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ROCKET RADIATION HANDBOOK, VOLUME II. MODEL EQUATIONS FOR PHOTON EMISSION RATES AND ABSORPTION CROSS-SECTIONS

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A review is given of model equations for the calculation of photon emission and absorption cross-sections and rate constants for gaseous molecules in bound-bound transitions. Approximate expressions for electronic, vibrational, and rotational transitions are discussed and a generalized line- and band-broadening formulation is employed which allows explicit calculation of cross-sections and rates at any gas temperature and pressure as a function of photon frequency. Such approximate model equations are quite useful in the applied sciences such as laser physics and gas radiations in space and in the atmosphere.

The formulas for the transition elements employed are based on idealized models of internal molecular forces and thus constitute only an approximation to the exact physical situation. Most of the transition element expressions come from well-known derivations given in the literature, but some new relations for anharmonic vibrational transitions are also provided which have not been previously reported. The derivations of new results are shown in some detail, but for the derivations of previously-established relations only references are given.

A novel feature presented is the use of generalized broadening functions applicable to both lines and bands. These functions have often been treated unsatisfactorily or incompletely. The new approach to calculate line- and band-broadening is treated in some detail and relies heavily on the so-called "law of spectroscopic stability" which essentially invokes conservation of the excitation energy that is distributed over the excited species.

With the first four chapters devoted mostly to a discussion of theoretical equations, the final chapter presents several explicit worked-out examples such as the absorption and stimulated emission cross-section of CO_2 as a function of pressure, temperature, and gas composition.

ERRATA

July 30, 1974
Page 1 of 3

VOLUME II, ROCKET RADIATION HANDBOOK

Location	Correction
Cover page and page i	Fill in: AF-FTD No. FTD-CW-01-01-74, Volume 2
p. 24, sixth line from bottom	Read: ....example that there are 8 upper states and 6 lower states and that only ....
p. 25, figure 2-1	Read: $w_m = 8$ states $w_n = 6$ states
p. 26, first and second line	Read: ....$C_{mn} = 6$. If finally anyone of the upper 8 states could make a transition to any one of the lower 6 states, $C_{mn} = 8 \times 6 = 48$. Thus in general many ....
p. 86, seventh line from top	.....eigenfunction, should read: eigenfunctions. ....
p. 99, Eq. (3.88)	$z_\alpha \vec{e}_\alpha$ should read: $z_\alpha \vec{e}_\alpha H(\Delta v_\alpha - 1)$ (Here H(x) is the unit step function defined by Eq. (3.156b))
p. 100, Eq. (3.89^a)	$(\lvert v_{\alpha m} - v_{\alpha n} \rvert + 1)$ should read: $(\lvert v_{\alpha m} - v_{\alpha n} \rvert + 1)^2$
p. 100, Eq. (3.89^b)	$(\lvert v_{\alpha m} - v_{\alpha n} \rvert + 1) z_\alpha \vec{e}_\alpha$ should read: $(\lvert v_{\alpha m} - v_{\alpha n} \rvert + 1) z_\alpha \vec{e}_\alpha H(\Delta v_\alpha - 1)$ (Here H(x) is the unit step function defined by Eq. (3.156^b))
p. 118, first line from top	Read: ....is $J_m = 1 \rightarrow J_n = 0$
p. 118, last line of text	Read: ....which is approximately given by (Ref. 6):
p. 162, fourth line from top	Read: ....and differs from zero only .... (not: differs only from zero).

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Location	Correction
p. 193, ninth line from top and at bottom of page	Read: sums are (Refs. 10 and 16):*) Add footnote on bottom of page: *) Z_v is also called the "vibrational sum-of-states" and Z_r the "rotational sum-of-states".
p. 194, Eq. (4.84), second line	Read: $= \frac{kT}{h\nu_B} + \ldots.$ (not: $\frac{kT}{h\nu_r} + \ldots\ldots$)
p. 243, Eq. (4.221), last term	Read: ....+1) +1)}]
p. 295, first line from top	Read: The dimensionless shape function .... (not: The dimensional shape function ....)
p. 315, Table 5-2, rows (c) and (d)	Read: $\ldots. = \frac{4.606 \times 10^{-2}}{\nu_{mn}(\text{Hz})}$ (not: $\ldots. = \frac{4.606 \times 10^{-12}}{\nu_{mn}(\text{Hz})}$)
p. 333, last line of footnote	Read: ....gives....(not: ....gave....).
p. 346, second line from bottom	Read: ....need....(not: ....needs....).
p. 348, Eq. (5.34)	Read: $\ldots. = w_v \exp-\left(\frac{V_1}{kT}\right) \ldots.$
p. 340, third line	Read: ....where w_v is the statistical weight of the internal excited level (electronic, ...
p. 348, Eq. (5.35)	Read: $\ldots. = w_v \exp-\left(\frac{V}{kT}\right)$

ERRATTA (CONTINUED)

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Location	Correction
p. 348, Eq. (5.38)	Read: .... $w_v \exp - \left(\frac{V}{KT}\right)$
p. 350, Eq. (5.43)	Read: .... $\frac{\Gamma(\nu,x)}{\Gamma(\nu,x=0)} =$ ....
p. 350, Eq. (5.47)	Read: ....$\left(\frac{1+\cos^2\theta}{16\pi/3}\right) z_{outer} = 5.3406 \times 10^{-29}$.....
p. 351, third line from top	Read: ....outer electrons.... (not: ....outer electron...)
p. 352, Eq. (5.51)	Read: .. $\sum_i$ ..
p. 416, fifth line from top	Read: .$\left[\int_{x=0}^{\infty} x^{p-1} (\exp -x)\, dx\right]^{-1}$
p. 444, thirteenth line from top	Read: α,β, ...of a polyatomic (not: ν,β, ...of a polyatomic)
p. A-12, Eq. (A.34)	$z_\beta \vec{e}_\beta$ should read: $z_\beta \vec{e}_\beta H(\Delta v_\beta - 1)$ (H(x) is unit step function defined by Eq. (3.156b).
p. B-12, third line from bottom	Read: Note that Eq. (B.12) differs....
p. B-24, footnote second line	Read: p. 51) on....
p. B-37, third line from top	Read: ....moment μ; .... not: ....moment υ, ...).
p. B-39, second line from bottom in text	Read: ....we have thus....(not: ....we hav thus...).
p. B-74, sixth line from bottom	Read: ....we wrote.... (not: ....we rote....).
p. B-75, Table B-7	Entry in next-to-last column for K_c of UF_6 (last row) should read: 0.1080 (not: 0.0108).

id

NOTICES

SPONSORSHIP

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This report was prepared by the Garrett Corporation, Airesearch Division, of Los Angeles, California, under contract with FTD, USAF.

Dr. J. W. Eerkens was the main author and principle investigator in the program which was carried out under the general technical direction of Mr. H. Lopez, Director of Engineering.

DISTRIBUTION

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PREFACE

The present monograph is the second volume of the Rocket Radiation Handbook series. The unclassified volumes of the series are entitled:

I. ROCKET RADIATION PHENOMENOLOGY AND THEORY

II. MODEL EQUATIONS FOR PHOTON EMISSION RATES AND ABSORPTION CROSS-SECTIONS

III. FUNDAMENTALS OF PHOTONICS

IV. GAS DYNAMICS AND FLOW-FIELDS OF ROCKET EXHAUSTS

V. ATMOSPHERIC PROPERTIES AND OPTICAL TRANSMISSION

VI. RADIATION SENSING SYSTEMS THEORY

Although each volume supports the others and covers a subject that is essential to rocket radiation science, most volumes stand on their own and their material can be used in other fields of applied physics and engineering.

The new Rocket Radiation Handbook contains the results of six years of fundamental research and experimental data analyses of the radiant emissions produced by rockets as they traverse the atmosphere and travel into space. At the present level of development, the theory appears to predict most observed radiations to within the margin of accuracy imposed by uncertainties in the values of some input parameters and observational conditions.

Some earlier attempts to derive theoretical models for observed rocket emissions were rather incomplete and unsatisfactory causing engineers in the field to become skeptical of any theoretical work. As a result the tendency has been to rely primarily on empirical information and the belief was held by many that satisfactory analytic expressions derived from theory, would be impossible to obtain in view of the perplexing multitude of phenomena which appear to be taking place simultaneously. It is my hope that the work presented here will dispel this notion.

That theoretical physics can correctly predict the overall results of a complex mixture of man-made physical events, if the theory is worked out properly and the basic phenomena are understood, was dramatically demonstrated during World War II by Enrico Fermi. Fermi and his associates developed the theory of neutron transport and nuclear chain reactors and designed the first nuclear reactor entirely from theory without the benefit of any data on an operating reactor. Their first nuclear reactor, when built, performed almost exactly according to calculation.

Another interesting example is the laser. Although the basic theory that could have predicted the principle of the laser existed in 1930, unfamiliarity of applied scientists and engineers with this theory, delayed the discovery of the laser until 1960.

The current Rocket Radiation Handbook, which is a complete revision and considerable expansion of an earlier version, was sponsored by the Foreign Technology Division of USAF-AFSC. In particular credit is due Capt. Roy Chardon who was the Technical Program Manager of the effort and who pushed most vigorously to have it compiled and issued. Col. G. R. Weinbrenner, Commander of FTD, Col. J. H. Mann, Mr. Ken Miller, Mr. Ted Larson, and Capt. Jeff Johnson under whose direction the work was carried out, also deserve full credit for backing this work.

In addition to the USAF, the Special Programs Office of the NASA must be mentioned. They sponsored most of the early work (1966-1970) on which the present Handbook is based. In particular Mr. Larry Gilchrist, Technical Program Manager, and Mr. Duff Gintner, Program Office Director at NASA H.Q. are thanked for their earlier support.

Finally I wish to express my gratitude to Dr. K. N. Satyendra under whose direction most of the early work which led to the present effort was initiated and to Mr. H. Lopez, Director of Engineering of the Garrett Corporation who saw to it that it was continued. For many valuable suggestions and assistance over the past six years I am indebted to Dr. R. Fairley, Dr. J. Robe, Mr. R. Proffitt, Mr. B. Bartholo, Dr. B. Stallwood, Dr. A. Bhattacharjie, Mr. C. Brooks, Mr. A. Gaede, and Mr. D. Ho. Many thanks also go to my Technical Typist, Editor, and Illustrator, Miss Frances Rossiter whose conscientious work and devotion made it possible to get all the material in a presentable form.

Data, figures, and derivations employed in the text which were obtained from other authors and organizations are too numerous to mention. They are referenced throughout the Handbook and use of their information is hereby gratefully acknowledged.

J. W. Eerkens

ABSTRACT

A review is given of model equations for the calculation of photon emission and absorption cross-sections and rate constants for gaseous molecules in bound-bound transitions. Approximate expressions for electronic, vibrational, and rotational transitions are discussed and a generalized line- and band-broadening formulation is employed which allows explicit calculation of cross-sections and rates at any gas temperature and pressure as a function of photon frequency. Such approximate model equations are quite useful in the applied sciences such as laser physics and gas radiations in space and in the atmosphere.

The formulas for the transition elements employed are based on idealized models of internal molecular forces and thus constitute only an approximation to the exact physical situation. Most of the transition element expressions come from well-known derivations given in the literature, but some new relations for anharmonic vibrational transitions are also provided which have not been previously reported. The derivation of new results are shown in some detail, but for the derivations of previously-established relations only references are given.

A novel feature presented is the use of generalized broadening functions applicable to both lines and bands. These functions have often been treated unsatisfactorily or incompletely. The new approach to calculating line- and band-broadening functions is treated in some detail and relies heavily on the so-called "law of spectroscopic stability" which essentially invokes conservation of the excitation energy that is distributed over the excited species.

With the first four chapters devoted mostly to a discussion of theoretical equations, the final chapter presents several explicit worked-out examples such as the absorption and emission rates of H_2O , CO_2 , CO, N_2O , NO_2 , and the stimulated emission cross-section of CO_2 as a function of pressure, temperature, and gas composition.

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I. INTRODUCTION

In the applied sciences there is a great need for moderately accurate model equations to calculate photon absorption cross-section and emission rates in molecular gases that are relatively easy to use but still contain all parametric dependencies. In particular equations are needed that give cross-sections and rate parameters explicitly as a function of the photon frequency ν, and the pressure p (or density n) and temperature T of the gas. Though some approximate model equations have been developed for selected photon-molecule interactions, generalizations to other molecules have been rather limited and the emphasis in the literature has been more on spectral details than on transition strengths. This monograph is an attempt to remedy this situation and to present and generalize in one place model expressions with which one can calculate pressure- and temperature-dependent cross-sections and transition rates explicitly as a function of the photon frequency ν. We are primarily considering here photons with energies below about 10 eV (frequency ν = 2,420 THz = 80,660 cm^{-1}) and above approximately 10^{-4} eV (ν = 0.0242 THz = 0.8066 cm^{-1}), that is those lying in the ultraviolet, visible, infrared, and radarwave portions of the spectrum,* which can cause bound-bound transitions in molecules. Only two-quanta interactions are considered. Bound-free and free-free electronic transitions as well as raman and double-photon interactions, which are essentially three-quanta problems are not treated here.

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*We shall call this region the UVIR region for short.

The model equations presented are those evolved by the author during several years of research on gas laser physics and gas radiations in space. The treatment is therefore somewhat biased towards problems in the latter fields of applied physics, but the material should be sufficiently general to allow its use in many other areas of physics.

In applied photonics work dealing with the movement of photons through gases, one repeatedly encounters relations like:

$$\frac{\text{Photon Absorptions}}{\text{(Unit Volume)(second)}} = \frac{\text{Photon Flux}}{\text{(Unit Area)(second)}} \times$$

$$\times \frac{\text{Absorption}}{\text{Unit Length of Photon Travel}},$$

where:

$$\frac{\text{Absorption}}{\text{Unit Length of Photon Travel}} = \frac{\text{Number of Molecules}}{\text{Unit Volume}} \times$$

$$\times \frac{\text{Absorption Cross-Section}}{\text{Molecule}} = N\sigma_{abs}$$

The basic parameter in such relations for which one seeks values is the microscopic absorption cross-section σ_{abs} which varies with photon frequency, gas temperature and gas pressure. The precise calculation of σ_{abs} for a molecule depends in a complicated manner on a molecule's physical makeup and can only be obtained correctly via the application of quantum mechanics.

It is this calculation of σ_{abs} (cm^2), and the stimulated emission cross-section $\sigma_{s.e.}$ (cm^2) and molecular emission rate A_{mn}(sec^{-1}) of a molecule which are simply related to σ_{abs}, that form the entire subject of this monograph. In Chapter 2, these parameters are discussed more fully.

While general microscopic relations governing the emission and absorption of radiation by molecules are derived in a number of books on quantum mechanics, details of the broadening of the frequencies of the basic emission and absorption lines into bands and band series are most often left to the applied science texts where usually only certain processes are treated that are of special interest. As a result most broadening widths and shape functions given in the literature are tailored to particular needs, and the underlying "law of spectroscopic stability" that governs all broadening processes is often obscured.

A novel feature in the present monograph is a unified treatment of all molecular broadening processes. This unified treatment can be applied to individual lines as well as bands and always ensures that conservation of energy and conservation of number-of-excited-species is obeyed. Although the basic features of the line-broadening functions and line-widths that are obtained are not new, the expressions that are derived for the contours of "rotationally broadened" vibrational transition bands and "vibrationally broadened" electronic transition band-systems are new in that they appear more convenient and of general use than what has been presented before in the literature. The approach of treating all broadening processes in one unified manner has proven to be very useful for gaseous laser processes and gas cloud radiation problems.

To illustrate our approach, consider radiative transitions* between two different excited states of a molecule. The first state might be designated by (J' , v' , Λ') and the second state by (J'' , v'' , Λ''), where J' is the rotational quantum number of the first state, v' represents the vibrational level of the first state and Λ' symbolizes the first state's electronic quantum state**, while doubly primed parameters indicate similar characteristics for the second state.

In general a transition from the single primed state to the double primed state can involve situations where $v'' > v'$, while $J'' < J'$ and $\Lambda'' = \Lambda'$, or $\Lambda'' > \Lambda'$, with $v'' < v'$ and $J'' < J'$, or any other combination. The relations between v'' and v', J'' and J', and Λ' and Λ'' are not completely arbitrary however but subject to certain constraints and selection rules, which we shall discuss in Chapters 2 through 4. That is we have in general that $v'' = v''(v')$, $J'' = J''(J')$, $\Lambda'' = \Lambda''(\Lambda')$.

Of course vibrational transitions can take place only for multi-atomic molecules in gases, liquids, or solids***, since a minimum of two charged atomic partners are needed for a vibrationally-excitable bond.

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*In what follows we shall use the word "transition" to mean "radiative transition" only, that is a transition involving a massless photon and a molecule. Transitions induced by a collision of a molecule with an electron or other molecule, that is "collisional" or "impact" transitions follow different rules and are not considered in this monograph.

**The electronic energy state is actually specified by three quantum numbers of course, namely the "principal," the "orbital" and the "spin" quantum numbers.

***In this monograph emphasis is placed on molecular transitions in gases. However many of the relations given are directly applicable or may be extended to liquids and solids.

Similarly rotational transitions require an axis of rotation between at least two separated, charged, atomic mass centers and thus only in multi-atomic gases and liquids do rotational transitions play a role. A monatomic gas such as Helium or Neon can only experience purely electronic transitions (as long as conditions are such that the molecules He_2^* or Ne_2^* cannot exist).

One glance at typical emissions from electronic, vibrational, and rotational transitions in a molecule, reveals that energy (or frequency) differences ΔE_e between electronic levels are an order of magnitude larger than typical differences between vibrational levels ΔE_v, and the latter are again much larger than the energy changes in rotational transitions ΔE_r. That is:

$$\Delta E_e \gg \Delta E_v \gg \Delta E_r \qquad (1.1)$$

or since the emission frequency $\nu_{mn} = \Delta E/h$,

$$(\nu_{mn})_e \gg (\nu_{mn})_v \gg (\nu_{mn})_r \qquad (1.2)$$

One also finds that in general the mean time τ for decay of an excited state is the shortest for the most energetic transitions and longest for the least energetic ones, that is:

$$\tau_e \ll \tau_v \ll \tau_r \qquad (1.3)$$

Typical order-of-magnitude values for the above parameters are:

$\Delta E_e \sim 3\text{eV}$; $(\nu_{mn})_e \sim 1000$ THz $\approx 30{,}000\ \text{cm}^{-1}$; $\tau_e \sim 10^{-7}$ sec

$\Delta E_v \sim 0.1$ eV ; $(\nu_{mn})_v \sim 100$ THz $\approx 1{,}000\ \text{cm}^{-1}$; $\tau_v \sim 10^{-3}$ sec

$\Delta E_r \sim 10^{-4}$ eV ; $(\nu_{mn})_r \sim 0.1$ THz $\approx 1\ \text{cm}^{-1}$; $\tau_r \sim 10$ sec

From this order-of-magnitude analysis it appears that we can treat the rotational transition that accompanies a pure vibrational transition (electronic state remains unchanged) as a perturbation, and similarly the simultaneous vibrational (and rotational) transition that may accompany an electronic transition can be considered as a small disturbance of a much larger change in electronic-state energy.

In the following, we shall employ the symbols m and n to indicate upper and lower quantum levels respectively. That is the state m possesses more internally stored molecular energy ("upper" state) than the state n ("lower" state). When considering a transition which is primarily electronic we then have an upper electronic level specified by the three-set $(n_m , \Lambda_m , \Omega_m)$ which we shall usually abbreviate Λ_m, and for the lower level we have the three-set $(n_n , \Lambda_n , \Omega_n)$ which we abbreviate Λ_n.* We shall consider Λ_m and Λ_n to be fixed in this case, while the vibrational and rotational quantum numbers v_m and J_m, and v_n and J_n can have various integral values though as remarked earlier, restrictions are placed on v_n and J_n by the selection rules, that is $v_n = v_n(v_m)$ and $J_n = J_n(J_m)$.**

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*An electronic level k is specified by three quantum numbers, a principle one n_k, an orbital one Λ_k, and a spin number Σ_k. Instead of Σ_k, usually one specifies the total angular momentum quantum number $\Omega_k = | \vec{\Lambda}_k + \vec{\Sigma}_k |$.

**For polyatomic molecules it is often necessary to specify two quantum numbers J and K to specify a rotational level. In this case $J_k \rightarrow (J_k, K_k)$ (see section 3.4).

For a transition that is primarily vibrational (i.e., $\Lambda_m = \Lambda_n$), the levels v_m and v_n are specified, while J_m and $J_n = J_n(J_m)$ can have various values. Finally for a pure rotational transition for which $\Lambda_m = \Lambda_n$ and $v_m = v_n$, we have one particular value J_m and one particular value $J_n = J_n(J_m)$.

To clarify this notation further, for example $A^{o}_{\substack{mn \\ elc}}$ is the symbol for the spontaneous deexcitation rate of a molecule from a particular upper electronic level $m = \Lambda_m$ to a particular lower electronic level $n = \Lambda_n$ for any accompanying values of $v_m \rightarrow v_n$ and $J_m \rightarrow J_n$ that can exist and are allowed. Since the transition rate $A^{o}_{\substack{mn \\ elc}}$ is, to first-order, only determined by the change in electronic energy $\Delta E_e = h(\nu_{mn})_e$, its value is the same whether we start out with $v_m = 5$, $J_m = 136$ or $v_m = 2$, $J_m = 25$.

The frequency ν of the photons emitted in the electronic $m \rightarrow n$ transition under discussion, is to first-order given by $\nu = (\nu_{mn})_e = \Delta E_e/h$. However because of the various possible vibrational sublevels v_m and their transition to $v_n = v_n(v_m)$ during the electronic transition $\Lambda_m \rightarrow \Lambda_n$, the actually emitted photon frequencies ν will vary within a small range about the central value ν_{mn}. That is, $\nu = \nu(v_m, v_n(v_m)) = \dfrac{\Delta E_e \pm \Delta E_v}{h} = \nu_{mn} \pm (\nu_{v_m} - \nu_{v_n(v_m)}) = \nu_{mn} \pm \Delta\nu_v(v_m)$, where ν_{mn} is fixed, and where the variable $\Delta\nu_v$ ($\Delta\nu_v \ll \nu_{mn}$) can take on any one value of a range of possible discrete values determined by the selection rules and other transitional constraints to be discussed in detail later.

As stated above, the rate $A^{o}_{\substack{mn \\ elc}}$ <u>for an individual molecule</u> is constant and independent of v_m and thus also independent of the emission perturbation frequency $\Delta\nu_v$. That is if we removed each molecule excited to the electronic level m from the gas and observed its decay to level n in isolation, we would find that the decay rate would be to first-order the same for each one, regardless of the initial value for v_m and J_m and the precise value ν of the emitted photon.

However, in a gas at thermal equilibrium, the population of molecules excited to $m = \Lambda_m$ with $v_m = 5$ is (usually) less than that of Λ_m - excited molecules with $v_m = 2$. As a result of this difference in population of initial vibrational sublevels, we will therefore find that the apparent value $A_{mn_{elc}}$ for a gas molecule does depend on v_m or $\Delta\nu_v(v_m)$. Since a particular lower sublevel v_n is specified for each v_m via certain selection rules,* the variation in the apparent value $A_{mn_{elc}}$ with the emitted photon frequency ν is directly related to the population distribution of states v_m . If we define the population distribution of sublevels v_m giving rise to emission of photons with frequencies in the range $\nu \pm 1/2\, d\nu$ by:

$$\frac{1}{N_{m_{tot}}}\,\frac{dN(v_m)}{d\nu} = g(v_m) = g\Big(\nu\big(v_m \to v_n(v_m)\big)\Big) = g(\nu,\nu_{mn},\Delta\nu_{mn})\ ;\ \mathrm{Hz}^{-1}\ , \tag{1.4}$$

where $N_{m_{tot}}$ is the total number of excited states m, then:

---

*In this case the selection rule is the "Franck-Condon Principle" (see Chapter 4).

$$\boxed{\frac{dA_{mn}}{d\nu} = A^{o}_{mn}\,\frac{dN(v_m)}{N_{m_{tot}}\,d\nu} = A^{o}_{mn}\,g(\nu,\nu_{mn},\Delta\nu_{mn})\ ,\ \sec^{-1}\ \mathrm{Hz}^{-1}} \tag{1.5}$$

The quantity $\Delta\nu_{mn}$ which we shall discuss in Chapter 4, is a measure of the average spread or "width" of the emitted photon frequencies about the central frequency ν_{mn} over which the variable $\Delta\nu_v$ will range. The magnitude of $\Delta\nu_{mn}$ for the electronic transition m → n is on the order of the value $(|E_{v_m} - E_{v_n=v_m\pm 1}|)/h$, but its exact value requires a more detailed analysis of the constraints imposed on $v_m \rightarrow v_n$ transitions when $\Lambda_m \rightarrow \Lambda_n$.

In the example above we considered an electronic transition $(m = \Lambda_m) \rightarrow (n = \Lambda_n)$, but the same can be said for a pure $(\Lambda_m = \Lambda_n)$ vibrational transition $(m = v_m) \rightarrow (n = v_n)$ in which the rotational sublevels cause a spreading of the emitted photon frequencies about ν_{mn} . Equation (1.5) applies therefore in general to both electronic and vibrational transitions and for that reason we have omitted subscripts "elc" or "vib" in it.

In fact, Eq. (1.5) can be applied to any frequency-spreading or "broadening" process, in which the basic transition energy quantum $h\nu_{mn}$ is slightly modified by another simultaneously-occurring process involving exchanges of smaller energy quanta, such as "collision-broadening," "doppler-broadening" and "stark-broadening" effects which we shall discuss in Chapter 4.

If we integrate Eq. (1.5) over all emitted photon frequencies ν from the $m \rightarrow n$ transition, we find that:

$$\frac{1}{N_{m_{tot}}} \int_{\nu = 0}^{\nu = \infty} \frac{dN(\nu_m)}{d\nu} \, d\nu = \int_{\nu = 0}^{\infty} g(\nu, \nu_{mn}, \Delta\nu_{mn}) \, d\nu = 1 \qquad (1.6)$$

Thus the distribution functions $g(\nu,\nu_{mn},\Delta\nu_{mn})$ of a broadening process must always be normalized to 1 to ensure that the law of conservation of the total number of excited states and emitted photons is obeyed. Spectroscopists will recognize that Eq. (1.6) expresses nothing but the so-called "law of spectroscopic stability" which states that an integration over the frequencies of an absorption or emission line or band must be constant regardless of how the line is broadened, provided that the energy supply rate is constant of course. The exact shape of the function $g(\nu,\nu_{mn},\Delta\nu_{mn})$ depends naturally on the particular broadening process that is in effect. It will be the subject of Chapter 4.

In Eq. (1.5), A_{mn} or $dA_{mn}/d\nu$ depends explicitly on ν. The function $g(\nu,\nu_{mn},\Delta\nu_{mn})$ contains all variations due to variations in the frequency ν while A^{o}_{mn} depends only on ν_{mn}. Let us compare this general form to the result which quantum mechanics usually yields for the transition probability. For a transition $(\Lambda_m \rightarrow \Lambda_n\ ,\ v_m \rightarrow v_n\ ,\ J_m \rightarrow J_n)$ quantum mechanics gives (see Refs. 1 and 2):

$$A\begin{pmatrix} \Lambda_m \rightarrow \Lambda_n \\ v_m \rightarrow v_n \\ J_m \rightarrow J_n \end{pmatrix} = \frac{64\ \pi^4 e^2 \nu^3_{mn}}{3hc^3} \left(\frac{S_{mn}}{w_m}\right)\ ,\quad \sec^{-1}\ , \qquad (1.7)^*$$

where for an electric-dipole transition between electronic levels $m \rightarrow n$ (i.e., $\Lambda_m \neq \Lambda_n$):

$$\left(S_{mn}\right)_{elc} \approx \sum \left| \iiint \psi^{\dagger}_{\Lambda_n}\ \psi^{\dagger}_{v_n}\ \psi^{\dagger}_{J_n}\ \vec{r}_{elc}\ \psi_{\Lambda_m}\ \psi_{v_m}\ \psi_{J_m}\ d\tau \right|^2 \approx$$

$$\approx \frac{\displaystyle\sum_{i,k} \left| \int \psi^{\dagger}_{J_{n_k}}\ \psi_{J_{m_i}}\ d\tau \right|^2 \sum_{i,k} \left| \int \psi^{\dagger}_{v_{n_k}}\ \psi_{v_{m_i}}\ d\tau \right|^2}{w_{e_n}(\Lambda_m)\ \ w_{v_m}(v_m)\ \ w_{r_m}(J_m)} \cdot$$

$$\cdot \sum_{i,k} \left| \int \psi^{\dagger}_{\Lambda_{n_k}}\ \vec{r}_{elc}\ \psi_{\Lambda_{m_i}}\ d\tau \right|^2 =$$

$$= \frac{C^{elc}_{mn} \circ C^{vib}_{mn} \circ C^{rot}_{mn}}{w_{e_m}(\Lambda_m)\ \ w_{v_m}(v_m)\ \ w_{r_m}(J_m)}\ R^2_{\substack{mn \\ elc}}\ ,\quad cm^2\ , \qquad (1.8)$$

---

*We prefer to remove the factor e^2 from the definition for the "strength" S_{mn} . Thus our "strength" is in units of cm^2 instead of erg - cm^3 employed by many others who use $\mathcal{S}_{mn} = e^2\ S_{mn}$.

Here the electronic transition matrix element $R^2_{\substack{mn\\elc}}$ is defined by:

$$R^2_{\substack{mn\\elc}} = R^2_{\substack{mn\\elc}}(\Lambda_m,\Lambda_n) = \left| \int \psi^\dagger_{\Lambda_{n_{k'}}} \vec{r}_{elc}\, \psi_{\Lambda_{m_{i'}}}\, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}} , \text{ cm}^2 , \qquad (1.9)$$

and the nondimensional "connection factors" C^{elc}_{mn} , ${}^\circ C^{vib}_{mn}$, and ${}^\circ C^{rot}_{mn}$ are formally given by:

$$C^{elc}_{mn} = C^{elc}_{mn}(\Lambda_m,\Lambda_n) = \frac{\displaystyle\sum_{i,k} \left| \int \psi^\dagger_{\Lambda_{n_k}} \vec{r}_{elc}\, \psi_{\Lambda_{m_i}}\, d\tau \right|^2}{\left| \displaystyle\int \psi_{\Lambda_{n_{k'}}} \vec{r}_{elc}\, \psi_{\Lambda_{m_{i'}}}\, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}}} \qquad (1.10)$$

$${}^\circ C^{vib}_{mn} = {}^\circ C^{vib}_{mn}(v_m,v_n;\Lambda_m,\Lambda_n) = \sum_{i,k} \left| \int \psi^\dagger_{v_{n_k}} \psi_{v_{m_i}}\, d\tau \right|^2 \qquad (1.11)$$

$${}^\circ C^{rot}_{mn} = {}^\circ C^{rot}_{mn}(J_m,J_n;\Lambda_m,\Lambda_n;v_m,v_n) = \sum_{i,k} \left| \int \psi^\dagger_{J_{n_k}} \psi_{J_{m_i}}\, d\tau \right|^2 \qquad (1.12)$$

The "weighting" factors or "degeneracies" w_{e_m}, w_{v_m}, and w_{r_m} in Eq. (1.8) are equal to the number of substates of exactly equal energy for respectively the electronic energy level Λ_m, the vibrational sublevel v_m, and the rotational sublevel J_m. The summations in Eqs. (1.10), (1.11), and (1.12) are over the allowed transitions (for which the integral $\int \psi_m^\dagger \psi_n \, d\tau \neq 0$) between degenerate substates i of the level m and degenerate substates k of the level n for respectively electronic, vibrational, and rotational levels. These degeneracies arise because of "space quantization." That is, not only the energy of the levels are quantized, but also the directions of the rotation vectors of orbital and spin quantum numbers of both electrons and molecules as a whole are quantized. Thus for a given energy level specified by a given quantum number(s), several substates or degeneracies can exist of equal energy but different spatial orientations of orbital or spin angular momentum vectors. Also for bending vibrations for example one can have a spatial degeneracy due to two possible identical bending vibrations in two mutually perpendicular planes.

Up to now we have used the words "levels," "sublevels," "states", and "substates" somewhat loosely. Following Condon and Shortley (Ref. 1) however, we shall from now on use the word "level" to indicate a particular energy level of a molecule, while a "state" of a molecule refers to a quantized energy level and a quantized orientation of the angular momentum. Thus a level can have various equally energetic states. We shall further call the electronic levels the "levels," and the vibrational and rotational levels the "sublevels," when we consider electronic transitions. For purely vibrational transitions, the vibrational energy levels are <u>the</u>

"levels" and the rotational energy levels are the "sublevels," while for purely rotational transitions the rotational levels are <u>the</u> "levels." Each level and sublevel can have states and substates of equal energy of course.*

For a vibrational electric-dipole transition with no electronic level change (i.e., $\Lambda_m = \Lambda_n$), the "strength" S_{mn} in Eq. (1.7) is similarly to Eq. (1.8)) given by:

$$\left(S_{mn}\right)_{vib} \approx \sum \left| \iiint \psi^{\dagger}_{\Lambda_n} \psi^{\dagger}_{v_n} \psi^{\dagger}_{J_n} \vec{r}_{vib} \, \psi_{\Lambda_m} \psi_{v_m} \psi_{J_m} \, d\tau \right|^2 \approx$$

$$\approx \frac{\sum\limits_{i,k} \left| \int \psi^{\dagger}_{J_{n_k}} \psi_{J_{m_i}} \, d\tau \right|^2 \sum\limits_{i,k} \left| \int \psi^{\dagger}_{v_{n_k}} \vec{r}_{vib} \, \psi_{v_{m_i}} \, d\tau \right|^2}{w_{v_m}(v_m) \; w_{r_m}(J_m)} =$$

$$= \frac{{}^{o}C^{rot}_{mn} \; C^{vib}_{mn}}{w_{v_m}(v_m) \; w_{r_m}(J_m)} \; R^2_{\substack{mn \\ vib}} \;, \; cm^2 \;, \qquad (1.13)$$

where ${}^{o}C^{rot}_{mn} = {}^{o}C^{rot}_{mn}(J_m, J_n; v_m, v_n; \Lambda_m = \Lambda_n)$ is again given by the expression (1.12) except that the dependencies on Λ_m and Λ_n must be set so that $\Lambda_m = \Lambda_n$. The factor C^{vib}_{mn} and the non-degenerate transition matrix $R^2_{\substack{mn \\ vib}}$ are formally given by:

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*In addition to the above definition, the word "state" is also used to indicate a general combination of an electronic, vibrational, and rotational level. Though perhaps confusing, it is usually clear from the context which meaning applies.

$$R^2_{\substack{mn\\vib}} = R^2_{\substack{mn\\vib}}(v_m, v_n; \Lambda_m = \Lambda_n) = \left| \int \psi^{\dagger}_{v_{n_{k'}}} \vec{r}_{vib} \, \psi_{v_{m_{i'}}} \, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}} , \ \text{cm}^2 , \qquad (1.14)$$

and:

$$C^{vib}_{mn} = C^{vib}_{mn}(v_m, v_n; \Lambda_m = \Lambda_n) = \frac{\sum\limits_{i,k} \left| \int \psi^{\dagger}_{v_{n_k}} \vec{r}_{vib} \, \psi_{v_{m_i}} \, d\tau \right|^2}{\left| \int \psi^{\dagger}_{v_{n_{k'}}} \vec{r}_{vib} \, \psi_{v_{m_{i'}}} \, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}}} \qquad (1.15)$$

Finally, for a pure rotational electric-dipole transition with $\Lambda_m = \Lambda_n$ and $v_m = v_n$, we get that:

$$\left(S_{mn}\right)_{rot} \approx \sum \left| \iiint \psi^{\dagger}_{\Lambda_n} \, \psi^{\dagger}_{v_n} \, \psi^{\dagger}_{J_n} \, \vec{r}_{rot} \, \psi_{\Lambda_m} \, \psi_{v_m} \, \psi_{J_m} \, d\tau \right| \approx$$

$$\approx \frac{\sum\limits_{i,k} \left| \int \psi^{\dagger}_{J_{n_k}} \vec{r}_{rot} \, \psi_{J_{m_i}} \, d\tau \right|^2}{w_{r_m}(J_m)} = \frac{C^{rot}_{mn} \, R^2_{\substack{mn\\rot}}}{w_{r_m}(J_m)} , \ \text{cm}^2 , \qquad (1.16)$$

where:

$$R^2_{\substack{mn\\ rot}} = R^2_{\substack{mn\\ rot}}(J_m, J_n; \Lambda_m=\Lambda_n; v_m=v_n) = \left| \int \psi^{\dagger}_{J_{n_{k'}}} \vec{r}_{rot}\, \psi_{J_{m_{i'}}}\, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}} ,\ cm^2 , \tag{1.17}$$

$$C^{rot}_{mn} = C^{rot}_{mn}(J_m, J_n; v_m=v_n; \Lambda_m=\Lambda_n) = \frac{\displaystyle\sum_{i,k} \left| \int \psi^{\dagger}_{J_{n_k}} \vec{r}_{rot}\, \psi_{J_{m_i}}\, d\tau \right|^2}{\left| \displaystyle\int \psi^{\dagger}_{J_{n_{k'}}} \vec{r}_{rot}\, \psi_{J_{m_{i'}}}\, d\tau \right|^2_{\substack{i' \to k'\\ \text{reference}}}} \tag{1.18}$$

Rewriting Eq. (1.7) for electronic transitions in the form:

$$A\begin{pmatrix} \Lambda_m \to \Lambda_n \\ v_m \to v_n \\ J_m \to J_n \end{pmatrix}_{elc} = \frac{64\,\pi^2 e^2 \nu^3_{mn}}{3hc^3} \left(\frac{C^{elc}_{mn}}{w_{e_m}(\Lambda_m)}\ R^2_{\substack{mn\\ elc}} \right) \cdot \left(\frac{{}^{\circ}C^{vib}_{mn}\ {}^{\circ}C^{rot}_{mn}}{w_{v_m}(v_m)\ \ w_{r_m}(J_m)} \right) =$$

$$= A^{\circ}_{\substack{mn\\ elc}} \cdot F^{vib/rot}_{mn} ,\ \frac{\text{photons/sec}}{\text{molecule }(\Lambda_m, v_m, J_m)} , \tag{1.19}$$

where:

$$F^{vib/rot}_{mn} = \frac{{}^{\circ}C^{vib}_{mn}\ {}^{\circ}C^{rot}_{mn}}{w_{v_m}(v_m)\ w_{r_m}(J_m)} \tag{1.20}$$

$$A^{\circ}_{\substack{mn\\ elc}} = \frac{64\ \pi^4 e^2 \nu^3_{mn}}{3hc^3}\left(\frac{C^{elc}_{mn}}{w_{e_m}(\Lambda_m)}\right) R^2_{\substack{mn\\ elc}}\ , \quad \sec^{-1}\ , \tag{1.21}$$

we have essentially separated it into a factor $A^{\circ}_{\substack{mn\\ elc}}$ that depends only on ν_{mn} and a factor $F^{vib/rot}_{mn}$ that depends only on the vibrational and rotational parameters. We can of course write expressions similar to (1.19) through (1.21) for pure vibrational and pure rotational transitions.

Now the factor $F^{vib/rot}_{mn}$, which we shall discuss in sections 4.7 and 4.8, is the probability for a transition from one particular sublevel v_m and sublevel J_m of the electronic level $m = \Lambda_m$ to any one equi-energetic (degenerate) sublevel v_n and sublevel J_n of the electronic level $n = \Lambda_n$ for a given molecule with v_m , J_m. Thus the expression for $A_{\substack{mn\\ elc}}$ given by (1.19) applies to very particular molecules, namely only those that are at energy level (Λ_m, v_m, J_m). In actual practice we wish to know the emission rate $A_{\substack{mn\\ elc}}$ for molecules in a gas of which we only know that they are excited to the electronic level Λ_m , but for which the sublevels v_m and J_m can have a variety of possible values. Similarly we wish to know in practical applications what $A_{\substack{mn\\ vib}}$ is for molecules in a gas of which we only know that they are excited to a particular vibrational level v_m , but for which J_m can vary from v_m-excited molecule to v_m-excited molecule. Finally it is of interest to determine what $A_{\substack{mn \\ rot}}$ is for molecules excited to a particular rotational level J_m, but whose translational kinetic energy can have different values from J_m-excited molecule to J_m-excited molecule.

Now in a gas of diatomic or linear molecules in thermodynamic equilibrium in which electronic excitations occur, we find from statistical mechanics that the probability of finding a molecule at sublevels (v_m, J_m) is (Ref. 2):

$$f_{v_m, J_m} = \frac{N(v_m, J_m)}{N_{tot}} = \frac{N(\Lambda_m, v_m, J_m)}{N_{\Lambda_m}} = \left[\frac{w_{v_m} \exp-\left[\sum_\alpha v_{\alpha_m} \nu_\alpha (hc/kT)\right]}{Z_v}\right] \cdot$$

$$\cdot \left[\frac{w_{r_m} \exp-\left[J_m(J_m+1)\nu_B(hc/kT)\right]}{Z_r}\right] = f_{v_m} f_{J_m} \qquad (1.22)$$

Equation (1.22) states that of all the molecules N_{tot} in the gas, a fraction f_{v_m, J_m} is at excited levels (v_m, J_m). Thus also of the Λ_m-electronically excited molecules $N_m \equiv N_{\Lambda_m}$, a fraction f_{v_m, J_m} is at sublevels (v_m, J_m). Z_v and Z_r in Eq. (1.22) are normalization factors (see Chapter 4) which are respectively called the rotational and vibrational "partition functions." For nonlinear molecules, the function f_{v_m, J_m} is somewhat different from Eq. (1.22) but similar (see Chapter 4).

For an equilibrium gas of linear molecules then we have for electronic transitions:

$$A\begin{pmatrix} \Lambda_m \rightarrow \Lambda_n \\ v_m \rightarrow v_n \\ J_m \rightarrow J_n \end{pmatrix} = A^{o}_{\substack{mn \\ elc}} F^{vib/rot}_{mn} f_{v_m, J_m} = A^{o}_{\substack{mn \\ elc}} G^{elc}_{mn}, \quad \frac{\text{photons/sec}}{\text{molecule } (\Lambda_m)}, \qquad (1.23)$$

where:

$$G^{elc}_{mn} = F^{vib/rot}_{mn} \cdot \left[\frac{w_{v_n} \exp -\left[\sum_\alpha v_{\alpha_m} \nu_\alpha hc/(kT) \right]}{Z_v} \right] \left[\frac{w_{r_n} \exp -\left[J(J+1) \nu_B hc/(kT) \right]}{Z_r} \right] \quad (1.24)$$

In the same manner we have for vibrational transitions (no electronic changes):

$$A_{\begin{pmatrix} v_m \to v_n \\ J_m \to J_n \end{pmatrix}} = A^{\circ}_{\substack{mn \\ vib}} F^{rot}_{mn} f_{J_m} = A^{\circ}_{\substack{mn \\ elc}} G^{vib}_{mn} , \quad \frac{\text{photons/sec}}{\text{molecule } (v_m)} \quad (1.25)$$

where:

$$G^{vib}_{mn} = F^{rot}_{mn} (2J_m+1) \frac{\exp -\left[J_m(J_m+1) \nu_B hc/(kT) \right]}{Z_r} \quad (1.26)$$

$$F^{rot}_{mn} = \frac{{}^{\circ}C^{rot}_{mn}}{w_{r_m}} \quad (1.27)$$

We use the superscripts elc and vib on G_{mn} to indicate that the function G_{mn} applies to the case that an electronic and a vibrational transition respectively is the primary internal-molecular change. Of course G^{elc}_{mn} contains all the fine-structure dependencies on the vibrational/rotational sublevels and similarly G^{vib}_{mn} contains all the dependence on the rotational fine-structure.

Equation (1.23) (and similarly Eq. (1.25)) is an improvement over (1.19) since it applies to arbitrary Λ_m-excited molecules and gives automatically the finer-detailed transition rates for different rotational sublevels J_m. However it is still awkward to use since in applied physics problems it is desirable to have the expression for the rate A_{mn} entirely in terms of the photon frequency ν , while (1.23) (and similarly (1.25)) still require auxiliary equations that relate J_m and ν . For example for electronic transition the photon frequency ν is related to J_m , v_m , J_n , v_n by:

$$\nu = \left[\nu_m(\Lambda_m) - \nu_n(\Lambda_n)\right] \pm f_{v_m} \frac{{}^{\circ}C^{vib}_{mn}}{w_{v_m}(v_m)} \cdot \left[\nu_{v_m}(v_m) - \nu_{v_n}(v_m)\right] \pm$$

$$\pm f_{J_m} \frac{{}^{\circ}C^{rot}_{mn}}{w_{r_m}(J_m)} \left[\nu_{J_m}(J_m) - \nu_{J_n}(J_m)\right] \equiv$$

$$\equiv \nu_{mn}(\Lambda_m, \Lambda_n) \pm f_{v_m} \frac{{}^{\circ}C^{vib}_{mn}}{w_{v_n}(v_m)} \Delta\nu_v(v_m) \pm f_{J_m} \frac{{}^{\circ}C^{rot}_{mn}}{w_{r_m}(J_m)} \Delta\nu_r(J_m) \qquad (1.28)$$

Here the values of $\Delta\nu_{v_m} = \nu_{v_m} - \nu_{v_n}$ and $\Delta\nu_{J_m} = \nu_{J_m} - \nu_{J_n}$ are determined by certain transition rules which we shall discuss in Chapter 4, and f_{v_m} and f_{J_m} are the "Boltzmann factors" for the vibrational and rotational levels (see Eq. (1.22)).

To carry out the program of rewriting G_{mn} in terms of ν instead of v_m or J_m , we assume that ν is continuous and that the discrete vibrational numbers v_m and rotational numbers J_m can be "smeared out." We shall do this in Chapter 4 where we essentially rewrite $G^{elc}_{mn}(v_m)$ and $G^{vib}_{mn}(J_m)$ as follows:

$G^{elc}_{mn}(v_m)$, probability at level v_m ⟶

$$g_e(\nu) \equiv \left(G^{elc}_{mn}(\nu)\right)\left(\frac{dv_m}{d\nu}\right), \text{ probability at frequency } \nu \text{ per unit } d\nu \qquad (1.29)$$

$G^{vib}_{mn}(J_m)$, probability at level J_m $\longrightarrow$

$$g_v(\nu) = \left(G^{vib}_{mn}(\nu)\right)\left(\frac{dJ_m}{d\nu}\right) \text{, probability at frequency } \nu \text{ per unit } d\nu \qquad (1.30)$$

The dimensions of $g_e(\nu)$ and $g_v(\nu)$ are Hz^{-1}, and when used in (1.25), this means that $A \rightarrow dA/d\nu$. We shall see in Chapter 4 that the expressions for the band-contour functions g_e and g_v always have ν_{mn} and $\Delta\nu_{mn}$ as parameters, where $\Delta\nu_{mn}$ gives the average width of the band and where for electronic transitions $\nu_{mn} = = \nu(\Lambda_m) - \nu(\Lambda_n)$ and for vibrational transitions $\nu_{mn} = \nu(v_m) - \nu(v_n)$. Thus we shall often write $g_e(\nu,\nu_{mn},\Delta\nu_{mn})$ and $g_v(\nu,\nu_{mn},\Delta\nu_{mn})$ to indicate the three key parameters on which g_e or g_v depends.

Before concluding this chapter, a few remarks concerning Eqs. (1.8), (1.12), and (1.16) are in order. The approximation signs used in these expressions indicate that all second-order mutual interactions between electronic, vibrational, and rotational forces are neglected. The ψ_{Λ_k} , ψ_{v_k} , ψ_{J_k} are of course the electronic, vibrational, and rotational eigenfunctions of state k, while $\psi^*_{\Lambda_k}$, $\psi^*_{v_k}$, $\psi^*_{J_k}$ are their complex conjugates.

Though the relations presented above appear rather formidable, they only look involved because of the formalistic manner in which equations in quantum mechanics are most conveniently expressed. We write them out in detail here only to show precisely how our approach is related to the expressions that appear in quantum mechanical treatments.

For applied physics work, it is sufficient to remember that the decay rate of a molecular excited state can always be written in the general form:

$$\boxed{\frac{dA_{mn}}{d\nu} = A^o_{mn}\ g_o(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{64\ \pi^4 e^2 \nu^3_{mn}}{3hc^3}\left(\frac{C_{mn}}{W_m}\right)_o \left(R^2_{mn}\right)_o g_o(\nu,\nu_{mn},\Delta\nu_{mn}),\ \sec^{-1}\ Hz^{-1},} \qquad (1.31)$$

where only the broadening function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ depends on ν and the remaining factors only depend on ν_{mn} and are independent of ν. The subscript o in Eq. (1.31) refers to an electronic, vibrational, or rotational transition whatever the case may be. For a pure rotational transition, $g_r(\nu,\nu_{mn},\Delta\nu_{mn})$ is the temperature or pressure-broadened line-contour function due to the translational molecular perturbations on the rotational transition.

In any particular problem, four parameters must be determined, namely R^2_{mn} , C_{mn} , w_m (or w_n), and the function $g(\nu,\nu_{mn},\Delta\nu_{mn})$. In the succeeding chapters we shall provide explicit expressions for these parameters. A review of the formal relations for cross-sections and rates derivable from the quantum theory of radiation is given in Chapter 2, while in Chapter 3, we give specific model expressions for the factors R^2_{mn} , C_{mn} , w_m , and w_n for electronic, vibrational, and rotational transitions. Chapter 4 covers broadening functions $g(\nu,\nu_{mn},\Delta\nu_{mn})$ for all the possible transitions.

After presenting detailed derivations in Chapters 3 and 4, summaries of the key expressions needed in most practical work are given in Chapter 5 in tabular form. Some practical examples are also worked out in Chapter 5, such as the stimulated emission cross-section for CO_2 in a He-N_2-CO_2 laser gas mixture and the emission rate (decay constant) for H_2O in a gaseous cloud. A nomenclature list and a list of the references are given at the end of the monograph.

Only one photon (one frequency ν) interactions are considered in this monograph. The extension of our review to (the much weaker) two-photon interactions involving two frequencies ν_1 and ν_2 (raman radiation, double absorption, etc.) will be left to a future effort.

2. GENERAL FORMULAS FOR DEEXCITATION RATES (LIFETIMES), PHOTON ABSORPTION CROSS-SECTIONS, AND CROSS-SECTIONS FOR PHOTON STIMULATED DEEXCITATION

2.1 PRELIMINARY CONSIDERATIONS

In this chapter we give for ready reference the general forms of the emission/absorption equations whose derivations are treated in most standard textbooks on quantum mechanics. We can divide first-order photon-molecule interactions into three groups; namely (1) spontaneous emission, (2) absorption, and (3) stimulated emission, and in the next three sections the general formulas are presented that are usually needed in applied physics work for these processes.

We use standard accepted symbols wherever possible, but for purposes of greater clarity we have introduced some new ones which reflect our general approach for treating broadening effects. The nomenclature is listed at the end of this monograph.

Besides some fundamental constants, we have seen that the general expressions for transitions between levels m and n contain four key factors, namely a transition element R^2_{mn}, a connection factor C_{mn}, a weighting factor w_m or w_n, and a broadening function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$. In Chapter 3 we shall give explicit model expressions for transition elements R^2_{mn}, connection factors C_{mn}, and weighting factors w_n, w_m for electronic, vibrational, and rotational transitions, while in Chapter 4, we consider explicit model equations for the broadening functions $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$.

In any particular application, the procedure is to determine first which general expression(s) in Chapter 2 is needed, secondly the appropriate expressions for R^2_{mn}, C_{mn} and the weighting factors w_m, w_n are obtained from Chapter 3, and finally the proper broadening function(s) $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ is selected from Chapter 4.

The matrix element R^2_{mn} (units of cm^2 for dipole transitions) gives the strength of an allowed transition between one reference upper state and one reference lower state of the possibly multiple number of equi-energetic states w_m in the upper level m and possibly multiple number of equi-energetic states w_n in the lower level n. The reference transition is usually defined to be the most probable one if there is a difference in the connection probability of allowed transitions between the w_m and w_n states.

The dimensionless connection factor C_{mn} as defined in Chapter 1, gives the total weighted number of allowed transitions between the w_m upper states and the w_n lower states. Referring to Figure 2-1, suppose for example that there are 7 upper states and 5 lower states and that only transitions as indicated by the solid lines are allowed. From the figure, it is clear that there are 12 such transitions, and thus $C_{mn} = 12$ if each transition is equally allowed. If in addition to the solid lines, the transitions indicated by the dotted lines would also be allowed, we would have on the other hand $C_{mn} = 18$. Or if only the dotted lines are allowed,

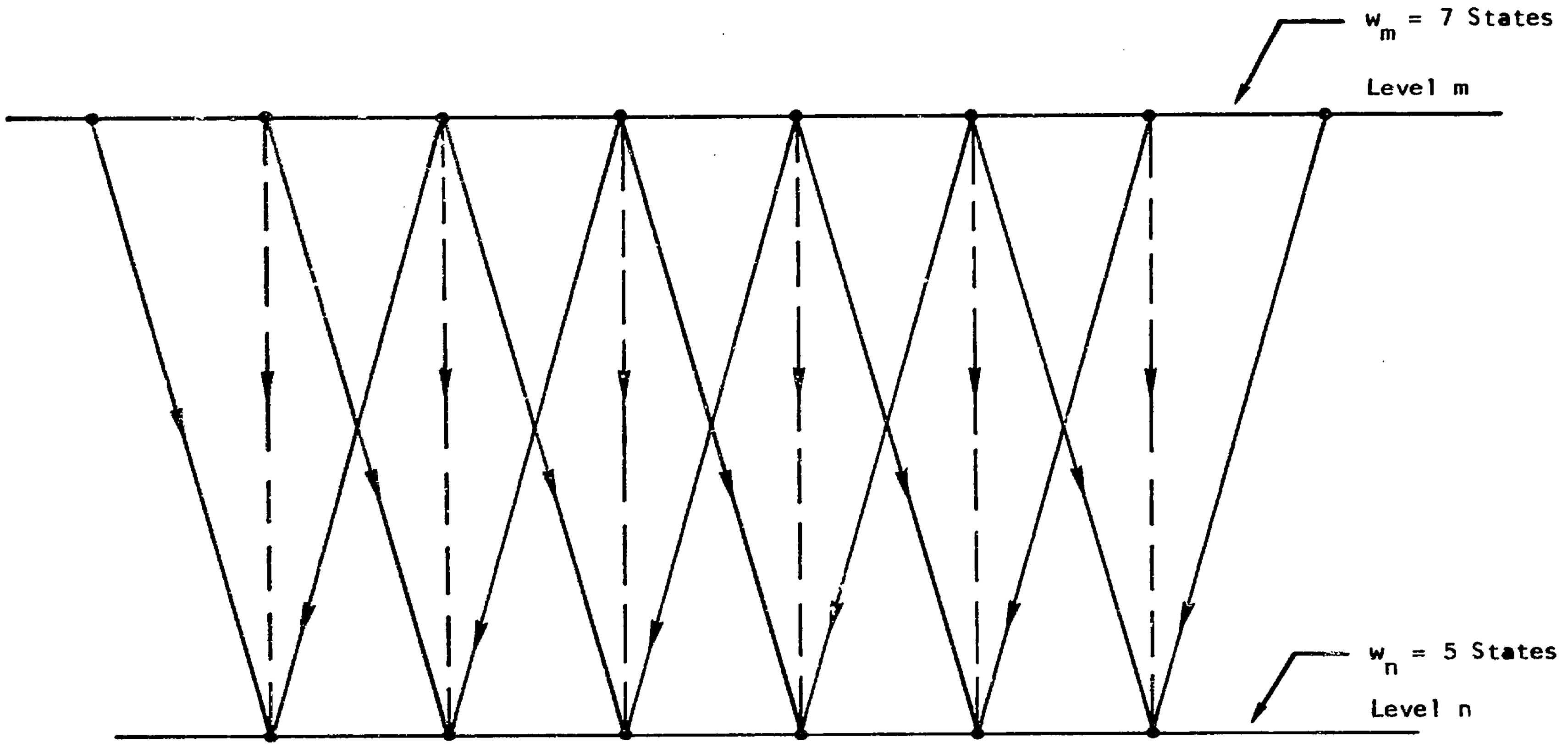

FIGURE 2-1. ILLUSTRATION OF CONNECTION FACTOR C_{mn}

$C_{mn} = 5$. If finally any one of the upper 7 states could make a transition to any one of the lower 5 states, $C_{mn} = 7 \times 5 = 35$. Thus in general many possibilities can exist depending on the exact selection rules.

Whether or not two states, say $w_m = k_m$ and $w_n = j_n$ are connected depends on whether the integral $\int \psi_{k_m} \vec{r}\, \psi_{j_n}\, d\tau$ is zero or nonzero. It is possible that the allowed transitions between states are not equally probable. For example let transitions between say state k_m and j_n be three times more probable than two other allowed transitions from k_m to say states p_n and q_n. In that case the transitions are weighted $(k_m \rightarrow j_n) = 1$, $(k_m \rightarrow p_n) = 1/3$, and $(k_m \rightarrow q_n) = 1/3$, if the calculation of the transition element R^2_{mn} is based on the strongest (most allowed) transition $k_m \rightarrow j_n$ between levels m and n. If in this case there is only one upper state k_m and three lower states (j_n, p_n, q_n) then $C_{mn} = 1 + 1/3 + 1/3 = 5/3$.

The reasons why R^2_{mn} and C_{mn} are usually calculated separately is that the summation calculation C_{mn} over allowed transitions between states can be done by a rather general mathematical methodology called "group theory," while the calculation of R^2_{mn} can be done by other convenient mathematical approximations. In group theory there is no need for a complete determination of the wave functions ψ_{k_m} and ψ_{j_n} to calculate C_{mn} and only the spatial symmetries of the quantum states m and n need to be known.

An important result from quantum mechanics is that the strength S_{mn} is symmetric. That is:

$$S_{mn} = S_{nm} \tag{2.1}$$

Since we defined R^2_{mn} to be a reference transition element between two particular states, we have also:

$$R^2_{mn} = R^2_{nm} , \tag{2.2}$$

and therefore since $S_{mn} = C_{mn} R^2_{mn}$ and $S_{nm} = C_{nm} R^2_{nm}$, we must have:

$$C_{mn} = C_{nm} \tag{2.3}$$

Now the transition parameters such as the decay constant A_{mn} must be specified on a per molecule basis, and since a single molecule can only be in one of the possible w_m upper states, the strength S_{mn} should be divided by w_m to give the average strength per molecule. This is the reason why we find the factor (S_{mn}/w_m) in expressions for A_{mn} such as Eq. (1.7).

In the following subsections we shall present without further explanation the standard expressions for the spontaneous emission rate A_{mn} (sec^{-1}), the stimulated emission cross-section σ_{mn} (cm^2) and the absorption cross-section σ_{nm} (cm^2). These three parameters, as will be shown, are interrelated of course. The reason for using cross-section σ as the basic parameter for the latter two processes instead of a rate parameter A, is that the former is independent of photon population while interaction rates are dependent on the photon fluence F_φ. The product $F_\varphi\sigma$ or $\int(dF_\varphi/d\nu)\sigma d\nu$ gives of course the rate.

2.2 SPONTANEOUS PHOTON EMISSIONS

The spontaneous deexcitation rate* A_{mn} or inverse decay constant τ_{mn}^{-1} for a transition from level m to n may in general be expressed by (Refs. 1 through 9):

$$A_{m \rightarrow n} \equiv A_{mn} = \frac{1}{\tau_{mn}} = \frac{64\,\pi^4 e^2 \nu_{mn}^3}{3hc^3} \left|\vec{r}_{mn}\right|^2 =$$

$$= \frac{64\,\pi^4 e^2 \nu_{mn}^3}{3hc^3} \frac{S_{mn}}{w_m} \;,\quad \text{sec}^{-1} \;, \tag{2.4}$$

where for an electric-dipole transition, the strength S_{mn} is formally defined by (Ref. 1):

$$S_{mn} = C_{mn}\, R_{mn}^2 = \sum_{i,k} \left| \int \psi_{n_k}^{*}\, \vec{r}\, \psi_{m_i}\, d\tau \right|^2 \;,\ \text{cm}^2\ ^{**} \tag{2.5}$$

---

*Also called the "Einstein A-Coefficient;" the subscript mn shall mean m → n in all the following.

**Note $C_{mn} R_{mn}^2 / w_{mn} = |\vec{r}_{mn}|^2 = |x_{mn}|^2 + |y_{mn}|^2 + |z_{mn}|^2 = 3\,|x_{mn}|^2 = 3\,|y_{mn}|^2 = 3\,|z_{mn}|^2$, for an isotropic homogeneous medium (Ref. 3, p. 405).

and the other parameters are defined in the nomenclature list. Equation (2.4) applies to any transition, whether electronic, vibrational, or rotational. Basic differences between these processes will appear in the parameter S_{mn}/w_m .

Now as shown in Chapter I (see Eq. (1.23)), we can write Eq. (2.4) in the form:

$$A_{mn} = A^{o}_{mn} \, G_{mn} \quad , \quad \sec^{-1} \quad , \tag{2.6}$$

or:

$$\frac{dA_{mn}}{d\nu} = A^{o}_{mn} \, g_{o}(\nu,\nu_{mn},\Delta\nu_{mn}) \ , \ \sec^{-1} \ \mathrm{Hz}^{-1} \tag{2.7}$$

Here G_{mn} or g_{mn} contains all the emission rate frequency dependencies due to broadening perturbations from the interaction of vibrational and/or rotational sublevels on electronic or vibrational levels during a transition, while the parameter A^{o}_{mn} depends only on ν_{mn} . That is A^{o}_{mn} is equal to Eq. (2.4) with the matrix element in (2.5) evaluated for the unbroadened, unperturbed, transition $m \rightarrow n$ as discussed in Chapter I. In other words $m = m(\Lambda_m)$ and $n = n(\Lambda_n)$ for an electronic transition, $m = m(v_m)$ and $n = n(v_n)$ for a vibrational transition, and $m = m(J_m)$, $n = n(J_n)$ for a rotational transition.

Using the results of Chapter I, we can write:

$$A^{o}_{mn} = \frac{1}{\tau^{o}_{mn}} = \frac{64\ \pi^4 e^2 \nu^3_{mn}}{3hc^3} \left(\frac{S_{mn}}{w_m}\right)_o = \frac{64\ \pi^4 e^2 \nu^3_{mn}}{3hc^3} \left(\frac{C_{mn}\ R^2_{mn}}{w_m}\right)_o \text{, sec}^{-1} \text{,}$$

(2.8)

where for an electronic electric-dipole (E.D.) transition:

$$\left(S_{mn}\right)_o = \left(S_{mn}\right)_{\substack{elc\\ E.D.}} = \left(C_{mn}\right)_{\substack{elc\\ E.D.}} \left(R^2_{mn}\right)_{\substack{elc\\ E.D.}} = \sum_{i,k} \left| \int \psi_{\Lambda_{n_i}}\ \vec{r}\ \psi_{\Lambda_{m_k}}\ d\tau \right|^2 \text{, cm}^2 \text{,}$$

(2.9)

while for a vibrational electric-dipole transition:

$$\left(S_{mn}\right)_o = \left(S_{mn}\right)_{\substack{vib\\ E.D.}} = \left(C_{mn}\right)_{\substack{vib\\ E.D.}} \left(R^2_{mn}\right)_{\substack{vib\\ E.D.}} = \sum_{i,k} \left| \int \psi_{v_{n_i}}\ \vec{r}\ \psi_{v_{m_k}}\ d\tau \right|^2 \text{, cm}^2 \text{,}$$

(2.10)

and for a rotational electric-dipole transition:

$$\left(S_{mn}\right)_o = \left(S_{mn}\right)_{\substack{rot\\ E.D.}} = \left(C_{mn}\right)_{\substack{rot\\ E.D.}} \left(R^2_{mn}\right)_{\substack{rot\\ E.D.}} = \sum_{i,k} \left| \int \psi_{J_{n_i}}\ \vec{r}\ \psi_{J_{m_k}}\ d\tau \right|^2 \text{, cm}^2$$

(2.11)

Since most transitions of interest are of the electric-dipole type, we shall omit the subscript E.D. from hereon, and only label parameters with M.D. (Magnetic Dipole) and E.Q. (Electric Quadrupole), if an E.D. transition is not under consideration.

If an E.D.-type transition is not allowed, the next possibly allowed radiative transitions are the much weaker magnetic dipole (M.D.) and/or electric quadrupole (E.Q.) type of single-photon transitions, and two-photon transitions. M.D. and E.Q. transitions are often also called "first-order forbidden" or simply "forbidden" transitions.

We shall not discuss second-order two-photon transitions here, but for completeness, we give the expressions for $(S_{mn})_o$ for M.D. and E.Q. transitions (Ref. 1), which must be used in Eq. (2.8) in place of the E.D. expressions (2.9) through (2.11):

$$\left(S_{mn}\right)_{o\ \mathrm{M.D.}} = \frac{h^2}{16\,\pi^2 m^2 c^2} \sum_{i,k} \left| \int \psi^*_{o_{n_i}} (\vec{r} \times \vec{\nabla})\, \psi_{o_{m_k}}\, d\tau \right|^2 =$$

$$= \left(C_{mn}\right)_{o\ \mathrm{M.D.}} \left(R^2_{mn}\right)_{o\ \mathrm{M.D.}} \text{, cm}^2 \text{ ,} \qquad (2.12a)$$

where:

$$\left(R^2_{mn}\right)_{o\ \mathrm{M.D.}} = \frac{h^2}{16\,\pi^2 m^2 c^2} \left| \int \psi^*_{o_{n_i'}} (\vec{r} \times \vec{\nabla})\, \psi_{o_{m_k'}}\, d\tau \right|^2 \text{, cm}^2 \text{ ,} \qquad (2.12b)$$

and:

$$\left(S_{mn}\right)_{o_{E.Q.}} = \frac{3\pi^2 \nu_{mn}^2}{10\,c^2} \sum_{i,k} \left| \int \psi^*_{o_{n_i}} (\vec{r}\,\vec{r})\, \psi_{o_{m_k}}\, d\tau \right|^2 =$$

$$= \left(C_{mn}\right)_{o_{E.Q.}} \left(R^2_{mn}\right)_{o_{E.Q.}} \text{ , cm}^2 \text{ ,} \qquad (2.13a)$$

where:

$$\left(R^2_{mn}\right)_{o_{E.Q.}} = \frac{3\pi^2}{10\,\lambda^2_{mn}} \left| \int \psi^*_{o_{n_i'}} (\vec{r}\,\vec{r})\, \psi_{o_{m_k'}}\, d\tau \right|^2 \text{ , cm}^2 \qquad (2.13b)$$

Here $(\vec{r}\,\vec{r})$ in Eq. (2.13) is a dyadic. As before, the subscripts $o = \text{elc} \equiv \Lambda$, $o = \text{vib} \equiv v$, or $o = \text{rot} \equiv J$, whatever applies.

In Chapter 3 we give explicit expressions for $(C_{mn})_o$ and $(R^2_{mn})_o$; here we shall simply assume that $(S_{mn})_o = (C_{mn})_o\,(R^2_{mn})_o$ is known. As mentioned, $(S_{mn})_o$ depends only on the central frequency ν_{mn} .

The transition probability $p_{mn}(\nu)$ that the emitted photon has a frequency ν in the range $\nu \pm \frac{1}{2}\,d\nu$ close to the resonant central frequency ν_{mn} may be defined formally by:

$$\frac{dp_{mn}(\nu)}{d\nu} = \frac{b(\nu, \nu_{mn}, \Delta\nu_{mn})}{\Delta\nu_{mn}} \text{ , Hz}^{-1} \qquad (2.14)$$

where the "spread" $\Delta\nu_{mn}$ is a constant, and the "shape function" $b(\nu,\nu_{mn},\Delta\nu_{mn})$ will be discussed more fully in Chapter 4. Then the average rate for the emission of photons of frequency ν close to the transition frequency ν_{mn} for a "broadened" transition $m \rightarrow n$ can be written:

$$\frac{dA_{mn}}{d\nu} = A^{\circ}_{mn} \frac{dp_{mn}(\nu)}{d\nu} = A^{\circ}_{mn} \frac{b(\nu,\nu_{mn},\Delta\nu_{mn})}{\Delta\nu_{mn}} \text{ , sec}^{-1}\text{ Hz}^{-1} \qquad (2.15)$$

Comparing Eq. (2.15) with (2.7), we see that we must have that:

$$\frac{dp_{mn}(\nu)}{d\nu} \equiv \frac{b(\nu,\nu_{mn},\Delta\nu_{mn})}{\Delta\nu_{mn}} = g(\nu,\nu_{mn},\Delta\nu_{mn}) \text{ , Hz}^{-1} \quad , \qquad (2.16)$$

Thus another way of looking at the broadening function $g(\nu,\nu_{mn},\Delta\nu_{mn})$ is to consider it to be the probability distribution of emitted photons to have a frequency ν in the vicinity of the central frequency ν_{mn} . We shall make use of relation (2.16) in Chapter 4 where we will evaluate $g(\nu,\nu_{mn},\Delta\nu_{mn})$ for specific cases by inverting G_{mn} as discussed in Chapter 1.

Because of Eq. (1.6), note that the shape function $b(\nu,\nu_{mn},\Delta\nu_{mn})$ and the spread $\Delta\nu_{mn}$ are so defined that:

$$\int_{\nu=0}^{\infty} \frac{b(\nu,\nu_{mn},\Delta\nu_{mn})}{\Delta\nu_{mn}}\, d\nu = \int_{\nu=0}^{\infty} g(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = 1 , \qquad (2.17a)$$

or since $\Delta\nu_{mn}$ is a constant:

$$\int_{\nu=0}^{\infty} b(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = \Delta\nu_{mn} , \text{ Hz} \qquad (2.17b)$$

As mentioned in Chapter 1, Eq. (2.17) expresses the so-called "law of spectroscopic stability" (Ref. 10). This law is also expressed by combining (2.15) and (2.17) in the relation:

$$\int_{\nu=0}^{\infty} \frac{dA_{mn}(\nu)}{d\nu}\, d\nu = A^{o}_{mn}(\nu_{mn}) , \text{ sec}^{-1} \qquad (2.18)$$

Summarizing our results for spontaneous photon emission, the general expression for the deexcitation rate is:

$$\frac{dA_{mn}}{d\nu} = \frac{64\,\pi^4 e^2 \nu_{mn}^3}{3hc^3}\left(\frac{S_{mn}}{w_m}\right)_o g_o(\nu,\nu_{mn},\Delta\nu_{mn}) =$$

$$= 2.6833 \times 10^{-21} \underset{(\mathrm{Hz}^3)}{\nu_{mn}^3} \underset{(\mathrm{cm}^2)}{\left(R_{mn}^2\right)_o} \left(\frac{C_{mn}}{w_m}\right)_o \underset{(\mathrm{Hz}^{-1})}{g_o(\nu,\nu_{mn},\Delta\nu_{mn})}\ ,\ \mathrm{sec}^{-1}\ \mathrm{Hz}^{-1} \tag{2.19}$$

where the subscript o must indicate whether the main transition is electronic, vibrational, or rotational, that is $o = \mathrm{elc}$, $o = \mathrm{vib}$, or $o = \mathrm{rot}$.

2.3 PHOTON ABSORPTION

The absorption cross-section $\sigma_{\substack{nm\\abs}}(\nu)$ is related to the spontaneous deexcitation rate A^{o}_{mn} and the broadening function $g_o(\nu_{mn},\nu,\Delta\nu_{mn})$ by the equivalent relations (Refs. 1 through 9):

$$\sigma_{\substack{nm\\abs}}(\nu) = \frac{\lambda^2_{mn}}{8\pi}\left(\frac{w_m}{w_n}\right)\frac{dA_{mn}(\nu)}{d\nu} = \frac{\lambda^2_{mn}}{8\pi}\left(\frac{w_m}{w_n}\right)A^{o}_{mn}\,\frac{dp_{mn}(\nu)}{d\nu} =$$

$$\sigma_{\substack{nm\\abs}}(\nu) = \frac{c^2}{8\pi\,\nu^2_{mn}}\left(\frac{w_m}{w_n}\right)A^{o}_{mn}\,g_o(\nu_{mn},\nu,\Delta\nu_{mn}) =$$

$$\sigma_{\substack{nm\\abs}}(\nu) = \frac{8\,\pi^3 e^2 \nu_{mn}}{3hc}\left(\frac{S_{mn}}{w_n}\right)_o g_o(\nu_{mn},\nu,\Delta\nu_{mn}) =$$

$$\boxed{\sigma_{\substack{nm\\abs}}(\nu) = 0.0960\,\underset{(Hz)}{\nu_{mn}}\left(\frac{C_{mn}}{w_n}\right)_o \underset{(cm^2)}{\left(R^2_{mn}\right)_o}\,\underset{(Hz^{-1})}{g_o(\nu,\nu_{mn},\Delta\nu_{mn})}\ ,\ cm^2} \tag{2.20}$$

The total absorption or excitation rate per molecule, K^{o}_{nm}, due to a fluence of photons $F_{\varphi}(\nu)$ whose frequencies are distributed over a range of values that cover the resonance width $\Delta\nu_{mn}$ in the region $\nu_{mn} - \frac{1}{2}\Delta\nu_{mn} < \nu < \nu_{mn} + \frac{1}{2}\Delta\nu_{mn}$, is related to A°_{mn} and $\sigma_{nm\,abs}$ by:

$$K^{\circ}_{nm} = \int_{\nu=0}^{\infty} \frac{dF_{\varphi}}{d\nu}\,\sigma_{nm\,abs}(\nu)\,d\nu =$$

$$K^{\circ}_{nm} = \frac{c^2}{8\pi\,\nu^2_{mn}} \left(\frac{dF_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}} \left(\frac{w_m}{w_n}\right) A^{\circ}_{nm} =$$

$$K^{\circ}_{nm} = \frac{8\,\pi^3\,e^2\,\nu_{mn}}{3hc} \left(\frac{C_{mn}}{w_n}\right)_{o} \left(R^2_{mn}\right)_{o} \left(\frac{dF_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}} =$$

$$K^{\circ}_{nm} = 0.0960\,\nu_{mn(\mathrm{Hz})} \left(\frac{C_{mn}}{w_n}\right)_{o} \left(R^2_{mn}\right)_{o\,(\mathrm{cm}^2)} \left(\frac{dF_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}\,(\mathrm{Hz}^{-1})}, \quad \mathrm{sec}^{-1}. \tag{2.21}$$

The omnidirectional photon flux or "fluence" is in units of photons · cm^{-2} · sec^{-1}, and is related to the photon density by:*

$$F_{\varphi}(\nu) = n_{\varphi}(\nu)\,c/\eta\,, \quad \frac{\text{photons}}{\mathrm{cm}^2 \cdot \mathrm{sec}}\,, \tag{2.22}$$

---

*We use the symbol F for fluence and the subscript φ to indicate we are dealing with photons. The molecular fluence would be designated by F_m, the electron fluence by F_e, etc. The word "flux" is often used instead of "fluence" in the older literature.

where $n_\varphi(\nu)$ is the density (cm^{-3}) of photons of frequency ν , c is the velocity of light (= 2.99793×10^{10} cm/sec), and η is the refractive index of the gas.

In a cavity, where the photon field is in equilibrium with the walls at temperature T, the photon fluence is given by (Ref. 6):

$$\frac{dF_\varphi}{d\nu} = \frac{\left(\frac{4\pi\ \nu^2}{c^2}\right)}{\exp\left(\frac{h\nu}{kT}\right) - 1} \ , \quad \frac{\text{photons}}{\text{cm}^2 \cdot \text{sec} \cdot \text{Hz}} \ , \qquad (2.23)$$

so that at equilibrium, the absorption rate per molecule in a gas-filled cavity is:

$$K^{o}_{\substack{nm\\ \text{equil.}\\ \text{cavity}}} = \frac{64\ \pi^4 e^2 \nu^3_{mn} \left(R^2_{mn}\right)_o \left(C_{mn}/w_n\right)_o}{3hc^3 \left\{\exp\left(\frac{h\nu_{mn}}{kT}\right) - 1\right\}} \ , \ \sec^{-1} \ , \qquad (2.24)$$

provided the presence of the absorbers does not significantly disturb the equilibrium photon frequency distribution given by Eq. (2.23).

For very monochromatic photons (such as those produced by a laser) whose frequency ν lies in the range $\nu_o - \frac{1}{2}\Delta\nu_o < \nu < \nu_o + \frac{1}{2}\Delta\nu_o$, where the "width" $\Delta\nu_o$ is very much smaller than the spread $\Delta\nu_{mn}$ about the resonance ν_{mn} , we have instead of Eq. (2.21) that:

$$\underset{\substack{\text{Monochromatic}\\ \text{Photons}\\ (\Delta\nu_o \ll \Delta\nu_{mn})}}{K^o_{nm}} = \frac{8\ \pi^3 e^2 \nu_{mn}}{3hc} \left(\frac{C_{mn}}{w_m}\right)_o \left(R^2_{mn}\right)_o F_\varphi \cdot g_o(\nu{=}\nu_o, \nu_{mn}, \Delta\nu_{mn})\ ,\ \text{sec}^{-1}\ , \qquad (2.25)$$

since in the integration of the function $dF_\varphi/d\nu$ over the small range $\Delta\nu_o$, we can replace the function $g_o(\nu, \nu_{mn}, \Delta\nu_{mn})$ by its value at $\nu = \nu_o$. F_φ is again the photon fluence (photons $\cdot$ cm^{-2} $\cdot$ sec^{-1}) of the very monochromatic photons.

In applied physics problems one often deals with a unidirectional photon stream Γ_φ (photons $\cdot$ cm^{-2} $\cdot$ sec^{-1}) rather than an omnidirectional photon fluence F_φ which occurs in cavities. For example the photon fluxes from lasers or light-beams received from distant stars are what we shall call photon "streams," designated by the symbol Γ_φ . Although the physical parameters Γ_φ and F_φ are by no means the same,* they both give the total number of crossings of photons (regardless of direction) through a 1 cm^2 area per second exposed to these fluxes. The excitation rate in a gas per molecule is therefore the same for molecules inside a flux Γ_φ or F_φ.** That is, for a beam of starlight incident on an absorbing gas:

$$\underset{(\text{starlight})}{K^o_{nm}} = 0.0960\ \underset{(\text{Hz})}{\nu_{mn}} \left(\frac{C_{mn}}{w_n}\right)_o \underset{(\text{cm}^2)}{\left(R^2_{mn}\right)_o} \left(\frac{d\Gamma_\varphi}{d\nu}\right)_{\nu=\nu_{mn}}\ ,\ \text{sec}^{-1}\ , \qquad (2.26)$$

---

*The unidirectional photon stream Γ_φ in a cavity with a homogeneous isotropic photon density n_φ is $\Gamma_\varphi = cn_\varphi/2\pi$ and thus in this case $\Gamma_\varphi = F_\varphi/2\pi$.

**It is assumed here also that the gas is isotropic and homogeneous.

where we simply replaced F_φ by Γ_φ in Eq. (2.25), and for a monochromatic laser beam:

$$\underset{\left(\Delta\nu_L \ll \Delta\nu_{mn}\right)}{\underset{\text{Laser}}{K^o_{nm}}} = 0.0960 \underset{(\text{Hz})}{\nu_{mn}} \left(\frac{C_{mn}}{w_n}\right)_o \underset{(\text{cm}^2)}{\left(R^2_{mn}\right)_o} \Gamma_L \underset{(\text{Hz}^{-1})}{g_o(\nu{=}\nu_L, \nu_{mn}, \Delta\nu_{mn})} \ , \ \text{sec}^{-1} \ , \tag{2.27}$$

where we replaced F_φ by Γ_L and ν_o by ν_L in Eq. (2.25).

Instead of the photon stream Γ_φ, the unidirectional intensity I_φ is often specified which is simply related to Γ_φ by:

$$I_\varphi(\nu) = h\nu \, \Gamma_\varphi(\nu) \quad , \quad \text{ergs} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \tag{2.28}$$

Similarly we can define the omnidirectional energy flux H_φ by the equation:

$$H_\varphi(\nu) = h\nu \, F_\varphi(\nu) \quad , \quad \text{ergs} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} \tag{2.29}$$

Substituting parameters H_φ or I_φ in Eqs. (2.26) and (2.27) instead of Γ_φ and Γ_L can of course be done directly by employing Eqs. (2.28) and (2.29).

Another transition parameter that is useful and which was first defined by Einstein, is the "induced absorption coefficient" B^{o}_{nm}:*

$$B^{o}_{nm} = \frac{c^3}{8\pi\, h\nu^3_{nm}} \left(\frac{w_m}{w_n}\right) A^{o}_{mn} = \frac{8\pi^3 e^2}{3h^2} \left(\frac{C_{mn}}{w_n}\right)_{o} \left(R^2_{mn}\right)_{o} =$$

$$= 4.342 \times 10^{35} \left(\frac{C_{mn}}{w_n}\right)_{o} \underset{(\mathrm{cm}^2)}{\left(R^2_{mn}\right)_{o}} , \quad \frac{\mathrm{cm}^3 \cdot \mathrm{Hz}}{\mathrm{erg} \cdot \mathrm{sec}} \qquad (2.30)$$

The relation between B^{o}_{nm} and K^{o}_{nm} is according to Eq. (2.21):

$$K^{o}_{nm} = B^{o}_{nm} \left(\frac{h\nu_{mn}}{c}\right) \left(\frac{dF_{\varphi}}{d\nu}\right)_{\nu=\nu_{nm}} = \frac{B^{o}_{nm}}{c} \left(\frac{dH_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}} , \quad \mathrm{sec}^{-1} \qquad (2.31)$$

---

*Also called the "Einstein B-Coefficient for Absorption," or simply the "Einstein B-Coefficient."

2.4 PHOTON STIMULATED EMISSION

So far we considered spontaneous emission and absorption parameters. The third important photon-molecule interaction is that of stimulated deexcitation in which a photon of resonant frequency $\nu = \nu_{mn}$, forces an excited molecule in state m to deexcite with the emission of a second photon of frequency $\nu = \nu_{mn}$.

The cross-section for stimulated emission, $\sigma_{\substack{nm\\ s.e.}}(\nu)$, is equal to the absorption cross-section $\sigma_{\substack{nm\\ abs}}(\nu)$, except for the factor (w_n/w_m) , that is (Ref 9):

$$\sigma_{\substack{mn\\ s.e.}}(\nu) = \left(\frac{w_n}{w_m}\right) \sigma_{\substack{nm\\ abs}}(\nu) = \frac{\lambda^2_{mn}}{8\pi} \frac{dA_{mn}(\nu)}{d\nu} =$$

$$\sigma_{\substack{mn\\ s.e.}}(\nu) = \frac{\lambda^2_{mn}}{8\pi} A^o_{mn}\, g_o(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{c^2}{8\pi\, \nu^2_{mn}} A^o_{mn}\, g_o(\nu,\nu_{mn},\Delta\nu_{mn}) =$$

$$\sigma_{\substack{mn\\ s.e.}}(\nu) = \frac{8\pi^3 e^2\, \nu_{mn}}{3hc} \left(\frac{C_{mn}}{w_m}\right)_o \left(R^2_{mn}\right)_o g_o(\nu,\nu_{mn},\Delta\nu_{mn}) =$$

$$\boxed{\sigma_{\substack{mn\\ s.e.}}(\nu) = 0.0960\, \underset{(Hz)}{\nu_{mn}} \left(\frac{C_{mn}}{w_m}\right)_o \underset{(cm^2)}{\left(R^2_{mn}\right)_o}\; \underset{(Hz^{-1})}{g_o(\nu,\nu_{mn},\Delta\nu_{mn})}\ ,\ cm^2} \tag{2.32}$$

The stimulated emission or deactivation rate D^o_{mn} due to a photon fluence F_φ $cm^{-2} \cdot sec^{-1}$ is analogously to Eq. (2.24) given by:

$$D^o_{mn} = \int_{\nu=0}^{+\infty} \frac{dF_\varphi}{d\nu} \, \sigma_{\underset{s.e.}{mn}}(\nu) \, d\nu = \frac{c^2}{8\pi \, \nu^2_{mn}} \left(\frac{dF_\varphi}{d\nu}\right)_{\nu=\nu_{mn}} A^o_{mn} =$$

$$D^o_{mn} = \frac{8\pi^3 e^2 \, \nu_{mn}}{3hc} \left(\frac{S_{mn}}{w_m}\right)_o \left(\frac{dF_\varphi}{d\nu}\right)_{\nu=\nu_{mn}} =$$

$$D^o_{mn} = 0.0960 \, \nu_{mn(Hz)} \left(\frac{C_{mn}}{w_m}\right)_o \left(R^2_{mn}\right)_o \left(\frac{dF_\varphi}{d\nu}\right)_{\nu=\nu_{mn}} \quad , \quad sec^{-1} \tag{2.33}$$

Again, another parameter called the "induced emission coefficient," B^o_{mn}, may be defined* which can be shown to be equal to the induced absorption coefficient multiplied by the weight ratio (Ref. 10), that is:

$$B^o_{mn} = \frac{w_n}{w_m} B^o_{nm} = 4.345 \times 10^{35} \left(\frac{C_{mn}}{w_m}\right)_o \underset{(cm^2)}{\left(R^2_{mn}\right)_o} \quad , \quad \frac{cm^3 \cdot Hz}{erg \cdot sec} \quad , \tag{2.34}$$

where B^o_{nm} was given by Eq. (2.30).

---

*Also called the "Einstein B-Coefficient for Emission," or simply the "Einstein B-Coefficient."

The deactivation rate D^{o}_{mn} due to a unidirectional beam of laser photons Γ_L of frequency $\nu = \nu_L$ is according to Eq. (2.27) then:

$$\left(D^{o}_{mn}\right)_{Laser} = 0.0960 \underset{(Hz)}{\nu_{mn}} \underset{(cm^{2})}{\left(\frac{C_{mn}}{w_m}\right)_{o}} \left(R_{mn}\right)^{2} \underset{(cm^{-2}\,\cdot\,sec^{-1})(Hz^{-1})}{\Gamma_L(\nu_L)\; g_o(\nu=\nu_L,\nu_{mn},\Delta\nu_{mn})}\ ,\ sec^{-1}\ , \qquad (2.35)$$

$$(\Delta\nu_L \ll \Delta\nu_{mn})$$

where the same argument applies for the integration over ν as was given for Eq. (2.25).

The parameters D^{o}_{mn} and B^{o}_{mn} are related by:

$$D^{o}_{mn} = B^{o}_{mn} \left(\frac{h\nu_{mn}}{c}\right)\left(\frac{dF_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}}\ ,\ sec^{-1} \qquad (2.36)$$

for the omnidirectional broad-spectrum case, or:

$$D^{o}_{mn} = B^{o}_{mn} \left(\frac{h\nu_{mn}}{c}\right) \Gamma_L\,(\nu_L) \cdot g_o(\nu=\nu_L,\nu_{mn},\Delta\nu_{mn})\ ,\ sec^{-1}\ , \qquad (2.37)$$

in case of the unidirectional monochromatic laser-beam Γ_L, or:

$$D^{\circ}_{mn} = B^{\circ}_{mn} \left(\frac{h\nu_{mn}}{c}\right)\left(\frac{d\Gamma_{\varphi}}{d\nu}\right)_{\nu=\nu_{mn}} , \text{ sec}^{-1} , \qquad (2,38)$$

for a unidirectional parallel beam Γ_{φ} of non-monochromatic photons, such as those coming from a distant star for example.

3. TRANSITION MATRIX ELEMENTS AND STRENGTH FACTORS

3.1 GENERAL CONSIDERATIONS

In this chapter we shall consider explicit expressions for th three main factors R^2_{mn}, C_{mn}, and w_m (or w_n) in the transition matrix element:

$$S_{mn} = C_{mn} R^2_{mn} = w_m \left| \vec{r}_{mn} \right|^2 = w_n \left| \vec{r}_{nm} \right|^2 , \text{ cm}^2 , \qquad (3.1)$$

where:

$$\left| \vec{r}_{mn} \right|^2 = \sum_k \left| \int \psi^*_{n_k} \vec{r} \, \psi_{m_i} \, d\tau \right|^2 , \text{ cm}^2 , \qquad (3.2)$$

and (R^2_{mn}) was defined by Eqs. (1.9), (1.14), and (1.17) for respectively electronic, vibrational, and rotational transitions. For convenience let us write $\left(R^2_{mn}\right)_o$ in the general form:

$$\left(R^2_{mn}\right)_o = \left| \int \psi^*_{o_{n_{k'}}} \vec{r}_o \, \psi_{o_{m_{i'}}} \, d\tau \right|^2_{\substack{i' \to k' \\ \text{reference}}} , \text{ cm}^2 , \qquad (3.3)$$

Here subscript o stands for elc, vib, or rot, whatever applies and the prime notation $'$ on the states k and i of respectively the levels m and n, indicate that the transition for which $\left(R^2_{mn}\right)_o$ is evaluated is for a particular allowed reference transition $i' \rightarrow k'$. In some problems, all allowed connections $i \rightarrow k$ are equally probable in which case the primes may be omitted. In some cases the reference transition (3.3) may be that of an idealized model, corresponding to for example a harmonic-oscillator approximation of the transition, or a transition in which spin is ignored. The factor C_{mn} then absorbs any discrepancies between the real and idealized transition. Sometimes R^2_{mn} is so chosen that $C_{mn}/(w_m w_n)$ is on the order of unity, so that R^2_{mn} is a coarse approximation for $S_{mn}/(w_m w_n)$, that is:

$$C_{mn} \sim w_m w_n \quad , \tag{3.4}$$

and:

$$R^2_{mn} \sim S_{mn}/(w_m w_n) \text{ , cm}^2 \tag{3.5}$$

The connection factor $\left(C_{mn}\right)_o$ which was defined in Chapter I for electronic, vibrational, and rotational transitions, can be written in the general form:

$$\left(C_{mn}\right)_o = \sum_{i,k} \left(C_{m_i n_k}\right)_o = \frac{\sum\limits_{i,k} \left| \int \psi^*_{o_{n_k}} \vec{r}_o \, \psi_{o_{m_i}} \, d\tau \right|^2}{\left| \int \psi^*_{o_{n_{k'}}} \vec{r}_o \, \psi_{o_{m_{i'}}} \, d\tau \right|^2_{\substack{i' \rightarrow k' \\ \text{reference}}}} \quad , \tag{3.6}$$

The parameter $C_{m_i n_k}$ appearing in Eq. (3.6), is called the "line-component" connection factor, while C_{mn} is referred to as the "line" connection factor. Similarly the parameters $S_{m_i n_k} = C_{m_i n_k} R^2_{mn}$ and $S_{mn} = C_{mn} R^2_{mn}$ are called the "line-component" strength and the "line" strength respectively. Note that because of the definition (3.6) we have for the reference line-component connection factor that:

$$C_{m_i', n_k'} = 1 \tag{3.7}$$

and the reference line-component strength:

$$S_{m_i', n_k'} = R^2_{mn} \tag{3.8}$$

The component lines due to transitions $m_i \rightarrow n_k$ all have, by definition, the same frequency, that is they are degenerate because of spatial quantization only. If due to the application of external fields, the line-components become resolved and have different frequencies, we must consider each such line separately and calculate separate values for the line's decay rate A_{mn}, and cross-sections σ_{nm} (absorption) or σ_{mn} (stimulated emission). The factor $(C_{mn})_o$ which previously represented the average of several degenerate component lines, now must be replaced by $\left(C_{m_i n_k}\right)_o$ = ([illegible])$_o$ since now the states m_i and n_k are no longer degenerate, and have become levels instead of states according to our definition of levels and states given in Chapter I.

The summation over allowed transitions between degenerate states m_i and n_k of levels m and n indicated in Eq. (3.6) is illustrated in Figure 2-1. If all connections (= upwards or downwards transitions) between the w_m spatially degenerate states of level m and the w_n spatially degenerate states of level n are allowed, we would have that $w_m = i$ and $w_n = k$ in the above, and the total number of possible non-identical connections would be $w_m w_n$. If furthermore all of these allowed connections were equally probable, we would have $C_{mn} = w_m w_n$, that is Eq. (3.4) would apply rigorously. In the general case, this situation does not apply however, that is neither all possible connections $w_m w_n$ are allowed, nor are all connections always equally probable (i.e., the primes on i and k in Eqs. (3.3) and (3.6) cannot be dropped).

As stated before, from quantum theory the so-called "principle of microscopic reversibility" can be proven, that is:

$$S_{m_i n_k} = S_{n_k m_i} , \qquad (3.9)$$

and thus:

$$R^2_{mn} = S_{m_i', n_k'} = S_{n_k', m_i'} \equiv R^2_{nm} , \qquad (3.10)$$

and therefore:

$$C_{m_i n_k} = C_{n_k m_i} \qquad (3.11)$$

Since the summation in Eq. (3.6) is symmetric in i and k, then also:

$$C_{mn} = C_{nm} \quad , \qquad (3.12)$$

and thus:

$$S_{mn} = S_{nm} \qquad (3.13)$$

A dimensionless transition parameter that is frequently used by absorption spectroscopists, is the so-called "oscillator strength" f_{nm} defined by:

$$f_{nm} = \frac{1}{3} \left(\frac{E_m - E_n}{Ry} \right) \frac{\left| \vec{r}_{nm} \right|^2_{elc}}{a_o^2} =$$

$$= \frac{8\,\pi^2 m_e}{3h} \nu_{mn} \left| \vec{r}_{nm} \right|^2_{elc} = \frac{8\,\pi^2 m_e\, \nu_{mn}}{3h} \left(R^2_{mn} \right)_{elc} \left(\frac{C_{mn}}{w_n} \right)_{elc} \qquad (3.14)$$

One often defines a similar "oscillator strength for emission" by:

$$f_{mn} = \frac{w_n}{w_m} f_{nm} = \frac{8\,\pi^2 m_e\, \nu_{mn}}{3h} \left(R_{mn} \right)^2_{elc} \left(\frac{C_{mn}}{w_m} \right)_{elc} \qquad (3.15)$$

In Eq. (3.14), the parameter Ry = Rydberg = $\frac{1}{2}\, e^2/a_o = 2.18 \times 10^{-11}$ ergs $= 13.605$ eV, and a_o = Bohr Radius $= h^2/(4\,\pi^2 m_e e^2) = 0.52917 \times 10^{-8}$ cm. The parameter m_e = electron mass $= 0.91083 \times 10^{-27}$ gm, and of course h = Planck's constant $= 6.6252 \times 10^{-27}$ erg-sec.

In atomic spectroscopy tables (Ref. 14), the strength for electric-dipole transitions is often expressed in units of $e^2 a_o^2 = 6.4589 \times 10^{-36}$ erg-cm^3, that is, writing $\mathscr{S}_{mn} = e^2\, S_{mn}$:

$$S_{mn} = \frac{\mathscr{S}_{mn}}{e^2} = a_o^2 \underset{(\text{units of } e^2 a_o^2)}{\mathscr{S}'_{mn}} \quad , \quad \text{cm}^2 \qquad (3.16)$$

where $\mathscr{S}'_{mn}$ is the tabulated strength (Ref. 14) expressed in units of $e^2 a_o^2$. Thus if we express S'_{mn} in units of a_o^2 ($= 0.2800 \times 10^{-16}$ cm^2), we have $S'_{mn} = \mathscr{S}'_{mn}$.

The strength of electric-quadrupole (E.Q.) transitions is usually tabulated in units of $e^2 a_o^4 = 1.8085 \times 10^{-52}$ erg-cm^5 (Ref. 14). That is:

$$\left(S_{mn}\right)_{E.Q.} = \frac{3\,\pi^2}{10\,\lambda_{mn}^2}\, \frac{\left(\mathscr{S}_{mn}\right)_{E.Q.}}{e^2} = \frac{3\,\pi^2 a_o^4}{10\,\lambda_{mn}^2} \underset{\left(\substack{\text{units of}\\ e^2 a_o^4}\right)}{\left(\mathscr{S}'_{mn}\right)_{E.Q.}} =$$

$$= \frac{2.3217 \times 10^{-33}}{\lambda_{mn}^2\ (\text{cm}^2)} \left(\mathscr{S}'_{mn}\right)_{E.Q.} \quad , \quad \text{cm}^2 \quad , \qquad (3.17)$$

where $(\mathscr{S}'_{mn})_{E.Q.}$ is in units of $e^2a_o^4$ (erg-cm^5), and λ_{mn} is in cm. Similarly, magnetic-dipole strengths are commonly given in units of $e^2h^2/(16\,\pi^2m_e^2c^2) = 8.5991 \times 10^{-41}$ erg-cm^3, and thus:

$$\left(S_{mn}\right)_{M.D.} = \frac{\left(\mathscr{S}_{mn}\right)_{M.D.}}{e^2} = \frac{h^2}{16\,\pi^2 m_e^2 c^2}\left(\mathscr{S}'_{mn}\right)_{M.D.} =$$

$$= 1.1711 \times 10^{-21} \underset{\left(\substack{\text{units of}\\ e^2h^2/(16\,\pi^2m_e^2c^2)}\right)}{\left(\mathscr{S}'_{mn}\right)_{M.D.}} \quad , \text{cm}^2 \,, \qquad (3.18)$$

where $(\mathscr{S}'_{mn})_{M.D.}$ is in units of $e^2h^2/(16\,\pi^2m_e^2c^2)$.

3.2 ELECTRONIC RADIATIVE TRANSITIONS

The matrix element $R^2_{\substack{mn \\ elc}}$ for an electronic transition between level $m = m(L_m, n_m, J_m)$ and a level $n = n(L_n, n_n, J_n)$, where L_k, n_k, J_k are quantum numbers for the orbital angular momentum, principal energy level, and total angular momentum (including spin) of an atom, has only been obtained exactly for the Hydrogen atom, whose wave functions can be represented by the Laguerre polynomials.* One finds for $n_m \neq n_n$ in this case that (Ref. 1):**

$$
\begin{aligned}
\left(R^2_{\substack{mn \\ elc}}\right)_H = {} & \left\{\frac{1}{(\ell_m + \ell_n)(\ell_m + \ell_n + 2)}\right\} \left\{\frac{(n_m + \ell_m)!\,(n_n + \ell_n)!}{(n_m - \ell_m - 1)!\,(n_n - \ell_n - 1)!}\right\} \cdot \\
& \cdot \left\{\frac{h^2}{4\pi^2 m_e e^2}\right\}^2 \left[\left\{\frac{1}{4(\ell_m + \ell_n)!}\right\}\left\{\frac{n_m - n_n}{n_m + n_n}\right\}^{(n_m + n_n)} \cdot \right. \\
& \cdot \left\{\frac{4 n_m n_n}{(n_m - n_n)^2}\right\}^{\left(\frac{\ell_m + \ell_n + 3}{2}\right)} \cdot \left\{ F(p_m; p_n; c; z) \quad + \right. \\
& \left. \left. - \left(\frac{n_m - n_n}{n_m + n_n}\right)^2 F(q_{mn}; q_{nm}; c; z) \right\} \right]^2 \cdot \delta(|\ell_m - \ell_n| - 1) \text{ , cm}^2 \qquad (3.19a)
\end{aligned}
$$

---

* The quantum number J will refer to the total angular momentum of the electrons of the atom here. For a molecule, J is the resultant angular momentum of the nuclei (the strongest effect usually) and the electrons.

**For a single electron, symbols ℓ and s are used instead of L and S by convention.

where we abbreviate:

$$p_k = -\left[n_k - \ell_k - 1\right] \tag{3.19b}$$

$$q_{ij} = -\left[n_i - \ell_j\right] \tag{3.19c}$$

$$c = \ell_m + \ell_n + 1 \tag{3.19d}$$

$$z = -\frac{4n_m n_n}{(n_m - n_n)^2} , \tag{3.19e}$$

and where the function F(a;b;c;z) is the "hypergeometric function" defined by:

$$F(a;b;c;z) = \sum_{n=0}^{\infty} k_n z^n = 1 + \frac{ab}{c} z + \frac{a(a+1)\,b(b+1)}{2!\,c(c+1)} z^2 + \ldots\ldots , \tag{3.20a}$$

in which:

$$k_n = \frac{a(a+1)\ldots\ldots(a+n-1)\;b(b+1)\ldots\ldots(b+n-1)}{(1.2\ldots\ldots n)\;c(c+1)\ldots\ldots(c+n-1)} \tag{3.20b}$$

$$k_0 = 1 \tag{3.20c}$$

The Dirac delta function $\left(\delta(x) = 1 \text{ for } x = 0\ ;\ \delta(x) = 0 \text{ for } x \neq 0\right)$ in Eq. (3.19a) specifies the selection rule:

$$\ell_n = \ell_m \pm 1 \tag{3.21a}$$

For convenience we shall adopt the convention that ℓ_m is the larger of ℓ_m and ℓ_n , and label it ℓ.* In this case (3.21a) reads:

$$\ell_m \equiv \ell = \ell_n + 1 \tag{3.21b}$$

Note that Eq. (3.19a) is independent of the quantum number J_k . Note also that Eq. (3.19a) is symmetric with respect to an interchange of (n_m,ℓ_m) and (n_n,ℓ_n) , (but not for $\ell_m \leftrightarrow \ell_n$ or $n_m \leftrightarrow n_n$ alone!), as it must be of course if R^2_{mn} is to be equal to R^2_{nm} . The Dirac delta function in (3.19a), that is condition (3.21), reduces the apparent number of independent variables in Eq. (3.19a) from four (n_m,n_n,ℓ_m,ℓ_n) to three (n_m,n_n,ℓ) of course, that is:

$$\left(R^2_{mn \atop elc}\right)_{\substack{\text{Hydrogenic} \\ \ell = \sup(\ell_m,\ell_n)}} = \left|\frac{1}{4\ell^2 - 1}\right| \left\{\frac{(n_m + \ell)!(n_n + \ell - 1)!}{(n_m - \ell - 1)!(n_n - \ell)!}\right\} .$$

---

*We shall denote this by $\ell = \sup(\ell_m,\ell_n)$.

$$\cdot \left\{ \frac{h^2}{4\pi^2 m_e e^2} \right\}^2 \left[\frac{1}{4(2\ell - 1)!} \left\{ \frac{n_m - n_n}{n_m + n_n} \right\}^{(n_m + n_n)} \cdot \right.$$

$$\cdot \left\{ \frac{4n_m n_n}{(n_m - n_n)^2} \right\}^{(\ell + 1)} \left\{ F(a_m; b_n; c; z) \right. +$$

$$\left. - \left(\frac{n_m - n_n}{n_m + n_n} \right)^2 F(a_m - 2; b_n; c; z) \right\} \Bigg]^2 , \ \mathrm{cm}^2 , \qquad (3.22a)$$

with:

$$a_m = -(n_m - \ell - 1) \qquad (3.22b)$$

$$b_n = -(n_n - \ell) \qquad (3.22c)$$

$$c = 2\ell \qquad (3.22d)$$

$$z = - \frac{4n_m n_n}{(n_m - n_n)^2} \qquad (3.22e)$$

In Table 3-1 adapted from Ref. 1, values for $\left(R^2_{\substack{mn \\ elc}}\right)_H$ are listed which were obtained via Eq. (3.22).

For transitions $n_m = n_n$, $\ell_m \neq \ell_n$, the matrix element is instead of (3.15a) given by (Ref. 1):

TABLE 3-1. VALUES OF R^2_{mn} FOR HYDROGENIC ATOMS IN UNITS OF $a_o^2 = 0.2880 \times 10^{-16}$ cm² (Adapted from Ref. 1)*

$n_m;\ell_m$	$n_n;\ell_n$	R^2_{mn} $(0.2800 \times 10^{-16}$ cm²)**
np	1s	$2^8\ 3^{-1}\ n^7(n - 1)^{2n-5}(n + 1)^{-2n-5}$
	2s	$2^{17}\ 3^{-1}\ n^7(n^2 - 1)(n - 2)^{2n-6}(n + 2)^{-2n-6}$
	3s	$2^8\ 3^6\ n^7(n^2 - 1)(n - 3)^{2n-8}(7n^2 - 27)^2(n + 3)^{-2n-8}$
	4s	$2^{26}\ 3^{-3}\ n^7(n^2 - 1)(n - 4)^{2n-10}(23n^4 - 288n^2 + 768)^2(n + 4)^{-2n-10}$
	5s	$2^8\ 3^{-3}\ 5^9\ n^7(n^2 - 1)(n - 5)^{2n-12}(91n^6 - 2545n^4 + 20625n^2 - 46875)^2(n + 5)^{-2n-12}$
nd	2p	$2^{19}\ 3^{-2}\ 5^{-1}\ n^9(n^2 - 1)(n - 2)^{2n-7}(n + 2)^{-2n-7}$
	3p	$2^{11}\ 3^8\ 5^{-1}\ n^9(n^2 - 1)(n^2 - 4)(n - 3)^{2n-8}(n + 3)^{-2n-8}$
	4p	$2^{30}\ 3^{-2}\ 5^{-2}\ n^9(n^2 - 1)(n^2 - 4)(n - 4)^{2n-10}(9n^2 - 80)^2(n + 4)^{-2n-10}$
	5p	$2^{11}\ 3^{-4}\ 5^8\ n^9(n^2 - 1)(n^2 - 4)(n - 5)^{2n-12}(67n^4 - 1650n^2 + 9375)^2(n + 5)^{-2n-12}$
nf	3d	$2^{13}\ 3^9\ 5^{-2}\ 7^{-1}\ n^{11}(n^2 - 1)(n^2 - 4)(n - 3)^{2n-9}(n + 3)^{-2n-9}$
	4d	$2^{38}\ 3^{-2}\ 5^{-2}\ 7^{-1}\ n^{11}(n^2 - 1)(n^2 - 4)(n^2 - 9)(n - 4)^{2n-10}(n + 4)^{-2n-10}$
	5d	$2^{13}\ 3^{-2}\ 5^{10}\ 7^{-2}\ n^{11}(n^2 - 1)(n^2 - 4)(n^2 - 9)(n - 5)^{2n-12}(11n^2 - 175)^2(n + 5)^{-2n-12}$

*Of course according to convention, the symbol s means $\ell_k = 0$; p means $\ell_k = 1$; d means ℓ_k 2; and f means $\ell_k = 3$.

**Tabulated values apply only if $n_m \neq n_n$.

$$\left(R^2_{mn \atop eic}\right)_{\substack{\text{Hydrogenic} \\ n_m = n_n}} = \frac{9}{4} \left| \frac{n_m^2 - \ell^2}{4\ell^2 - 1} \right| \left(\frac{h^2 n_m}{4\pi^2 m_e e^2} \right)^2 , \ \text{cm}^2 , \qquad (3.23)$$

where we already used the condition (3.21b) in Eq. (3.23), that is we choose ℓ to equal the larger of ℓ_m and ℓ_n and applied the selection rule for changes in ℓ_k. Equation (3.23) does not apply to the Hydrogen atom itself but is important in the Stark Effect, when the degeneracy of states at a level n_k is lifted.

Equations (3.22) and (3.23) can also be used for transitions in atoms which have closed inner cores of electrons and one outer electron, that is "Hydrogen-resembling" or "Hydrogenic" atoms such as the alkalis. In Table 3-2, values of R^2_{mn} calculated from Eq. (3.22) as well as from (3.23) are listed for specific transitions in Hydrogen or Hydrogenic atoms.

The energy levels E_k of Hydrogen are (Ref. 1):

$$E_k = E_{ion} - \left(\frac{m_e M_H}{m_e + M_H} \right) \frac{e^4 Z_H^2}{2\hbar^2 n_k^2} = 13.60 \left[1 - \frac{1}{n_k^2} \right] , \ \text{eV} , \qquad (3.24)$$

where m_e and M_H are the electron and Hydrogen atom mass, Z_H is the charge of the Hydrogen atom, and E_{ion} is the ionization energy = 13.60 eV. Emitted photons have of course the frequency $\nu = (E_m - E_n)/h$, with E_m and E_n in ergs (1 eV = 1.6021×10^{-12} ergs).

The quantum number ℓ_k in the above is the orbital quantum number of the single electron in the Hydrogen atom at level k. Since there is only

TABLE 3-2. VALUES FOR R_{mn}^2 IN UNITS OF a_0^2 (= 0.2800×10^{-16} cm^2) FOR SPECIFIC TRANSITIONS IN HYDROGENIC ATOMS (Adapted from Ref. 1)*

n \ m	2p	3p	4p	5p	6p	7p	8p
1s	0.111	0.00763	0.0015	0.00044	0.00017	0.000077	0.000039
2s	1.800	0.269	0.0260	0.006	0.0020	0.00087	0.00039
3s	0.060	4.63	0.475	0.051	0.013	0.0046	0.0020
4s	0.010	0.171	8.57	0.726	0.083	0.029	0.0082
5s	0.0035	0.026	0.336	1.125	0.937	0.212	0.0855
6s	0.0017	0.0094	0.046		19.82		
7s	0.0009	0.0046	0.022			27.14	
8s	0.0006	0.0026	0.012				35.58

n \ m	3d	4d	5d	6d	7d	8d
2p	0.6434	0.0463	0.0095	0.0031	0.00124	0.000584
3p	2.891	0.908	0.088	0.021	0.00738	0.00321
4p	0.049	6.86	1.219	0.135	0.0395	0.0125
5p	0.0066	0.144	11.81	1.42	0.185	0.0482
6p	0.0023	0.021		3.12		
7p	0.00086	0.008			25.44	
8p	0.00057	0.003				33.88

n \ m	4f	5f	6f	7f	8f
3d	1.66	0.11	0.022	0.00718	0.0031
4d	4.00	1.98	0.188	0.0441	0.015
5d	0.044	9.0			
6d	0.0051		15.29		
7d	0.0013			22.62	
8d	0.0006				31.06

*Of course according to convention, the symbol s means $\ell_k = 0$; p means $\ell_k = 1$; d means $\ell_k = 2$; and f means $\ell_k = 3$.

one electron in Hydrogen, we can set $\ell_k = L_k$ in the generalized language for multi-electronic atoms, if we consider Hydrogen as a special case in the class of all atoms. For the Russell-Saunders approximation which we shall assume to hold for all cases of interest, an electronic level k is completely specified by the three quantum numbers (n_k, L_k, J_k) for atoms or $(n_k, \Lambda_k, \Omega_k)$ for molecules (Refs. 1 and 2). Here:

$$L_k = |\vec{L}_k| = |\sum_i \vec{\ell}_{k_i}| \tag{3.25}$$

$$J_k = |\vec{J}_k| = |\vec{L}_k + \vec{S}_k| \tag{3.26}$$

$$\vec{S}_k = \sum_i \vec{s}_{k_i} \tag{3.27}$$

$$\Lambda_k = |\vec{L}_k \cdot \vec{a}| \tag{3.28}$$

$$\Omega_k = \Lambda_k + \Sigma_k \tag{3.29}$$

$$\Sigma_k = \vec{S}_k \cdot \vec{a} \tag{3.30}$$

$$S_k = |\vec{S}_k| \tag{3.31}$$

The summations in (3.25) and (3.27) are over the i electrons of the atom or molecule, $\vec{\ell}_{k_i}$ is the orbital momentum quantum vector and $\vec{s}_{k_i}$ the spin quantum vector of electron i of the atom or molecule* whose energy level is designated by k.** The vector $\vec{a}$ is a unit vector along the principal axis of the molecule, which for a diatomic molecule for example passes through the centers of the nuclei. Actually only for linear molecules are Λ_k and Σ_k well defined and useful for describing quantum states. The appropriate quantum numbers for nonlinear molecules will be discussed later.

Quantization rules dictate that L_k and Λ_k can only take on integral values, while S_k and Σ_k can have half-integral values in addition to integral values. From the definitions (3.26) and (3.29) we see then that J_k can only take on positive integer or half-integer values, the largest of which is $(J_k)_{max} = |\vec{L}_k| + |\vec{S}_k|$ and the smallest of which equals $(J_k)_{min} = |\vec{L}_k|$ or $(J_k)_{min} = |\vec{S}_k|$ whichever is smaller. On the other hand Ω_k for molecules can take on both positive and negative integer or half-integer values if Σ_k is larger than Λ_k.

It can be shown (Ref. 1) that the atomic level k specified by the set of quantum numbers (n_k, L_k, J_k) has $(2J_k + 1)$ degenerate states of equal energy due to the fact that a given value J_k can be obtained by $(2J_k + 1)$ different vectorial combinations of differently oriented vectors $\vec{L}_k$ and $\vec{S}_k$. Thus the "degeneracy" or "statistical" weight w_k of atomic level k is given by the formula:

---

* For molecules, the summation of angular momenta must also include the momentum of the rotating nuclei. We shall discuss this later and not consider it here however.

**By "quantum vectors" we shall mean here the integrally or half-integrally valued angular momenta or spins with their directions in atomic units of $\hbar$.

$$(w_k)_{\substack{\text{atom}\\(L_k,J_k)}} = 2J_k + 1 \qquad (3.32)$$

If we consider the multiplet splitting (see below) due to spin to be negligibly small (as is usually the case) and assume that the sublevels with different values of S (and therefore J) belong to one energy level or "term" (n_k, L_k), the statistical weight (= number of substates) is however instead of (3.32):

$$(w_k)_{\substack{\text{atom}\\(S_k,L_k)}} = (2S_k + 1)(2L_k + 1) \qquad (3.33)$$

For linear molecules (which include all diatomic molecules), there is a twofold degeneracy with respect to the quantum number Λ_k for each level (n_k, Λ_k) if $\Lambda_k \neq 0$, since there are two possible spatial directions for $\vec{L}_k$ giving the same value for Λ_k (see Eq. (3.26)). If $\Lambda_k = 0$, there is no degeneracy with respect to Λ_k. There is a $(2S_k + 1)$ degeneracy (= multiplicity) due to the spin S_k, if we consider the small energy differences of the members of the multiplets insignificant and treat them as states of the level or term (n_k, Λ_k). Thus:

$$\boxed{(w_k)_{(S_k,\Lambda_k)} = 2(2S_k + 1) \text{ , if } \Lambda_k \neq 0} \qquad (3.34a)$$

Linear Molecules

$$\boxed{(w_k)_{(S_k,\Lambda_k)} = (2S_k + 1) \text{ , if } \Lambda_k = 0} \qquad (3.34b)$$

Linear Molecules

For nonlinear molecules, one can no longer describe the electronic levels adequately via the quantum number Λ (with levels Σ, Π, Δ, Φ, etc.). Instead the electronic levels are described by their symmetry properties (Refs. 10 through 13). For example designations A, B and A', A'' are used to describe the non-degenerate symmetric and antisymmetric levels of molecules who have symmetries of respectively the C_2 and C_s point groups; for molecules with symmetries of point groups C_{2v} and C_{2h}, the four possible non-degenerate levels are designated A_1, A_2, B_1, B_2 and A_g, A_u, B_u, B_g respectively (Ref. 11). Molecules with more symmetry such as those with point group C_{3h} can have, in addition to non-degenerate levels A', A'', also doubly degenerate levels E' and E'', while molecules with even more symmetry (e.g., those belonging to point group T_d or O_h) have in addition to singly degenerate levels A, B and doubly degenerate levels E, also triply degenerate levels that are designated by the symbol F.

For the purpose of determining the statistical weight of the electronic level of a nonlinear (polyatomic) molecule then, we may write:

$$\boxed{w_{k(S_k, X_k)\,(\text{nonlinear polyatomic molecule})} = d_{X_k}\,(2S_k + 1),} \qquad (3.35a)$$

where X = A, B, E, F, and where:*

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*In Herzberg's tables of molecular properties (Refs. 2 and 11), electronic levels for nonlinear polyatomic molecules are designated by one of the symbols A, B, E, F, hence the value of d_{X_k} is quickly determined.

$$d_{A_k} = 1 \tag{3.35b}$$

$$d_{B_k} = 1 \tag{3.35c}$$

$$d_{E_k} = 2 \tag{3.35d}$$

$$d_{F_k} = 3 \tag{3.35e}$$

The spin degeneracy or multiplicity $(2S_k + 1)$ is usually written as a left superscript on the level designation A, B, E or F for nonlinear molecules. For example $^2A'$ is a level with $S = 1/2$ and species A', while ^3A_u has $S = 1$ and species A_u .

Comparing (3.33) with (3.34) and (3.35), we see that atomic states are more degenerate than molecular states. The reason for finding less degeneracy in a molecule then in an atom is due to the fact that a molecule is less symmetric (as "seen" by the electrons) than an atom and therefore it has more energy levels for a given number of states.[*]

Both for atoms and molecules, energy levels with the same values of n_k and L_k or n_k and Λ_k (or X_k for non-linear molecules[**]) are called

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[*] See Chapter 1 for our definition of "levels" and "states."

[**] We shall keep the designation Λ_k in what follows for all molecules even though it has little meaning for nonlinear molecules. For the latter we shall assume that Λ_k stands for X_k and that the value for Λ_k equals $\left(d_{X_k} - 1\right)$.

"terms" (Ref. 1), while the various levels of a term (n_k, L_k) or (n_k, Λ_k) with different values for J_k or Ω_k are called the term's sublevels. The assembly of allowed transitions between the various sublevels of one term say $(n_m, \Lambda_m$ or $L_m)$ and the various sublevels of another term say $(n_n, \Lambda_n$ or $L_n)$ is called a "multiplet."

Because of the selection rules, there are for an atom $(2S + 1)$ multiplet members if $S > L$, and $(2L + 1)$ multiplet members if $L > S$. The number $(2S + 1)$ is called the "multiplicity" of the multiplet even in case $L > S$. If $2S + 1 = 1$, $(S = 0)$, the multiplet is called a "singlet"; if $2S + 1 = 2$, $(S = 1/2)$ it is called a "doublet" ; if $2S + 1 = 3$, $(S = 1)$ it is called a "triplet," etc.

For molecules, provided $\Lambda \neq 0$, the multiplicity is always equal to $(2S + 1)$, that is it is equal to the number of Σ values, regardless of whether S is smaller or larger than Λ. If $\Lambda = 0$, the multiplicity is 1, that is we have a singlet.

For atoms (including of course the Hydrogen atom), the connection factors $C_{mn} = C\Big((n_m, L_m, J_m) \rightarrow (n_n, L_n, J_n)\Big)$ for dipole transitions are given by (Ref. 1):

$$C_{\substack{mn\\ elc}}\begin{pmatrix} J_m \rightarrow J_n = J_m - 1 \\ L_m \rightarrow L_n = L_m - 1 \\ S_m \rightarrow S_n = S_m \end{pmatrix} = \left| \frac{(J_m + 1 + S_m + L_m)(J_m + S_m + L_m)(J_m - 1 - S_m + L_m)(J_m - S_m + L_m)}{4J_m} \right| \qquad (3.36a)$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m\\ L_m\rightarrow L_n=L_m-1\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(2J_m+1)(J_m+1+S_m+L_m)(J_m+1+S_m-L_m)(J_m-S_m+L_m)(S_m+L_m-J_m)}{4J_m(J_m+1)}\right| \tag{3.36b}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m+1\\ L_m\rightarrow L_n=L_m-1\\ S_n\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(J_m+2+S_m-L_m)(J_m+1+S_m-L_m)(S_m+L_m-J_m-1)(S_m+L_m-J_m)}{4(J_m+1)}\right| \tag{3.36c}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m-1\\ L_m\rightarrow L_n=L_m\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(J_m+S_m-L_m)(J_m-S_m+L_m)(J_m+1+S_m+L_m)(S_m+L_m-J_m+1)}{4J_m}\right| \tag{3.36d}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m\\ L_m\rightarrow L_n=L_m\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(2J_m+1)\left\{J_m(J_m+1)\ -\ S_m(S_m+1)\ +\ L_m(S_m+1)\right\}^2}{4J_m(J_m+1)}\right| \tag{3.36e}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m+1\\ L_m\rightarrow L_n=L_m\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(J_m+1-S_m+L_m)(J_m+1+S_m-L_m)(J_m+2+S_m+L_m)(S_m+L_m-J_m)}{4(J_m+1)}\right| \tag{3.36f}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m-1\\ L_m\rightarrow L_n=L_m+1\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(J_m+S_m-L_m)(J_m-1+S_m-L_m)(S_m+L_m-J_m+1)(S_m+L_m-J_m+2)}{4J_m}\right| \tag{3.36g}$$

$$C_{\substack{mn\\elc}}\begin{pmatrix}J_m\rightarrow J_n=J_m\\ L_m\rightarrow L_n=L_m+1\\ S_m\rightarrow S_n=S_m\end{pmatrix}=\left|\frac{(2J_m+1)(J_m+1-S_m+L_m)(J_m+2+S_m+L_m)(J_m+S_m-L_m)(S_m+L_m-J_m+1)}{4J_m(J_m+1)}\right| \tag{3.36h}$$

$$C_{\substack{mn\\ elc}}\begin{pmatrix} J_m \rightarrow J_n = J_m - 1 \\ L_m \rightarrow L_n = L_m + 1 \\ S_m \rightarrow S_n = S_m \end{pmatrix} = \left| \frac{(J_m+1-S_m+L_m)(J_m+2-S_m+L_m)(J_m+2+S_m+L_m)(J_m+3+S_m+L_m)}{4(J_m+1)} \right| \tag{3.36i}$$

For (electric) quadrupole transitions the connection factors are more complicated. We shall not write them out completely here; they may be obtained however from the formulas given by Condon & Shortley (Ref. 1) via the relations:

$$C_{\substack{mn\\ elc\\ E.Q.}}\begin{pmatrix} J_m \rightarrow J_n = J_m \\ L_m \rightarrow L_n \\ S_m \rightarrow S_n = S_m \end{pmatrix} = \frac{2}{3}\, J_m(J_m+1)(2J_m+1)(2J_m-1)(2J_m+3)\left(D^2 \Big/ R^2_{\substack{mn\\ E.Q.}} \right) \tag{3.37a}$$

$$C_{\substack{mn\\ elc\\ E.Q.}}\begin{pmatrix} J_m \rightarrow J_n = J_m - 1 \\ L_m \rightarrow L_n \\ S_m \rightarrow S_n = S_n \end{pmatrix} = \frac{1}{2}\, J_m(J_m+1)(J_m-1)(2J_m+1)(2J_m-1)\left(E^2 \Big/ R^2_{\substack{mn\\ E.Q.}} \right) \tag{3.37b}$$

$$C_{\substack{mn\\ elc\\ E.Q.}}\begin{pmatrix} J_m \rightarrow J_n = J_m - 2 \\ L_m \rightarrow L_n \\ S_m \rightarrow S_n = S_m \end{pmatrix} = J_m(J_m-1)(2J_m+1)(2J_m-1)(2J_m-3)\left(F^2 \Big/ R^2_{\substack{mn\\ E.Q.}} \right) \tag{3.37c}$$

Here D^2, E^2 and F^2 (see Ref. 1, pp 95 and 96 for their definitions) each have three possible values depending on whether $\Delta J = J_m - J_n = 0, -1, -2$, which are the three allowed possible changes in J for a quadrupole transition.

It should be remarked that the connection factors (3.36) are applicable to both electric as well as magnetic dipole transitions. The relations (3.36) for C_{mn} apply to all atoms in contrast to the expression (3.22) for R^2_{mn} which applies strictly only to Hydrogenic atoms.

In many problems, the small energy differences between levels of various J values is small and we want to consider the totality of transitions from one term (n_mL_m) to another term (n_nL_n). In that case, summing the specific connection factors in (3.36) over the various allowed values for J_m and J_n, we find (Ref. 1, p. 239) for dipole transitions:

$$C_{mn}\begin{pmatrix} L_m \rightarrow L_n = L_m - 1 \\ S_m \rightarrow S_n = S_m \end{pmatrix} = (2S_m+1)(2L_m+1)L_m(2L_m-1) \qquad (3.38a)$$

$$C_{mn}\begin{pmatrix} L_m \rightarrow L_n = L_m \\ S_m \rightarrow S_n = S_m \end{pmatrix} = (2S_m+1)(2L_m+1)L_m(L_m+1) \qquad (3.38b)$$

$$C_{mn}\begin{pmatrix} L_m \rightarrow L_n = L_m + 1 \\ S_m \rightarrow S_n = S_m \end{pmatrix} = (2S_m+1)(2L_m+1)(L_m+1)(2L_m+3) \qquad (3.38c)$$

It should be noted that we have only provided transition connection factors in which the spin quantum number $S_n = S_m$ in Eqs. (3.36) and (3.38). It has been found that transitions in which $S_m \neq S_n$ are very weak and often do not exist at all, hence in first approximation one may assume that transition elements for such transitions are zero. For electronic transitions in general then, the rules are that:

$$\Delta S = 0 \tag{3.39}$$

$$\Delta L = L_m - L_n = 0 \text{ , provided } \vec{L}_m \neq \vec{L}_n \text{ , or} \tag{3.40a}$$

$$\Delta L = \pm 1 \tag{3.40b}$$

$$\Delta J = J_m - J_n = 0 \text{ , provided } J_m = J_n \neq 0 \text{ , or} \tag{3.41a}$$

$$\Delta J = \pm 1 \tag{3.41b}$$

Whereas, as remarked, the factors C_{mn} apply to any atom, the expression R^2_{mn} in (3.19) or (3.22) applies strictly only to Hydrogenic atoms. A general expression for R^2_{mn} applying to any atom is not available and only special calculations for R^2_{mn} of some selected atoms of the periodic table employing various approximations are available in the general literature.

An approximate relation for R^2_{mn} for multi-electron atoms may be obtained by using the hydrogenic relation (3.22), setting $\ell = L$, and assuming that: (a) only the outermost electron of the multi-electron atom makes a transition, and (b) that this transition takes place in an electric central field potential whose strength is $Z_{eff}e^2/r$ instead of e^2/r as is the case for the Hydrogen atom. Z_{eff} is then the average effective nuclear charge that the outer electron experiences after we take into account the screening effect by the inner electrons. Assumption (b) is not too bad, but the assumption that only one outer electron in the valence shell is jumping is more serious since in reality a radiative transition in a multi-electron atom involves adjustments by all the valence electrons. However the "outer-jumping-electron approximation" appears to give fair results for many atoms and suffices for order-of-magnitude calculations, if no other relations are available.

The effective charge Z_{eff} may be determined from the experimentally measured ionization energy E_{ion} by the equation:

$$Z_{eff} = n_v \left(E_{ion}/Ry \right)^{1/2} \quad , \qquad (3.42)$$

where:

n_v = Principal Quantum Number of Jumping Valence Electron ($n_v \leq n_n, n_m$)

Ry = Rydberg constant = 13.605 eV

E_{ion} = Ionization Potential, eV

In Table 3.3, values of Z_{eff} and n_v are listed for the first thirty-six elements of the periodic table.

TABLE 3-3. PRINCIPAL QUANTUM NUMBER OF THE EMITTING ELECTRON, IONIZATION POTENTIAL, EFFECTIVE NUCLEAR CHARGE, AND SHIELDING CONSTANTS FOR THE FIRST 36 ELEMENTS OF THE PERIODIC TABLE

Element	Atomic Number, $Z = N$	Valence-Band Principal Quantum Number, n_v	Ionization Energy, E_{ion} ev	Effective Nuclear Charge, $n_v \sqrt{\frac{E_i}{Ry}} = Z_{eff}$
H	1	1	13.595	1.00
He	2	1	24.580	1.35
Li	3	2	5.390	1.25
Be	4	2	9.320	1.66
B	5	2	8.296	1.56
C	6	2	11.264	1.82
N	7	2	14.54	2.07
O	8	2	13.614	2.00
F	9	2	17.42	2.26
Ne	10	2	21.559	2.52
Na	11	3	5.138	1.84
Mg	12	3	7.644	2.25
Al	13	3	5.984	1.99
Si	14	3	8.149	2.32
P	15	3	10.43	2.62
S	16	3	10.357	2.62
Cl	17	3	13.01	2.93
A	18	3	15.755	3.23
K	19	4	4.339	2.26
Ca	20	4	6.111	2.68
Sc	21	4	6.56	2.78
Ti	22	4	6.83	2.84
V	23	4	6.738	2.82
Cr	24	4	6.76	2.82
Mn	25	4	7.432	2.96
Fe	26	4	7.896	3.05
Co	27	4	7.86	3.04
Ni	28	4	7.633	3.00
Cu	29	4	7.723	3.01
Zn	30	4	9.391	3.32
Ga	31	4	5.97	2.66
Ge	2	4	8.13	2.09
As	33	4	10.05	3.43
Se	34	4	9.750	3.38
Br	35	4	11.84	3.73
Kr	36	4	13.996	4.06

Applying the above indicated modifications to Eq. (3.23) for the case that $n_m = n_n$ yields then:

$$\left(R^2_{mn}\right)_{\substack{\text{Atom}\\ n_m = n_n \geq n_v \\ L = \sup(L_m, L_n)}} \approx \frac{9}{4} \left| \frac{n_m^2 - L^2}{4L^2 - 1} \right| \left(\frac{h^2 n_m}{4\pi^2 Z_{eff} m_e e^2} \right)^2 =$$

$$= 0.595 \times 10^{-16} \left| \frac{n_m^2 - L^2}{4L^2 - 1} \right| \frac{n_m^2}{Z^2_{eff}} \quad , \quad \text{cm}^2 \quad , \qquad (3.43)$$

where we wrote out the value for the square of the Bohr radius a_o , that is:

$$a_o^2 = \left(\frac{h^2}{4\pi^2 m_e e^2} \right)^2 = \left(0.52917 \times 10^{-8} \text{ cm}\right)^2 = 0.2800 \times 10^{-16} \text{ cm}^2 \ , \qquad (3.44)$$

which is the natural unit for atomic cross-sections.

For transitions in which $n_n \neq n_m$, we modify the hydrogenic equation (3.22) in a similar manner to serve as an approximation for multi-electron atoms. The result is as follows.

$$\left(R^2_{mn}\right)_{\substack{\text{Atom}\\ n_m \neq n_n \\ n_m, n_n \geq n_v \\ L = \sup(L_m, L_n)}} \approx \frac{0.2800 \times 10^{-16}}{Z^2_{\text{eff}}} \left| \frac{1}{4L^2-1} \right| \left\{ \frac{(n_m+L)!\,(n_m+L-1)!}{(n_m-L-1)!\,(n_m-L)!} \right\} \cdot$$

$$\cdot \left[\frac{1}{4(2L-1)!} \left\{ \frac{n_m-n_n}{n_m+n_n} \right\}^{(n_m+n_n)} \left\{ \frac{4n_m n_n}{(n_m-n_n)^2} \right\}^{(L+1)} \cdot \right.$$

$$\left. \cdot \left\{ F(a_m\,;\, b_n\,;\, c\,;\, z) - \left(\frac{n_m-n_n}{n_m+n_n} \right)^2 F(a_m-2\,;\, b_n\,;\, c\,;\, z) \right\} \right]^2 ,\ \text{cm}^2 \tag{3.45a}$$

Here we used (3.44). The functions F(a;b;c;z) are again the hypergeometric functions defined by Eq. (3.20) in which the parameters are defined by:

$$a_m = -(n_m-L-1) \tag{3.45b}$$

$$b_n = -(n_n-L) \tag{3.45c}$$

$$c = 2L \tag{3.45d}$$

$$z = \frac{4n_m n_n}{(n_m-n_n)^2} \tag{3.45e}$$

For molecules, the electric field in which the valence electrons move is not radially symmetric as it is for atoms, hence the "central field approximation" on which (3.43) and (3.45) are based and which is fair for atoms, is somewhat uncertain for molecules. Nevertheless in lieu of a detailed calculation using approximate molecular orbital wave functions (which are available for only a few molecules), we may use expressions similar to (3.43) and (3.45) as a coarse approximation:

$$\boxed{\begin{aligned}\left(R^2_{mn}\right)_{\begin{pmatrix}\text{elc}\\ \text{molecule}\\ \Lambda = \sup(\Lambda_m,\Lambda_n)\\ n_m = n_n\end{pmatrix}} &\approx 0.595 \times 10^{-16}\left(\frac{n_m}{Z_{\text{eff}}}\right)^2 \left|\frac{n_m^2 - \Lambda^2}{4\Lambda^2 - 1}\right| = \\ &= 0.595 \times 10^{-16}\left(\frac{n_m}{n_v}\right)^2 \left(\frac{Ry}{E_{\text{ion}}}\right)\left|\frac{n_m^2 - \Lambda^2}{4\Lambda^2 - 1}\right| \quad, \quad \text{cm}^2\end{aligned}} \tag{3.46}$$

$$\boxed{\begin{aligned}\left(R^2_{mn}\right)_{\begin{pmatrix}\text{elc}\\ \text{molecule}\\ \Lambda = \sup(\Lambda_m,\Lambda_n)\\ n_m \neq n_n\end{pmatrix}} &\approx \frac{0.2800 \times 10^{-16}}{n_v^2\,\left|4\Lambda^2 - 1\right|}\left(\frac{Ry}{E_{\text{ion}}}\right)\left\{\frac{(n_m+\Lambda)!\,(n_m+\Lambda-1)!}{(n_m-\Lambda-1)!\,(n_m-\Lambda)!}\right\} \cdot \\ &\left[\frac{1}{4(2\Lambda-1)!}\left\{\frac{n_m - n_n}{n_m + n_m}\right\}^{(n_m + n_n)} \cdot \left\{\frac{4n_m n_n}{(n_m - n_n)^2}\right\}^{(\Lambda + 1)} \cdot \right. \\ &\left. \cdot\left\{F(a_m\ ;\ b_n\ ;\ c\ ;\ z) - \left(\frac{n_m - n_n}{n_m + n_n}\right)^2 F(a_m - 2\ ;\ b_n\ ;\ c\ ;\ z)\right\}\right]^2 , \quad \text{cm}^2\end{aligned}} \tag{3.47a}$$

Here we used Eq. (3.42) and as before Ry = 13.605 eV , while:

$$a_m = -(n_m - \Lambda - 1) \qquad (3.47b)$$

$$b_n = -(n_n - \Lambda) \qquad (3.47c)$$

$$c = 2\Lambda \qquad (3.47d)$$

$$z = \frac{4n_n n_m}{(n_n - n_m)^2} \qquad (3.47e)$$

We substituted Λ for L in Eq. (3.47) which is actually not quite correct since $L = |\vec{L}|$, while $\Lambda = |\vec{L} \cdot \vec{a}|$ (see Eqs. (3.25) through (3.31). However in most cases of interest we are considering only small integer values of Λ in which case $\Lambda \sim L$.* The real difficulty here is of course that we are trying to fit a radially symmetric solution to a non-radially symmetric problem. The approximations (3.46) and (3.47) can therefore at best be expected to give only order-of-magnitude answers, which are still better than no answers at all.

The parameter Z_{eff} , n_v , and E_{ion} appearing in Eqs. (3.46) and (3.47) were defined in Eq. (3.42). In Table 3-4 values for Z_{eff} , E_{ion} and

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*By convention, for linear molecules, levels with $\Lambda = 0$ are designated Σ , levels with $\Lambda = 1$ are designated Π , levels with $\Lambda = 2$ are designated Δ , and levels with $\Lambda = 3$ are designated Φ . For nonlinear molecules, which are designated by the symmetry species A , B , E , and F , we may set $\Lambda = 0$ for A and B species, $\Lambda = 1$ for E species and $\Lambda = 2$ for F species as an approximation.

TABLE 3-4. EFFECTIVE CHARGE NUMBERS OF MISCELLANEOUS MOLECULES

Molecule	Ionization Energy, E_{ion} (eV)	Valence-Band Equivalent Principal Quantum Number, n_v	Equivalent Principal Quantum Number for Lowest Excitations, n_m	$Z_{eff} = n_v \sqrt{\frac{E_{ion}}{Ry}}$
H_2	15.422	1	2	1.065
O_2	12.2	3	3	2.842
N_2	15.576	3	3	3.211
F_2	15.7	3	4	3.224
$C\ell_2$	11.48	4	4	3.676
CO	14.009	3	3	3.091
$HC\ell$	12.74	3	4	2.904
HF	15.77	2	3	2.154
NO	9.25	3	3	2.475
OH	13.17	2	2	1.968
HS	10.50	3	3	2.636
H_2O	12.618	2	3	1.927
CO_2	13.769	4	4	4.026
N_2O	12.893	4	4	3.895
NO_2	9.78	4	4	3.393
SO_2	12.34	4	4	3.811
H_2S	10.472	3	4	2.633
HCN	13.91	3	3	3.035
OCS	11.24	4	4	3.637
CS_2	10.079	5	5	4.305
O_3	12.800	4	4	3.881
NH_3	10.154	2	3	1.728
CH_4	12.99	2	3	1.955

equivalent n_v numbers are listed for some of the more common molecules. For n_m and n_n in Eqs. (3.45) and (3.47) we must take values that correspond to assuming that the nuclei making up the molecule are merged and have a total electric charge and electron cloud equal to that of an atom whose charge and electron cloud are the same as the sum of the charges and electrons of the nuclei. In most problems if n_n is the lower of n_m and n_n, we have that $n_n = n_v$, that is it equals the equivalent principal quantum number of the valence orbital based on the assumption that the nuclei are merged.

For the purpose of obtaining order-of-magnitude estimates of the transition elements of purely electronic transitions, $R^2_{mn_{elc}}$, it is sometimes useful to consider the transitions of an ideal three-dimensional harmonic oscillator model in which an electron is assumed to oscillate in a three-dimensional potential well, experiencing a restoring force whose magnitude is proportional to the square of the displacement of the electron from the center of the well, that is $F = k_o r^2$ instead of $F = Ze^2/r^2$. The electric dipole transition element R^2_{mn} for the three-dimensional harmonic oscillator has the very simple form (Refs. 4 and 6):

$$\left(R^2_{mn}\right)_{H.O.} = \frac{\left(\frac{m+n+1}{2}\right)h}{8\pi^2 m_e \nu_o} = a_o^2 \left(\frac{Ry}{E_o}\right)\left(\frac{m+n+1}{2}\right), \ \text{cm}^2, \qquad (3.48)$$

where m_e is the electron mass and ν_o is the fundamental frequency of the harmonic oscillation which is related to the force constant k_o by:

$$\nu_o^2 = k_o/m_e \tag{3.49}$$

E_o is given by $E_o = h\nu_o$, Ry is the Rydberg constant (=13.605 eV), and as before, a_o is the Bohr radius (= 0.52917×10^{-8} cm).

The indices m and n give the order of the allowed oscillating levels. The allowed energy levels of the three-dimensional harmonic oscillator are found to be:

$$E_m = h\nu_o \left(m + \frac{3}{2}\right) \quad , \quad m = 0 , 1 , 2 , 3 \ldots. \tag{3.50}$$

and the selection rule for transitions m → n is:

$$m - n = \pm 1 \quad , \tag{3.51}$$

thus:

$$\left(E_m - E_n\right)_{(m - n) = 1} = E_{mn} = h\nu_{mn} = E_o = h\nu_o \quad , \tag{3.52a}$$

or:

$$\nu_{mn} = \nu_o \tag{3.52b}$$

The statistical weights of level k of the three-dimensional harmonic oscillator are (Ref. 4):

$$\left(w_k\right)_{3D.H.O.} = \frac{1}{2}(k + 1)(k + 2) , \qquad (3.53)$$

and if we assume that m is the larger of m and n and m - n = 1, we have:

$$\left(C_{mn}\right)_{3D.H.O.} = w_m w_n = \frac{1}{4}(m + 1)(m + 2)^2(m + 3) \qquad (3.54)$$

When substituting Eqs. (3.51) and (3.52) into Eq. (3.48) we find for transitions between the ground state n = 0 and m = 1 that:

$$\left(R^2_{mn}\right)^o_{3D.H.O.} = \frac{h}{8\pi^2 m_e \nu_{mn}} = a_o^2 \left(\frac{Ry}{E_{mn}}\right) , \text{cm}^2 , \qquad (3.55)$$

while for this transition:

$$\left(C_{mn}\right)^o_{3D.H.O.} = \frac{1}{2}(1 + 1)(1 + 2) = 3 \qquad (3.56)$$

When (3.55) and (3.56) are substituted into Eq. (3.14), we find that the dimensionless oscillator strength f_{nm} is:

$$\left(f_{nm}\right)^o_{3D.H.O.} = 1 \qquad (3.57)$$

Thus measured or caluculated values of f_{nm} for actual electronic transitions give a measure of the deviation of the actual situation from that of the ideal three-dimensional harmonic oscillator model (for the ground-state-connected transition n = 0 → m = 1).

Values for the oscillator strengths f_{nm} of atoms and molecules vary usually between 10^{-2} and 10 (Ref. 14) and many of the important ones lie in the range $0.1 \lesssim f_{nm} \lesssim 2$ as may be seen from Table 3-5. Thus in cases where information about a transition is very scanty, one may take as a crude estimate:

$$f_{\substack{nm\\ elc}} \sim 0.5 \left(f_{nm}\right)^{0}_{3D.H.O.} \tag{3.58}$$

and therefore according to Eq. (3.55):

$$\boxed{\begin{aligned} \underset{\left(\substack{\text{crude approximation}\\ \text{for atoms and molecules}}\right)}{\left(R^{2}_{\substack{mn\\ elc}}\right)} &\approx \frac{a_{0}^{2}}{2}\left(\frac{Ry}{E_{mn}}\right) = 0.14 \times 10^{-16}\left(\frac{13.605}{E_{\substack{mn\\ (eV)}}}\right) = \\ &= \frac{1.5365 \times 10^{-12}}{\nu_{mn}(cm^{-1})} = \frac{4.606 \times 10^{-14}}{\nu_{mn}(THz)} \quad , \quad cm^{2} \quad , \end{aligned}} \tag{3.59}$$

where we used (3.44) again and where E_{mn} is in eV , and ν_{mn} is in units of cm^{-1} or THz (= 10^{12} Hz).

TABLE 3-5. MEASURED OSCILLATOR STRENGTHS AND WEIGHTS OF TYPICAL DIPOLE TRANSITIONS IN THE NEUTRAL ATOMS HYDROGEN THROUGH NEON

(Data from Ref. 14)

Atom	Transition $n \rightarrow m$	Wavelength λ_{mn} (Angstroms)	f_{nm}	w_n	w_m
H	$1 \rightarrow 2$	1215.67	0.4162	2	8
He	$1s^2(^1S) \rightarrow 1s2p(^1P^o)$	584.33	0.2762	1	3
Li	$2s^2(^2S) \rightarrow 2p(^2P^o)$	6707.8	0.753	2	6
Be	$2s^2(^1S) \rightarrow 2s2p(^2S)2p(^1P^o)$	2348.61	1.36	1	3
B	$2s^22p(^2P^o) \rightarrow 2s2p^2(^2P)$	1378.7	0.66	6	6
C	$2s^22p^2(^3P) \rightarrow 2s2p^3(^3S^o)$	945.44	0.27	9	3
N	$2p^3(^4S^o) \rightarrow 2p^2(^3P)3s(^4P)$	1199.9	0.35	4	12
O	$2p^33s(^5S^o) \rightarrow 2p^3(^4S^o)3p(^5P)$	7773.4	0.922	5	15
F	$2p^43s(^4P) \rightarrow 2p^4(^3P)3p(^4D^o)$	6859.2	0.55	12	20
Ne	$2p^53s(3/2^o) \rightarrow 2p^5(^2P^o_{3/2})3p(1/2^o)$	6402.25	0.373	5	7

The utter simplicity of Eq. (3.59) gives it much to recommend it in place of the much more complicated molecular expressions (3.46) or (3.47), particularly in such applications as preliminary engineering design problems which rely on this parameter. Even though Eq. (3.59) may be off by a factor of 10 (high or low), it may be preferred over (3.46) or (3.47) since the accuracy of the latter expressions is not well known (very few data have been published on molecular oscillator strengths or related parameters with which one could check Eqs. (3.46) and (3.47)). Note here that we have only approximated the R^2_{mn} portion of S_{mn} by the expression obtained for the three-dimensional oscillator model; not the weights w_m, w_n or the connection factor C_{mn} which we will discuss next.

The connection factors for molecules which give the possible transitions between states with total angular momentum J_m to states with total angular momentum J_n are determined primarily by the rotational quantum number J due to the nuclei, rather than J due to the electrons (though the electronic J also plays a role). Since we shall take up the rotational transitions separately later on, and include them in the term $G(\nu, \nu_{mn}, \Delta\nu_{mn})$ or $g(\nu, \nu_{mn}, \Delta\nu_{mn})$, we need only consider the total connection factor between levels (n_m, Λ_m) and (n_n, Λ_n) here. If we consider the levels due to different values of the spin quantum number S to be substates of the energy levels or terms (n_k, Λ_k) or (X_k), we have:

$$\boxed{\left(C_{mn}\right)_{\substack{\text{elc}\\ \text{molecules}}} = w_m w_n = d_{X_m}(2S_m + 1)\, d_{X_n}(2S_n + 1) ,} \tag{3.60}$$

where S_k is the total electron spin quantum number of level k, and:

$$\boxed{\begin{aligned}
&d_{X_k} = 1 \text{, if level or species } X = \Sigma \text{; } A \text{, } B && (3.61a)\\
&d_{X_k} = 2 \text{; if species or level } X = E \text{; } \Pi \text{, } \Delta \text{, } \Phi \text{, } \ldots && (3.61b)\\
&d_{X_k} = 3 \text{, if species } X = F && (3.61c)
\end{aligned}}$$

For molecules then, we may obtain approximate model expressions for electronic transitions by using the simple expressions (3.59), (3.60), and (3.61), that is:

$$\boxed{\begin{aligned}
\left(S_{mn}\right)_{\substack{\text{elc}\\ \text{molecules}}} &= \left(C_{mn}\right)_{\substack{\text{elc}\\ \text{molecules}}} \left(R^2_{mn}\right)_{\substack{\text{elc}\\ \text{molecules}}} = \frac{1.5365 \times 10^{-12}\, w_m w_n}{\nu_{mn}(\text{cm}^{-1})} = \\
&= \frac{4.606 \times 10^{-14}\, w_m w_n}{\nu_{mn}(\text{THz})} \text{, cm}^2 \text{,}
\end{aligned}} \qquad (3.62)$$

where:

$$\boxed{\begin{aligned} w_m &= d_{\chi_m}(2S_m + 1), \qquad (3.63) \\ w_n &= d_{\chi_n}(2S_n + 1), \qquad (3.64) \end{aligned}}$$

with d_{χ_m} and d_{χ_n} as defined in Eq. (3.61).

3.3 VIBRATIONAL RADIATIVE TRANSITIONS

3.3.1 Diatomic Molecules

For vibrational transitions in diatomic molecules, or transitions in one vibrating bond of a linear polyatomic molecule, one can approximate the vibrations quite well by using the one-dimensional harmonic oscillator model. For transitions between vibrational levels v_m and v_n one finds, using harmonic oscillator eigenfunction in Eq. (1.14) (Refs. 2,7, and Appendix A):

$$\left(R^2_{mn}\right)_{\substack{\text{vib}\\ \Delta v = 1\\ \text{diatomic}}} = \frac{\left(\frac{v_m + v_n + 1}{2}\right) h\mu_1^2}{8\pi^2 \bar{M}_{AB} \nu_e e^2} = \frac{|v_m - v_n| \, (v_m + v_n + 1) \, \hbar z_1^2}{16\pi^2 \bar{M}_{AB} \nu_{mn}}, \text{ cm}^2 \qquad (3.65)^*$$

In Eq. (3.65) z_1 is the effective charge of the derivative of the dipole formed by the separation of unequal average charges that are distributed around the two atoms of the molecule which are spaced on the average a distance r_e, that is $z_1 = (r_e e)^{-1} \cdot [\partial\mu(s)/\partial s]_{s=r_e} = [\partial z(s)/\partial s]_{s=r_e}$, where z(s) is given by (see also Appendix B):

$$z(s) = z_1 + (z_0 - z_1)(r_e/s) , \qquad (3.66)$$

The parameter $\bar{M}_{AB}$ in (3.65) is the reduced mass:

$$\bar{M}_{AB} = \frac{M_A \, M_B}{M_A + M_B} \quad , \quad \text{gms} \quad , \qquad (3.67)$$

---

*Since $|v_m - v_n| \equiv \Delta v = 1$ we could omit this term in (3.65); we leave it in since we shall later generalize to the case $\Delta v \neq 1$.

where:

M_A, M_B = Masses of respectively component A and component B of the vibrating molecular bond A - B, gms

Instead of the charge parameters given in (3.66), dipole moment parameters μ are often used, that is (Ref. 7):

$$\mu = zes = z_o e r_e + z_1 e(s - r_e) = \mu_o + \mu_1(s - r_e) \text{ , erg}^{1/2} \cdot \text{cm}^{3/2} \text{ ,} \qquad (3.68)$$

where:

$$\mu_o = z_o \, e \, r_e \text{ , erg}^{1/2} \cdot \text{cm}^{3/2} \qquad (3.69)$$

$$\mu_1 = z_1 \, e \text{ , erg}^{1/2} \cdot \text{cm}^{1/2} \qquad (3.70)$$

The other parameters are:

s = $s(t)$ = Instantaneous relative separation of molecular components A and B , cm

r_e = Equilibrium separation between molecular components A and B , cm

ν_{mn} = Fundamental frequency of vibration of bond A - B , Hz

In Figure 3-1, curves of Eqs. (3.66) and (3.68) are shown to illustrate the behaviour of z and μ for the cases $z_1 = z_o$, $z_1 = 2z_o$, and $z_1 = -2z_o$. Note that $z = z_1$ at $r = \infty$, and $z = z_o$ at $r = r_e$.

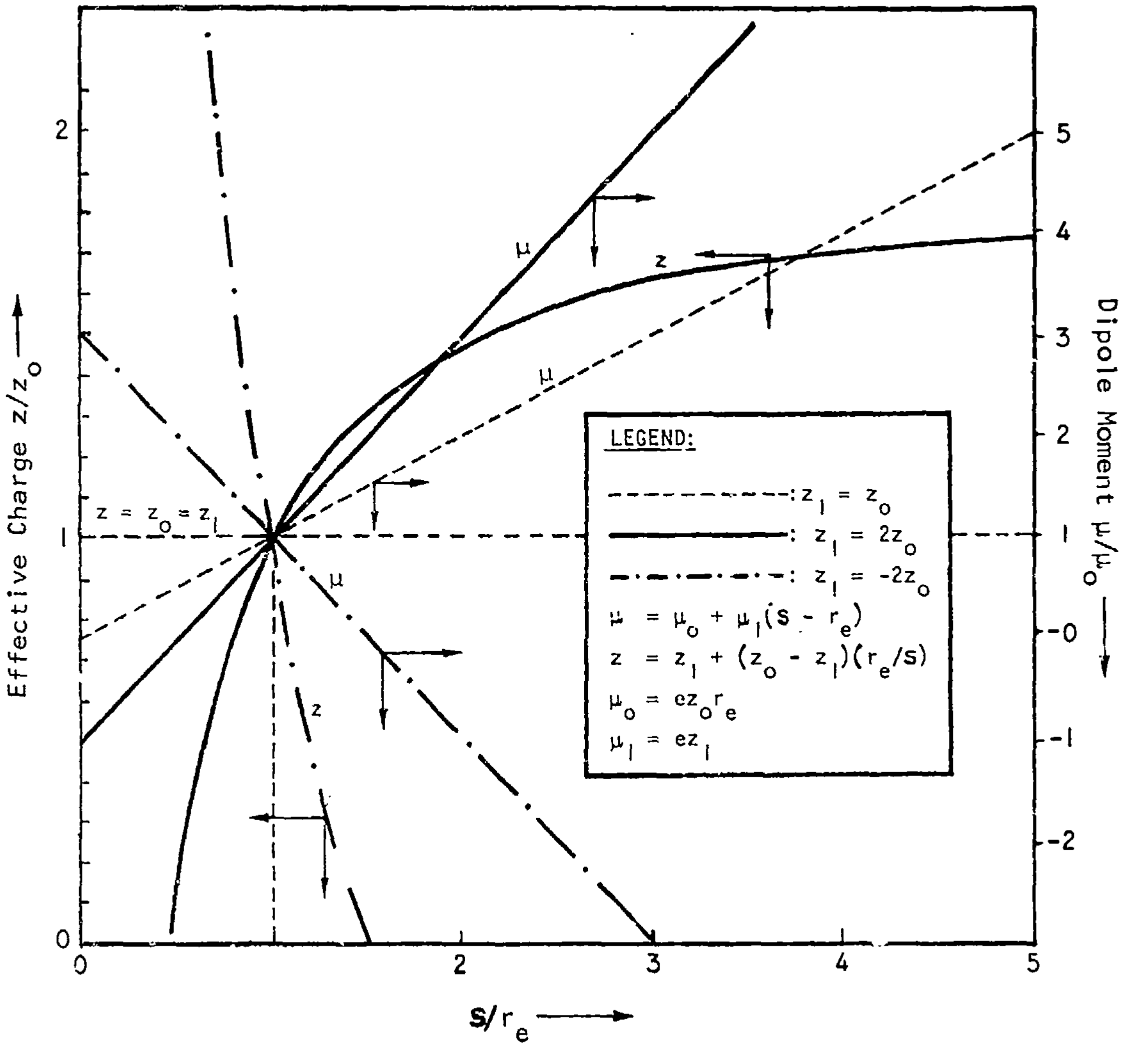

FIGURE 3-1. DEPENDENCE OF THE DIPOLE MOMENT μ AND EFFECTIVE CHARGE z ON INTERNUCLEAR DISTANCE FOR THE CASES THAT $z_1 = z_o$, $z_1 = 2z_o$, AND $z_1 = -2z_o$

In Appendix B it is shown that if z_o and r_e are given, it is possible to calculate z_I by means of basic microscopic relations of atomic physics. Thus (see Eqs. (B.52) and (B.53)) we have:

$$z_I = z_I(p_d) = z_I(z_o, r_e) \qquad (3.71)$$

The relation (3.71) between z_I and z_o is plotted in Figure B-2 on page B-27 of Appendix B. Note that for positive values of z_o, the solutions for z_I is double-valued. Also note that z_o can be positive or negative. It is usually not too difficult to determine which z_I value applies however, since the intermediary parameter $p_d = 0.922\ Z_d r_e$ which relates z_I and z_o must be such that $Z_d = Z_A^{eff} - Z_B^{eff}$ has a reasonable value. For example in obtaining the z_I value for OH from the literature value of $z_o = \pm 0.3561$, we find that $z_I = 0.096$ ($Z_d = 0.447$) or $z_I = -0.3$ ($Z_d = 1.565$), if $z_o = +0.3561$, and $z_I = -2.0$ ($Z_d = 1.676$), if $z_o = -0.3561$. Only the solution $z_I = 0.096$, $z_o = 0.3561$ with $Z_d = 0.447$ is compatible with the fact that H can at most have a value of $Z_A^{eff} = 1$.

In Table 3-6, values for μ_o, r_e, z_o, and z_I for some selected diatomic molecules are listed taken from data given in Refs. 2, 15, and 16. Additional values for some other molecules may be found in Appendix B. Data on directly measured values for z_I (or μ_I) are rather scarce and thus Figure B-2 of Appendix B was used if such experimental values are unavailable.

Note from Table 3-6 that the more homopolar the molecular bond is (e.g., CO) the smaller z_o is, while the more ionic it is (e.g., KCℓ), the larger the value of z_o as one would expect. However z_I may be quite different from the value of z_o and may not follow this rule. Also note

TABLE 3-6. DIPOLE MOMENTS, EQUIVALENT DIPOLE LENGTHS AND CHARGES, AND VIBRATIONAL PARAMETERS OF SELECTED DIATOMIC MOLECULES (Refs. 2, 15, 16, and Appendix B)

Molecule	Reduced Mass $\bar{M}_{AB}$ (amu)*	Permanent Electric Dipole Moment μ_o (debyes)**	Equivalent Electric Dipole Length, $d_o = \mu_o/e = z_o\, r_e$ (pm)***	Equilibrium Distance Between Molecular Components, r_e (pm)***	Effective Dipole Charge Number z_o	Effective Dipole Charge Number z_1	Fundamental Vibration Frequency**** ν_e (cm^{-1})	Anharmonic Constant x_e
HCl	0.979889	1.08	22.49	127.5	0.176	0.075	2989.74	0.01741
HO	0.948376	1.66	34.56	97.1	0.356	0.093	3735.21	0.007713
HBr	0.99558	0.82	17.07	141.4	0.121	0.067	2649.67	0.01706
HF	0.957347	1.82	37.89	91.7	0.413	0.082	4138.52	0.02176
CO	6.85841	0.112	2.332	112.8	0.0207	1.033	2170.21	0.006203
NO	7.46881	0.153	3.186	115.1	0.0277	0.985	1904.03	0.007337
ClF	12.31410	0.88	18.32	162.8	0.113	0.075	793.2	0.0125
BrF	15.3542	1.29	26.85	175.9	0.153	0.105	671	0.00447
KCl	18.599	10.27	213.8	266.7	0.802	1.585	280	0.0032
ICl	27.4221	0.65	13.52	232.1	0.058	0.047	384.18	0.003813
H_2	0.504066	0	0	74.16	0	0	4395.24	0.02683
N_2	7.00377	0	0	109.4	0	0	2359.61	0.006126
O_2	8.00000	0	0	120.74	0	0	1580.361	0.007639
Cl_2	17.48942	0	0	198.8	0	0	564.9	0.00708
F_2	9.50227	0	0	143.5	0	0	892.1	0.01043

* 1 amu = 1.660×10^{-24} gram; masses of the most abundant isotopes are assumed in this column.

** 1 debye = 10^{-18} $ergs^{1/2} \cdot cm^{3/2}$.

*** 1 pm = 1 picometer = 10^{-12} m = 10^{-10} cm .

**** Herzberg labels this parameter ω_e .

that for homonuclear diatomic molecules such as H_2 , O_2 , and N_2 the dipole moment $\mu_o = 0$ and $z_o = 0$ as one would expect since they are completely symmetric. The same applies for the vibrational ground state of a symmetric linear polyatomic molecule such as O-C-O. However whereas $z_o = 0$ for the vibrational ground state ($v = 0$) of O-C-O, $z_1 \neq 0$ for the nonsymmetric vibrations of OCO. For molecules such as O_2 , N_2 , and H_2 on the other hand, $z_o = z_1 = 0$ for all vibrational levels. We shall discuss the polyatomic situation more fully in subsection 3.3.2.

Statistical weights for the vibrational levels of diatomic molecules are:

$$w_{v_k} = 1 \quad , \tag{3.72}$$

and therefore:

$$C_{mn} = w_{v_m} w_{v_n} = 1 \tag{3.73}$$

The spatial orientation of the axis of the diatomic molecule is quantized into various allowed rotational states which we shall take up in the next section. That is, degeneracies due to spatial orientation of the vibrating molecular axis will be incorporated in the formulas for the rotational sublevels which we shall consider later. As far as vibrations alone are concerned, Eqs. (3.72) and (3.73) apply (for diatomic molecules).

The one-dimensional harmonic oscillator model allows only transitions for which:

$$\Delta v = v_m - v_n = \pm 1 \quad , \tag{3.74}$$

while its energy levels are given by:

$$E_{v_k} = h\nu_e \left(\frac{1}{2} + v_k\right) , \; v_k = 0 \; , \; 1 \; , \; 2 \; \ldots \; , \tag{3.75}$$

where:

$$h\nu_e = E_{v_k=1} - E_{v_k=0} \tag{3.76}$$

Because of the selection rule (3.74), we see that for allowed transitions $v_m \rightarrow v_n$, the energy of the emitted (absorbed) photon is:

$$E_{v_m} - E_{v_n} = E_{mn} = h\nu_{mn} = h\nu_e \; , \tag{3.77}$$

and thus substituting ν_{mn} for ν_e in Eq. (3.65), as we did, is justified.

In conclusion then for $\Delta v = 1$ transitions in diatomic molecules, we have (taking for convenience v_m to be the larger of v_m and v_n):

$$\boxed{\begin{aligned} \left(S_{mn}\right)_{\substack{\text{vib}\\ \text{diatomic}\\ (v_m - v_n = 1)}} &= \left(C_{mn} R^2_{mn}\right)_{\substack{\text{vib}\\ \text{diatomic}\\ (v_m - v_n = 1)}} = \frac{v_m h z_1^2}{8\pi^2 \bar{M}_{AB} \nu_{mn}} = \\ &= 1.6861 \times 10^{-15} \underset{(\text{amu})(\text{cm}^{-1})}{\left(\frac{v_m z_1^2}{\bar{M}_{AB}\nu_{mn}}\right)} = 5.0548 \times 10^{-18} \underset{(\text{amu})(\text{THz})}{\left(\frac{v_m z_1^2}{\bar{M}_{AB}\nu_{mn}}\right)} \text{ cm}^2 \; , \end{aligned}} \tag{3.78}$$

where $\bar{M}_{AB}$ is in atomic mass units (amu) and ν_{mn} is in cm^{-1} or in THz (TeraHerz = 10^{12} Hz). Values for z_1 must be taken from Appendix B or Table 3-6. Of course according to (3.72), $w_{v_m} = w_{v_n} = 1$.

Now the actual vibrational motion of a molecule is not quite harmonic but more like that of the anharmonic oscillator. Although to first-order all the above relations for R^2_{mn} and S_{mn} which were derived using the harmonic oscillator model still hold (Refs. 2 and 16), an important change is that for the anharmonic oscillator, transitions with $\Delta v > 1$ are also allowed though with much lower probability. From the work of Heaps and Herzberg (Ref. 17), we find that to accommodate anharmonic transitions we must multiply S_{mn} and R^2_{mn} of Eq. (3.78) by the factor:

$$\underset{\left(\begin{smallmatrix} v_m > v_n \\ \text{diatomic} \end{smallmatrix}\right)}{k'(v_m \rightarrow v_n)} = \frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)^2} \frac{(v_m - 1)!}{v_n!} \qquad (3.79)$$

where v_m is taken as the larger of v_m and v_n. The factor x_e is the so-called anharmonic constant which has been tabulated by Herzberg (Ref. 2). Values for x_e for selected diatomic molecules are listed in Table. 3-6. In Appendix C, a general method is given to calculate x_e for other molecules.

Multiplying (3.79) with (3.78), we obtain:

$$\boxed{\begin{aligned}
\left(S_{mn}\right)_{\substack{\text{vib}\\ \text{diatomic}\\ (v_m > v_n)}} &= \left(C_{mn}\, R^2_{mn}\right)_{\substack{\text{vib}\\ \text{diatomic}}} = \frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)^2}\,\frac{v_m!}{v_n!}\,\frac{hz_1^2}{8\pi^2 \bar{M}_{AB}\,\nu_e} = \\
&= \frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)^2}\,\frac{v_m!}{v_n!}\,\frac{hz_1^2\,(v_m - v_n)}{8\pi^2 \bar{M}_{AB}\nu_{mn}} = \\
&= \frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)}\,\frac{v_m!}{v_n!}\,\frac{1.6861 \times 10^{-15}\, z_1^2}{\bar{M}_{AB}(\text{amu})\,\nu_{mn}(\text{cm}^{-1})}\ ,\ \text{cm}^2
\end{aligned}} \tag{3.80}$$

In Eq. (3.80) we replaced $\nu_{mn} = \nu_e$ of (3.78) by $\nu_{mn} = (v_m - v_n)\nu_e$, since for transitions with $\Delta v \neq 1$, Eq. (3.77) no longer holds, but (3.75) still holds approximately, that is for the anharmonic oscillator:

$$E_{v_k} = h\nu_e(v_k + \tfrac{1}{2}) - hx_e\nu_e(v + \tfrac{1}{2})^2 \approx h\nu_e(v_k + \tfrac{1}{2})\ , \tag{3.81}$$

where the anharmonic term with x_e is small and may be neglected to first-order. Values for ν_e of selected diatomic molecules are listed in Table 3-6.

Note that if $v_m - v_n = 1$, Eq. (3.80) reduces to (3.78) as it should of course. Comparing (3.80) with (3.78) we see that the factor $v_m = (v_m + v_n + 1)/2$ of Eq. (3.65) has been replaced by the factor:

$$\underset{\left(\substack{v_m > v_n \\ \text{diatomic}}\right)}{k(v_m \rightarrow v_n)} = \frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)} \frac{v_m!}{v_n!} \tag{3.82}$$

3.3.2 Polyatomic Molecules

In treating vibrational transitions of polyatomic molecules, it is convenient to divide them into the following classes (Ref. 10):

1. Linear Molecules
2. Planar Molecules
3. Pyramidal Molecules
4. Tetrahedral Molecules
5. Octahedral Molecules
6. Other Molecules

When molecular vibrations are considered together with molecular rotations, another classification is often employed:

1. Linear Molecules
2. Symmetric Top Molecules
3. Spherical Top Molecules
4. Asymmetric Top Molecules

It can be shown (Ref. 10) that linear molecules (such as O-C-O or H_2-C-C-H_2) have in general (3N - 5) so-called "normal vibrations" while nonlinear molecules (such as NH_3) possess in general (3N - 6) normal vibrations whose frequencies are labeled ν_1 , ν_2 , ν_3 , ν_4 , ... N stands here for the number of atoms in the molecule. If several atoms of the molecule are the same, or groups of atoms are the same, several normal vibrations will be identical however, and the effective number of different normal vibrations is less than (3N - 5) or (3N - 6). For example tetrahedral CH_4 could have (3 x 5 - 6) = 9 normal vibrations but because of its high symmetry, only 4 of these normal vibrations are distinct and 5 of them are degenerate. Similarly octahedral SF_6 could have as many as 15 normal vibrations if each atom were different, but because of its high symmetry we find that there are only 6 distinct normal vibrations, ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 and the other 9 possible vibrations are degenerate, that is they have the same value for ν as one of these 6. As a final example, the linear molecule CO_2 should have (3 x 3 - 5) = 4 normal vibrations. But two of these four correspond to bending vibrations, ν_{2a} and ν_{2b} whose frequencies are the same $(\nu_{2a} = \nu_{2b})$, but whose planes of vibration are at right angles to each other. Thus CO_2 has only three distinct normal vibrational frequencies ν_1 , ν_2 , ν_3 , of which ν_2 is doubly degenerate.

The general method by which to determine the distinct normal vibration of a polyatomic molecule are given by Herzberg (Ref. 10). We shall assume here that they are known by consulting Herzberg's tables of polyatomic molecular properties (Ref. 11) which list the fundamental frequencies of the normal vibrations of most commonly known gaseous molecules. We shall use the subscript α to denote a general normal vibration with fundamental frequency ν_α and vibrational quantum numbers $v_\alpha = 0$, 1 , 2 .... , β for another normal vibration with frequency ν_β , etc.

It can be shown, analogous to Eq. (3.65) for diatomic molecules, that the parameter R^2_{mn} in the case of transitions with $\Delta v_\alpha = 1$ within one normal vibration α of a polyatomic molecule has the general form (see Appendix A):

$$\boxed{\begin{aligned}\left(R^2_{mn}\right)_{\substack{vib\\ \Delta v_\alpha = 1\\ \text{polyatomic}}} &= \frac{\left|v_{\alpha_m} - v_{\alpha_n}\right| \left(v_{\alpha_n} + v_{\alpha_n} + 1\right) hz^2_\alpha}{16\pi^2 \nu_{\alpha_{mn}} M_\alpha} = \\ &= \frac{\left(v_{\alpha_m} + v_{\alpha_n} + 1\right) hz^2_\alpha}{16\pi^2 \nu_\alpha M_\alpha} \quad , \ \text{cm}^2\end{aligned}} \qquad (3.83)$$

Here $\nu_{\alpha_{mn}} = \left(v_{\alpha_m} - v_{\alpha_n}\right) \nu_\alpha = \nu_\alpha$ since $\Delta v_\alpha = v_{\alpha_m} - v_{\alpha_n}$ is restricted to the value 1. M_α is the effective mass of the normal vibration α if treated by the harmonic oscillator model, and z_α is the first-derivative dipole charge number* for the α vibration (see Appendices A and B).

The values to be used for the various M_α of a polyatomic molecule depend in a complicated way on the masses and relative arrangements of the atoms that make up the molecule. Similarly z_α varies considerably for the different normal vibrations of different types of molecules. We shall give expressions and tables for M_α and z_α for the five major classes of polyatomic molecules later on. For the moment we shall assume that they are known.

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*We shall omit the subscript 1 in z_1 from here on and write $(z_1)_\alpha = z_\alpha$ for convenience.

Now just like anharmonicity removed the $\Delta v = 1$ selection rule for diatomic molecules, the same occurs for polyatomic molecules. However for polyatomic molecules we not only introduce the possibility of overtone transitions $v_{\alpha_m} - v_{\alpha_n} \equiv \Delta v_\alpha = 2$, 3 , etc., the anharmonicity also allows so-called "combination-band" transitions $\left(v_{\alpha_m}, v_{\beta_m}, v_{\gamma_m}, \ldots\right) \rightarrow \left(v_{\alpha_n}, v_{\beta_n}, v_{\gamma_n}, \ldots\right)$ in which level changes in several of the normal vibrations take place simultaneously. The latter would be strictly forbidden if the vibrations were purely harmonic.

By including first-order anharmonic corrections in the transition element (see Appendix A), we find that for "overtone" and "combination-band" transitions of polyatomic molecules one obtains:

$$\boxed{\begin{aligned} \left(R^2_{mn}\right)_{\substack{\text{vib}\\ \text{polyatomic}}} &= \left(\frac{hz^2_{mn}}{8\pi^2 \nu_{mn} M_{mn} x_{mn}}\right) \prod_{\alpha} \left[\frac{x_\alpha^{|v_{\alpha_m}-v_{\alpha_n}|}}{\left(|v_{\alpha_m}-v_{\alpha_n}|+1\right)^2} \left(\frac{v_{\alpha_m}!}{v_{\alpha_n}!}\right)^{\delta_\alpha} \right] = \\ &= 1.6867 \times 10^{-15} \underset{(\text{amu})(\text{cm}^{-1})}{\left(\frac{z^2_{mn}}{M_{mn}\nu_{mn}x_{mn}}\right)} \prod_{\alpha} \left[\frac{x_\alpha^{|v_{\alpha_m}-v_{\alpha_n}|}}{\left(|v_{\alpha_m}-v_{\alpha_n}|+1\right)^2} \left(\frac{v_{\alpha_m}!}{v_{\alpha_n}!}\right)^{\delta_\alpha} \right], \ \text{cm}^2 \end{aligned}} \tag{3.84}$$

Here ν_α is the fundamental frequency of normal vibration α , v_{α_m} is the upper initial (final) and v_{α_n} the lower final (initial) vibrational quantum number of vibration α in the transition $m \longleftrightarrow n$; v_{β_m} is the upper initial (final) vibrational quantum number of normal vibration β , etc. The parameter z_{mn} for a combination-band transition we shall discuss later; for an overtone transition in a single vibration α , we have that $z_{mn} = z_\alpha$. The transition frequency ν_{mn} in Eq. (3.84) is:

$$\nu_{mn} = \sum_\alpha \left(v_{\alpha_m} - v_{\alpha_n} \right) \nu_\alpha , \qquad (3.85)$$

while the parameter $\delta_\alpha = 1$, if $v_{\alpha_m} > v_{\alpha_n}$, and $\delta_\alpha = -1$, if $v_{\alpha_m} < v_{\alpha_n}$. The parameters M_{mn}, x_{mn}, and z_{mn} are discussed in Appendix A and are defined by:

$$M_{mn} = \left[\sum_\alpha M_\alpha^{-1/2} \left| v_{\alpha_m} - v_{\alpha_n} \right| \right]^{-2} \qquad (3.86)$$

$$x_{mn} = \left[\sum_\alpha x_\alpha^{-1/2} \left| v_{\alpha_m} - v_{\alpha_n} \right| \right]^{-2} \qquad (3.87)$$

$$z_{mn} = \left(\nu_{mn} M_{mn} x_{mn} \right)^{1/2} \left| \sum_\alpha \left(\frac{\left| v_{\alpha_m} - v_{\alpha_n} \right| + 1}{\left| v_{\alpha_m} - v_{\alpha_n} \right|} \right) \frac{z_\alpha \vec{e}_\alpha}{M_\alpha^{1/2} \nu_\alpha^{1/2} x_\alpha^{1/2}} \right| \qquad (3.88)$$

The M_α , x_α , and z_α of a normal vibration α of a molecule, may be obtained by methods discussed in Appendices A, B, and C if experimental data are unavailable. Tables of values for these parameters are given in subsections 3.3.2.1 through 3.3.2.5.

Equation (3.84) which is based on a first-order anharmonic approximation is in reasonable agreement with experiment for first overtones and double combination bands. However it predicts progressively less correct values (too low) for triple and higher combinations and higher overtones. Agreement is better if (3.84) is modified to (see Appendix A):

$$\boxed{\left(R^2_{mn}\right)_{\substack{vib\\ polyat.}} = 1.6867 \times 10^{-15} \underset{(amu)(cm^{-1})}{\left(\frac{z^2_{mn}}{M_{mn}\nu_{mn}x_{mn}}\right)} \prod_{\alpha} \left(\frac{x_{\alpha}^{|v_{\alpha_m}-v_{\alpha_n}|\cdot f}}{\left(|v_{\alpha_m}-v_{\alpha_n}|+1\right)^2}\left(\frac{v_{\alpha_m}!}{v_{\alpha_n}!}\right)^{\delta_{\alpha}}\right),\ cm^2} \tag{3.89a}$$

$$\boxed{z_{mn} = \left(\nu_{mn}M_{mn}x_{mn}\right)^{1/2} \left| \sum_{\alpha} \frac{\left(|v_{\alpha_m}-v_{\alpha_n}|+1\right) z_{\alpha}\vec{e}_{\alpha}}{M_{\alpha}^{1/2}\,\nu_{\alpha}^{1/2}\,\left(x_{\alpha}^{1/2}\right)^{f\left(|v_{\alpha_m}-v_{\alpha_n}|\right)}}\right|} \tag{3.89b}$$

$$\boxed{f = 1 - \frac{1}{2}\left(\frac{\left(\sum_{\alpha}|v_{\alpha_m}-v_{\alpha_n}|\right)! - 1}{\left(\sum_{\alpha}|v_{\alpha_m}-v_{\alpha_n}|\right)! + 1}\right)} \tag{3.89c}$$

Like Eq. (3.84), Eq. (3.89) will reduce to Eq. (3.83) for transitions with $\sum_{\alpha}|v_{\alpha_m} - v_{\alpha_n}| = 1$ (i.e., a $\Delta v_{\alpha} = 1$ transition within only one normal vibration α).

Whereas for diatomic molecules the weights w_{v_m}, w_{v_n}, and connection factors $(C_{mn})_{vib}$ equaled unity, for polyatomic molecules this is not the case since some normal vibrations can be degenerate. To determine the degeneracy of a normal vibration, symmetry considerations play a vital role (Refs. 10 and 11). Normal vibrations in polyatomic molecules, like electronic excitations, can be classified according to their symmetry properties. For nonlinear molecules, symbols A and B (with subscripts) denote in general that the vibration is non-degenerate, while the symbol E is used for doubly-degenerate vibrations, and the symbol F for triply-degenerate vibrations. For linear molecules, vibrations designated by Σ are non-degenerate, while vibrations designated Π , Δ , Φ , ... are doubly-degenerate (Ref. 10). If we use the symbol d_{X_α} to indicate the degeneracy of the normal vibration α of a polyatomic molecule, we have:

$$d_{X_\alpha} = 1 \text{ , if } X_\alpha = A \;\; ; \;\; X_\alpha = B \;\; ; \text{ or } X_\alpha = \Sigma \tag{3.90a}$$

$$d_{X_\alpha} = 1 \text{ , if } X_\alpha = E \;\; ; \;\; X_\alpha = \Pi \;\; ; \; X_\alpha = \Delta \; ; \; X_\alpha = \Phi \tag{3.90b}$$

$$d_{X_\alpha} = 3 \text{ , if } X_\alpha = F \tag{3.90c}$$

The weight w_{α_k} of a general vibrational level k of a normal vibration α with vibrational quantum number v_{α_k} is then (Ref. 10):

$$w_{\alpha_k} = 1 \text{ , if } d_{X_\alpha} = 1 \tag{3.91a}$$

$$w_{\alpha_k} = \left(v_{\alpha_k} + 1\right) \text{ , if } d_{X_\alpha} = 2 \tag{3.91b}$$

$$w_{\alpha_k} = \frac{1}{2}\left(v_{\alpha_k} + 1\right)\left(v_{\alpha_k} + 2\right) \text{ , if } d_{X_\alpha} = 3 \tag{3.91c}$$

Note that we can combine (3.91a), (3.91b), and (3.91c) into the single expression:

$$w_{\alpha_k} = \delta\left(d_{X_\alpha} - 1\right) + \left(v_{\alpha_k} + 1\right)\delta\left(d_{X_\alpha} - 2\right) + \frac{1}{2}\left(v_{\alpha_k} + 1\right)\left(v_{\alpha_k} + 2\right)\delta\left(d_{X_\alpha} - 3\right) , \tag{3.91d}$$

where $\delta(x)$ is the Dirac delta function. Note that for the fundamental vibration $v_{\alpha_k} = 1$, Eq. (3.91b) yields $w_{\alpha_k} = 2 = d_{X_\alpha}$ and Eq. (3.91c) gives $w_{\alpha_k} = 3 = d_{X_\alpha}$ as they must of course.

For vibrational combination band transitions, the weights w_{v_m} and w_{v_n} are given by:

$$\boxed{w_{v_k} = \prod_\alpha w_{\alpha_k}} \tag{3.92}$$

where the product is over the normal vibrations α whose levels change in the transition. The connection factor for the most general vibrational transition is then:

$$\boxed{\left(C_{mn}\right)_{vib} = w_{v_m} w_{v_n} = \prod_\alpha w_{\alpha_m} w_{\alpha_n}} \tag{3.93}$$

For a transition within one normal vibration β , we have simply $(C_{mn})_{vib} =$ $= w_{\beta_m} w_{\beta_n}$ according to Eq. (3.93).

The emitted (absorbed) photon frequencies are of course $\nu_{mn} =$ $= \left(E_{v_m} - E_{v_n}\right)/h$ for a vibrational transition in a polyatomic molecule, where:

$$E_{v_k} = \sum_\alpha \left[h\nu_\alpha \left(v_{\alpha_k} + \frac{d_\alpha}{2}\right) - h x_\alpha \nu_\alpha \left(v_{\alpha_k} + \frac{d_\alpha}{2}\right)^2 \right] \tag{3.94}$$

Here we abbreviate $d_\alpha \equiv d_{X_\alpha}$; the symbol v_{α_k} is the level of excitation of the normal vibration α in the general state k.

As an illustration, let us consider the transition $\nu_3 \rightarrow 2\nu_2$ in CO_2 . Here $v_{3_m} = 1$, $v_{2_m} = 0$, $v_{3_n} = 0$, $v_{2_n} = 2$. Since the ν_2 vibration (with fundamental frequency ν_2) in CO_2 is doubly-degenerate, while ν_3 is non-degenerate, we have $w_m = w_{3_m} w_{2_m} = 1 \times 1 = 1$, and $w_n = w_{3_n} w_{2_n} = 1 \times 3 = 3$.

Having determined what the general form of the relations for R^2_{mn}, C_{mn}, w_m, and w_n should be for polyatomic molecules, we next turn to the problem of obtaining values for M_α, z_α, and x_α which enter into the equations for R^2_{mn}. For the anharmonic constant x_α, there is an analytic relation that may be used if no other data are available. This relation is (Ref. 16):

$$x_\alpha = \frac{h\nu_\alpha}{4D_\alpha} = 3.099 \times 10^{-5} \frac{\nu_\alpha(\mathrm{cm}^{-1})}{D_\alpha(\mathrm{eV})} , \tag{3.95}$$

where D_α is the dissociation limit energy for the normal vibration α and ν_α is its fundamental frequency. For diatomic molecules Eq. (3.95) can be readily applied but for polyatomic molecules values for D_α are not always available. Appendix C discusses ways of estimating D_α for polyatomic molecules.

As mentioned the parameters M_α, z_α, M_{mn}, and z_{mn} depend strongly on the molecular configuration and are best discussed on a class-for-class basis. In general one finds that the frequency of the normal vibration α can be expressed in terms of the atomic masses and force constants of the molecule by a relation of the form (Ref. 10):

$$4\pi^2\nu_\alpha^2\ (\mathrm{sec}^{-2}) = \sum_s \frac{k_{\alpha s}(\mathrm{dynes/cm})}{M_{\alpha s}(\mathrm{gm})} \tag{3.96}$$

For the simplest type of polyatomic molecule such as symmetric triatomic YXY, there is only one component s for each normal vibration, that is:

$$4\pi^2\nu_\alpha^2 = \frac{k_\alpha}{M_\alpha} \tag{3.97}$$

This relation is identical to that for a diatomic molecule (Ref. 2), except that there are three normal vibrations $\alpha = 1, 2, 3$ for a triatomic molecule as opposed to only one for a diatomic molecule ($M_\alpha = \bar{M}_{AB}$ given by Eq. (3.67) for a diatomic molecule). However for the slightly more complex linear XYZ molecule, we have:

$$4\pi^2\nu_1^2 = \frac{k_{11}}{M_{11}} + \frac{k_{12}}{M_{12}} \tag{3.98a}$$

$$4\pi^2\nu_2^2 = \frac{k_{21}}{M_{21}} + \frac{k_{22}}{M_{22}} + \frac{k_{23}}{M_{23}} \tag{3.98b}$$

$$4\pi^2\nu_3^2 = \frac{k_{31}}{M_{31}} + \frac{k_{32}}{M_{32}} \tag{3.98c}$$

Appendix B gives explicit expressions for $k_{\alpha s}$ and $M_{\alpha s}$ for a number of commonly-occurring classes of molecules.

Values for the effective dipole charge z_α are shown in Appendices A and B to be derivable from values $z_{\alpha s}$ of the s components that participate in a normal vibration via the relation:

$$z_\alpha = \frac{\sum_s \left(\frac{k_{\alpha s}}{M_{\alpha s}}\right)^{1/4}}{\sum_s M_{\alpha s}^{-1/2}} \left| \sum_s \frac{\gamma_{\alpha s} z_{\alpha s} \vec{e}_{\alpha s}}{(k_{\alpha s} M_{\alpha s})^{1/4}} \right| \tag{3.99}$$

where the $\vec{e}_{\alpha s}$ are unit vectors of the dipole direction along the component bonds and the $\gamma_{\alpha s}$ or +1 or -1 depending on whether a component vibration is stretching or contracting with respect to others (see Appendix B). The absolute value in (3.99) is to be taken with respect to the vectors $\vec{e}_{\alpha s}$, that is $|\vec{V}| = \sqrt{\vec{V} \cdot \vec{V}}$.

We shall now briefly review values of M_α , x_α , and z_α for the various classes of molecules as calculated according to the relations developed in Appendices A, B, and C and/or from data supplied by Refs. 2, 10, 11, 15, 16, and 20.

3.3.2.1 Linear Molecules (XY_2 , XYZ)

In Table 3-7 some of the more common linear molecules are listed together with some of their vibrational properties. We can distinguish between symmetric linear molecules (such as OCO and SCS) and unsymmetric linear molecules (e.g., NNO, OCS, and HCN). Most linear molecules are triatomic although four-atomic and more-than-four atomic linear molecules do exist also. However as more and more atoms are present in a molecule the chance becomes increasingly larger that the atoms form bonds with more than just one or two neighbors thus causing nonlinear, planar, and three-dimensional molecular configurations.

To obtain a convenient mathematical description of the vibrations of linear symmetric triatomic molecules XY_2 such as CO_2 , or linear triatomic molecules XYZ like OCS, the most convenient and satisfoactory mechanical model appears to be the so-called "valence-force" model. In this model, harmonic-oscillator stretching force constants k_1 and k_2 (dynes/cm) are used

TABLE 3-7. BASIC VIBRATIONAL PARAMETERS OF SELECTED TRIATOMIC MOLECULES

(Refs. 10, 11, 15, 16)*

Molecule XYZ	Interatomic Distance Angstrom (10^{-8} cm)		Frequencies (cm^{-1}) of the Normal Vibrations			Masses (amu) of the Normal Vibrations			Anharmonic Constants of the Normal Vibrations**			Dipole Charges of the Normal Vibrations		
	ℓ_{XY}	ℓ_{YZ}	ν_1	ν_2	ν_3	M_1	M_2	M_3	x_1	x_2	x_3	z_1	z_2	z_3
LINEAR														
OCO (CO$_2$)	1.162	1.162	1388.2	667.4	2349.2	16.000	2.182	4.364	{ $\underline{0.00281}$ 0.00520	$\underline{0.00327}$ 0.00360	$\underline{0.01132}$ 0.00879 }	0	0.2862	1.2602
SCS (CS$_2$)	1.555	1.555	658.0	396.7	1532.5	32.000	2.526	5.052	0.00355	0.00346	0.00826	0	0.0423	0.2040
SCO (OCS)	1.561	1.161	860.0	520.4	2062.2	13.246	1.954	2.254	0.00428	0.00364	0.00913	0.1326	0.1139	0.4376
NNO (N$_2$O)	1.126	1.191	1284.9	588.8	2223.8	8.272	1.625	2.312	{ $\underline{0.00679}$ 0.00783	$\underline{0.00572}$ 0.00740	$\underline{0.01369}$ 0.01349 }	0.0738	0.1602	0.5726
HCN	1.068	1.156	2096.7	713.5	3311.5	1.709	0.413	1.069	{ $\underline{0.02645}$ 0.03968	$\underline{0.00814}$ 0.00473	$\underline{0.02176}$ 0.01560 }	0.2474	0.2119	0.3413
ICN	1.995	1.159	470	321	2158	139.471	2.406	2.168	0.00543	0.00164	0.00892	0.2142	0.2602	0.8446
BrCN	1.789	1.160	580	368	2187	30.083	2.243	2.170	0.00463	0.00185	0.00886	0.1252	0.2653	0.9132
CℓCN	1.629	1.163	729	397	2201	18.907	1.903	2.097	0.00359	0.00205	0.00886	0.1559	0.3053	0.8884
OUO (UO$_2$)	1.58	1.58	860	220	940	16.000	7.052	14.104	0.01930	0.00233	0.00498	0	0.4201	2.3233
NONLINEAR (PLANAR) XY$_2$														
H$_2$O	0.956	0.956	3657	1594.7	3755.7	0.19046	1.04375	0.92706	{ $\underline{0.04952}$ 0.02395	$\underline{0.01824}$ 0.01982	$\underline{0.02923}$ 0.02460 }	{ $\underline{0.1055}$ 0.0961	$\underline{0.2735}$ 0.0971	$\underline{0.1531}$ 0.1528 }
D$_2$O	0.955	0.955	2666	1179	2784	0.35933	1.95671	1.72808	0.01686	0.01392	0.01761	0.0879	0.0893	0.1401
H$_2$S	1.328	1.328	2614.6	1182.7	2627.5	0.20253	0.93100	0.96867	0.02687	0.04730	0.02700	0.0703	0.0692	0.1079
D$_2$S	1.330	1.330	1892	934	1999	0.39191	1.83185	1.87850	0.01942	0.03885	0.02051	0.0635	0.0658	0.0975
H$_2$Se	1.460	1.460	2344.5	1034.2	2357.8	0.20184	1.05503	0.98750	0.02706	0.07203	0.02722	0.0982	0.0986	0.1488
D$_2$Se	1.461	1.461	1630	745	1696	0.39488	2.19374	1.95062	0.01878	0.05564	0.01954	0.0883	0.0916	0.1318
CH$_2$	1.029	1.029	2968	1444	3000	0.19809	0.76959	0.89401	0.02400	0.02806	0.02424	0.0836	0.0818	0.1434
SO$_2$	1.432	1.432	1151.3	517.6	1361.7	2.14598	10.82905	9.14286	0.00663	0.00565	0.00784	0.3139	0.3271	0.5543
NO$_2$	1.193	1.193	1320	648	1621	1.62391	5.35349	5.89474	0.00853	0.00892	0.01048	0.8852	0.8360	1.6861
F$_2$O	1.55	1.55	830	490	1110	1.69184	10.83874	7.67745	0.01029	0.01321	0.01376	0.5427	0.6633	0.9447
Cℓ$_2$O	1.47	1.47	680	330	973	2.05266	17.20668	8.81294	0.00958	0.01077	0.01371	0.5614	0.6550	1.0293

*All molecules are assumed to be composed of the most abundant atomic isotope. For other isotopic compositions, see Ref. 16.

**The constants listed are for x_α [illegible], that is [illegible] x_α [illegible] x_α^i (see Appendix C); the underlined values are deduced from measurements (Ref. 10), all others are calculated (Appendix C).

to describe motions along the molecular axis for relative displacements of the XY and YZ bonds, while angular or bending force constants k_δ (dyne-cm/radian) are used for motions of the atoms perpendicular to this axis (Ref. 10, p. 172). In Appendix B, expressions are given for the normal vibrational frequencies ν_1, ν_2, and ν_3 in terms of these force constants, the atomic masses, and the equilibrium atomic separations, based on the valence-force mechanical model. It is shown there further how to calculate M_1, M_2, M_3, z_1, z_2, and z_3 from these basic atomic constants. Appendix C shows how to get estimates for the anharmonic constants x_1, x_2, and x_3.

Table 3-7 summarizes calculated and/or measured values for ν_α, x_α, M_α, and z_α for the three normal vibrations of most common linear XY_2 and XYZ molecules according to the formulas given in Appendices B and C and/or data supplied by Refs. 2, 10, 11, 15, 16, and 20.

3.3.2.2 Planar Molecules (XY_2, XY_3)

Although other types exist, we shall consider here only planar (nonlinear) triatomic XY_2 and four-atomic XY_3 which are the most common chemical formulas for molecules in this class. Table 3-7 lists values for ν_α, x_α, M_α and z_α for the three normal vibrations of XY_2 while in Table 3-8 values for the four normal vibrations of planar XY_3 are given as obtained from the general relations for these molecules developed in Appendices B and C. Of the nonlinear XY_2 group, H_2O is probably the best known one, while BF_3 is the most commonly quoted representative of the planar XY_3 group.

TABLE 3.8 BASIC VIBRATIONAL PARAMETERS OF SELECTED FOUR-ATOMIC XY$_3$ MOLECULES (Refs. 11, 15, 16)*

Molecule XY$_3$	Frequencies (cm^{-1}) of the Normal Vibrations				Masses (amu) of the Normal Vibrations				Anharmonic Constants of the Normal Vibrations**				Dipole Charges of the Normal Vibrations			
	ν_1	ν_2	ν_3	ν_4	M_1	M_2	M_3	M_4	x_1	x_2	x_3	x_4	z_1	z_2	z_3	z_4
PLANAR																
BF_3	888	691	1446	480	19	3.0735	0.4335	6.2250	0.00408	0.00317	0.00905	0.00458	0	0.5958	1.8454	2.2326
BCl_3	471	462	958	243	35	3.31[illegible]	0.4573	16.0525	0.00225	0.00220	0.00562	0.00239	0	0.3095	0.9992	1.3544
BBr_3	279	372	[illegible]	151	80	3.5060	0.4765	33.0719	0.00139	0.00186	0.00495	0.00149	0	0.2762	0.9775	1.2216
SO_3	1069	652	1330	532	16	6.4000	0.9426	5.1988	0.00368	0.00303	0.00700	0.00428	0	0.3261	1.8437	1.7871
CO_3^{--}	1063	879	1415	680	16	3.2000	0.4587	3.3183	0.00253	0.00210	0.00443	0.00426	0	0.5474	1.6358	1.8581
NO_3^-	1050	831	1390	720	16	3.6129	0.5559	3.7465	0.00383	0.00303	0.00800	0.00826	0	0.5036	1.6018	1.8535
PYRAMIDAL																
NH_3	3337	950	3414	1628	0.2370	2.1807	0.2611	1.2926	0.01457	0.00415	0.02204	0.01710	0.0336	0.0313	0.0895	0.0354
ND_3	2419	749	2555	1191	0.4382	3.5821	0.3138	1.5816	0.01034	0.00320	0.01600	0.01230	0.0317	0.0298	0.0797	0.0313
PH_3	2327	991	2421	1121	0.2176	1.4414	0.2632	1.1897	0.01222	0.00521	0.02240	0.01878	0.0247	0.0248	0.0500	0.0261
PD_3	1694	730	1780	806	0.4136	2.2300	0.3569	1.5700	0.00882	0.00380	0.01623	0.01350	0.0232	0.0232	0.0434	0.0225
PF_3	890	531	840	486	2.6216	7.0402	2.6059	8.1343	0.00257	0.00153	0.00293	0.00251	0.4903	0.4546	0.8474	0.4555
PCl_3	510	257	480	190	3.3136	13.6883	3.5678	21.2442	0.00144	0.00072	0.00161	0.00095	0.3069	0.3108	0.6484	0.3101
PBr_3	380	162	400	116	4.1310	25.1541	3.8056	47.4070	0.00118	0.00050	0.00146	0.00061	0.2413	0.1576	0.5593	0.2638
AsF_3	707	341	644	274	4.0779	16.1788	3.0727	15.8047	0.00255	0.00123	0.00296	0.00185	0.4948	0.4448	0.8235	0.4670
$AsCl_3$	410	193	370	159	4.5784	19.8416	5.7164	15.8232	0.00141	0.00067	0.00158	0.00099	0.2874	0.2847	0.5078	0.2346
$SbCl_3$	360	165	320	134	5.1995	24.2393	5.6972	32.1376	0.00139	0.00064	0.00157	0.00092	0.2740	0.2727	0.4330	0.2804
$BiCl_3$	288	130	242	96	5.7869	32.6258	6.0588	38.3057	0.00172	0.00077	0.00217	0.00121	0.2278	0.2358	0.3572	0.2288
[illegible]I_3	(157)	(66)	(159)	(57)	14.3865	84.0355	17.1539	134.4159	0.00117	0.00051	0.00162	0.00080	0.1329	0.1340	0.2405	0.1565

*All molecules are assumed to be composed of the most abundant atomic isotopes. For other isotope compositions, see Ref. 16.

**The constants listed were calculated for $v_\alpha = 1$, that is $x_\alpha - x'_\alpha$ (see Appendix C).

3.3.2.3 Pyramidal Molecules (XY_3)

Of the three-dimensionally structured four-atomic molecules, the pyramidal XY_3 group represented by NH_3 is probably the most studied. Table 3-8 lists values of ν_α , M_α , x_α , and z_α for the four normal vibrations of a number of XY_3 molecules which have been extensively investigated. These parameters were calculated from the relations developed in Appendices B and C.

3.3.2.4 Tetrahedral Molecules (XY_4)

The highly symmetric XY_4 molecule represented by CH_4 is another well-studied three-dimensionally structured molecule. Table 3-9 lists values of ν_α , M_α , x_α , and z_α for the four normal vibrations of commonly-occurring XY_4 molecules, obtained from the relations in Appendices B and C.

3.3.2.5 Octahedral Molecules (XY_6)

Values of ν_α , M_α , x_α , and z_α for the six normal vibrations of the very symmetric XY_6 molecules such as SF_6 and UF_6 are listed in Table 3-10. These parameters were calculated from equations discussed in Appendices B and C.

TABLE 3.9. BASIC VIBRATIONAL PARAMETERS OF SELECTED TETRAHEDRAL XY_4 MOLECULES (Refs. 11, 15, 16)

Molecule XY_4	Frequencies (cm^{-1}) of the Normal Vibrations				Masses (amu) of the Normal Vibrations				Anharmonic Constants of the Normal Vibrations*				Dipole Charges of the Normal Vibrations		
	ν_1	ν_2	ν_3	ν_4	M_1	M_2	M_3	M_4	x_1	x_2	x_3	x_4	$z_1 = z_2$	z_3	z_4
CH_4	2914	1526	3020	1306	1	0.3333	0.1747	0.8880	0.01115	0.01314	0.01783	0.00692	0	0.3250	0.0982
CD_4	2085	1054	2258	996	2	0.6667	0.3011	1.6302	0.00793	0.00907	0.01320	0.00528	0	0.3091	0.0959
SiH_4	2187	978	2183	910	1	0.3333	0.1816	1.3121	0.01342	0.05511	0.03075	0.01007	0	0.1456	0.0472
NH_4^+	3033	1685	3134	1397	1	0.3333	0.1818	0.8304	0.00895	0.00870	0.01270	0.00525	0	0.1862	0.0510
CF_4	904	437	1265	630	19	6.3333	0.8282	9.4276	0.00189	0.00112	0.00302	0.00145	0	2.7472	1.0907
SiF_4	800	260	1022	420	19	6.3333	1.4417	21.3957	0.00231	0.00100	0.00354	0.00138	0	4.7344	1.8238
$CC\ell_4$	458	218	776	314	35	11.6667	0.9014	16.3366	0.00107	0.00063	0.00207	0.00081	0	1.7718	0.7126
$SiC\ell_4$	424	150	608	221	35	11.6667	1.7739	28.7485	0.00148	0.00073	0.00262	0.00090	0	2.4651	0.9132
$TiC\ell_4$	386	120	495	141	35	11.6667	2.5293	41.7076	0.00260	0.00177	0.00529	0.00130	0	3.3423	1.1005
$GeC\ell_4$	396	134	453	172	35	11.6667	3.2380	41.0046	0.00146	0.00058	0.00210	0.00090	0	2.2825	0.8124
$SnC\ell_4$	366	104	403	134	35	11.6667	3.9356	66.6070	0.00143	0.00048	0.00200	0.00076	0	3.1315	1.1215
CBr_4	267	123	672	183	79	26.3333	0.9541	36.0855	0.00069	0.00038	0.00197	0.00052	0	1.5432	0.6118
$SiBr_4$	249	90	487	137	79	26.3333	2.0589	54.1529	0.00092	0.00044	0.00217	0.00057	0	2.0300	0.7466
$GeBr_4$	234	78	328	111	79	26.3333	4.4201	74.7884	0.00094	0.00042	0.00161	0.00051	0	1.7788	0.6428
$SnBr_4$	220	64	279	88	79	26.3333	5.9996	109.4183	0.00096	0.00039	0.00153	0.00045	0	2.5150	0.8937
CI_4	164	45	216	49	127	42.3333	10.8429	210.1158	0.00094	0.00036	0.00159	0.00103	0	0.9707	0.2971
OsO_4	971	335	960	328	16	5.3333	2.5304	29.6751	0.00211	0.00113	0.00270	0.00087	0	5.4600**	1.8076**
SO_4^{--}	981	451	1104	613	16	5.3333	1.5277	11.1255	0.00253	0.00203	0.00391	0.00201	0	3.3215	1.2449
$C\ell O_4^-$	935	462	1102	628	16	5.3333	1.6280	10.2254	0.00513	0.02603	0.01423	0.00628	0	2.1487	0.7861
PO_4^{---}	980	363	1082	515	16	5.3333	1.4434	15.6739	0.00221	0.00130	0.00319	0.00143	0	2.5642	0.9834

*The constants listed were calculated for $v_\alpha = 1$, that is $x_\alpha = x'_\alpha$ (see Appendix C).

**A value of $(z_o)_{XY} = 0.53$ was assumed for OsO_4.

TABLE 3-10. BASIC VIBRATIONAL PARAMETERS OF SELECTED OCTAHEDRAL XY_6 MOLECULES (Refs. 22 and 27)

Molecule XY_6	Frequencies (cm^{-1}) of the Normal Vibrations						Masses (amu) of the Normal Frequenci		
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$M_1 = M_2 = M_5 = M_6$	M_3	M_4
SF_6	773.5	641.7	939	614	525	347	19	18.7653	29.5252
SeF_6	706.9	658.7	780	437	405	264	19	41.4122	143.4663
TeF_6	697.1	6[illegible].3	752	327	314	197	19	65.3099	396.9187
MoF_6	741.5	651.6	741.1	264	318	116	19	49.1339	310.1968
WF_6	771.0	677.2	711	258	320	127	19	92.9541	875.0934
UF_6	667.1	532.5	624.4	186.2	202	134	19	119.8799	1321.4626

Molecule XY_6	Anharmonic Constants of the Normal Vibrations*						Dipole Charges of the Normal Vibrations		
	x_1	x_2	x_3	x_4	x_5	x_6	$z_1 = z_2 = z_5 = z_6$	z_3	z_4
SF_6	0.002[illegible]6	0.00512	0.00293	0.00184	0.00181	0.00119	0	3.6809	3.2735
SeF_6	0.00266	0.00500	0.00375	0.00196	0.00226	0.00145	0	3.5549	4.0109
TeF_6	0.00251	0.00720	0.00340	0.00139	0.00163	0.00103	0	3.5711	4.4020
MoF_6	0.00191	0.00497	0.00227	0.00079	0.00107	0.00080	0	3.8232	4.1521
WF_6	0.00198	0.00519	0.00215	0.00074	0.00107	0.00072	0	4.3047	5.7200
UF_6	0.00157	0.00375	0.00171	0.00050	0.00060	0.00043	0	3.2599	4.3192

*The constants listed were calculated for $v_\alpha = 1$, that is $x_\alpha = x_\alpha'$ (see Appendix C).

3.4 ROTATIONAL RADIATIVE TRANSITIONS

As mentioned earlier, rotational states and transitions in molecules are best treated in five groups as follows (Ref. 16):

a. Diatomic Molecules

b. Linear Polyatomic Molecules

c. Symmetric Top Molecules

d. Spherical Top Molecules

e. Asymmetric Top Molecules

We shall briefly consider the pertinent transition relations for these five classes of molecules in the order given.

3.4.1 Diatomic Molecules

For molecular rotation, the eigenfunctions to be used in Eq. (1.17) are essentially associated Laguerre functions for the ideal rotator (Ref. 2). For diatomic molecules, the transition element can be shown to equal (Ref. 16, pp. 20-24):

$$\left(R^2_{mn}\right)^{\mathrm{rot.}}_{\mathrm{diatomic}} = d_o^2 \frac{\frac{1}{2}(J_m + J_n + 1)}{(2J_m + 1)(2J_n + 1)} \;,\quad \mathrm{cm}^2 \;, \tag{3.100}$$

where the effective dipole "length" d_o is related to the permanent dipole moment μ_o of the molecule by:

$$d_o = \frac{\mu_o}{e} = z_o r_e \tag{3.101}$$

Here r_e is the equilibrium interatomic distance of the molecule XY, and z_o is the permanent dipole charge. Measured or estimated values of z_o and r_e (and therefore d_o) of various diatomic molecules and radicals are given in Table B-3 of Appendix B.

Note from Table B-3 that all homonuclear diatomic molecules (H_2, N_2, O_2, $C\ell_2$, etc.), have a zero permanent dipole moment as one would expect. Thus although these molecules do rotate and can possess rotational levels J = 0, 1, 2, ... , which can be excited or deexcited in molecular collisions, they cannot interact (via a first-order electric-dipole) with the radiation field and absorb or emit photons in a pure rotational transition.

The parameters J_m and J_n in Eq. (3.100) are the rotational quantum numbers of rotational levels m and n respectively. In contrast to vibrational transitions, rotational transitions obey the selection rules rigorously. These rules hold that for a rotational radiative dipole transition in a diatomic molecule:

$$\Delta J = J_m - J_n = \pm 1 \qquad (3.102)$$

Since a rotational angular momentum of J units of $\hbar$ can be oriented in (2J + 1) different directions in space according to the space quantization laws (Ref. 1), the degeneracies w_{r_m} and w_{r_n} of the rotational states m and n are simply:*

---

*Of course the total degeneracy of a molecule at level k is equal to the product $w_{e_k} w_{v_k} w_{r_k}$ (see Chapter 1).

$$w_{r_m} = 2J_m + 1 \tag{3.103a}$$

$$w_{r_n} = 2J_n + 1 \tag{3.103b}$$

Furthermore since all w_{r_m} states can connect to any one of the w_{r_n} states in a transition with $\Delta J = \pm 1$, we have for the connection factor C_{mn}^{rot} that:

$$C_{mn}^{rot} = w_{r_m} w_{r_n} = (2J_m + 1)(2J_n + 1) \tag{3.104}$$

The rotational energy levels of a diatomic molecule are given by (Ref. 16):

$$\left(E_J\right)_{\substack{\text{diatomic}\\ \text{molecule}}}^{rot} = hc\left[B_e J(J + 1) - \alpha_e\left(v + \frac{1}{2}\right) J(J + 1) - D_e J^2(J + 1)^2\right] \approx$$

$$\approx hc\left[B_e J(J + 1) - \alpha_e\left(v + \frac{1}{2}\right) J(J + 1)\right] \text{, ergs ,} \tag{3.105}$$

where:

$$B_e = h/(8\pi^2 c I_e) \text{ , cm}^{-1} \tag{3.106}$$

$$D_e = 4B_e^3/\nu_e^2 \text{ , cm}^{-1} \tag{3.107}$$

$$\alpha_e = 6(x_e B_e^3/\nu_e)^{1/2} - 6B_e^2/\nu_e \text{ , cm}^{-1} \tag{3.108}$$

Here B_e is the main rotational energy constant often called "the rotational constant" which is related to the molecular moment of inertia

I_e (gram - cm^2) via (3.106). The much smaller constants α_e and D_e are corrections of the main rotational energy for respectively the change in the average moment of inertia due to vibrations, and centrifugal stretching. The parameter ν_e(cm^{-1}) is the fundamental vibrational frequency of the molecule, v is the vibrational energy level quantum number, and x_e is the anharmonic constant which were all discussed in the previous section. Values of the rotational constant B_e for some selected diatomic molecules are listed in Table 3-11. Table 3-11 also lists values of d_o for these molecules.

If we define J to be the larger of J_m and J_n (we denote this by $J = \sup(J_m, J_n)$), Eq. (3.100) can be rewritten with the aid of Eq. (3.102) in the simple form:

$$\boxed{\underset{(J = \sup(J_m, J_n))}{\left(R^2_{mn}\right)_{\substack{\text{rot}\\ \text{diatomic}}}} = d_o^2 \frac{J}{(2J + 1)(2J - 1)} \text{ , cm}^2 \text{ ,}} \tag{3.109}$$

or:

$$\boxed{\underset{(J = \sup(J_m, J_n))}{\left(S_{mn}\right)_{\substack{\text{rot}\\ \text{diatomic}}}} = C^{\text{rot}}_{mn} \left(R^2_{mn}\right)_{\text{rot}} = J\, d_o^2 \text{ , cm}^2 \text{ ,}} \tag{3.110}$$

and:

TABLE 3-11. ROTATIONAL CONSTANTS AND DIPOLE LENGTHS OF SELECTED DIATOMIC MOLECULES (Refs. 1, 16)*

Molecule	Rotational Constant B_e (cm^{-1})	Vibrational Correction Constant α_e (cm^{-1})	Dipole Length d_o (Angstrom = 10^{-8} cm)
H_2	60.800	2.993	0
HO	18.871	0.714	0.3456
HN	16.65	0.64	0.2115
HF	20.939	0.770	0.3789
$HC\ell$	10.5909	0.3019	0.2249
HBr	8.473	0.226	0.1707
HI	6.551	0.183	0.0916
DO	10.0202	0.295	(0.3272)
CO	1.9313	0.01748	0.0233
CS	0.8205	0.00624	0.4123
CN	1.8996	0.01735	0.0800
CH	14.457	0.534	0.3040
CD	7.808	0.212	(0.2815)
N_2	2.010	0.0187	0
NO	1.7046	0.0178	0.0319
NS	(1.0480)	(0.01475)	(0.3599)
$C\ell F$	0.51651	0.004358	0.1832
BrF	0.35717	0.005214	0.2685
$IC\ell$	0.11416	0.000536	0.1352
$KC\ell$	0.1250	0.0000756	2.138
O_2	1.44566	0.01579	0
F_2	(0.8618)	(0.01627)	0
$C\ell_2$	0.2438	0.0017	0

*NOTE:

The most abundant isotopes are assumed for the atoms in each molecule. Values in parentheses are estimates. All values are for the electronic ground state of the molecule.

$$\boxed{C^{\text{rot}}_{\substack{mn\\ \text{diatomic}\\ (J\,=\,\sup(J_m,J_n))}} = (2J+1)(2J-1)} \qquad (3.111)$$

Note that we could also have taken our reference transition as the $J_m = 1 \rightarrow J_n = 0$ transition in which case:

$$\boxed{\left(R^2_{o_{mn}}\right)_{\substack{\text{rot}\\ \text{diatomic}}} = d_o^2 \quad , \quad \text{cm}^2} \qquad (3.112)$$

and C^{rot}_{mn} would have to be defined as:

$$\boxed{C^{\text{rot}}_{\substack{o_{mn}\\ \text{diatomic}\\ (J\,=\,\sup(J_m,J_n))}} = J} \qquad (3.113)$$

The advantage of this latter approach is that $\left(R^2_{o_{mn}}\right)_{\text{rot}}$ is constant, while all dependencies on J (and thus ν) reside in the connection factor $C^{\text{rot}}_{o_{mn}}$. Of course physically $C^{\text{rot}}_{o_{mn}}$ does not represent the sum of all possible transitions between the states at level m and the states at level n any more, but it gives the effect on S_{mn} of increasing J relative to the case that the transition is $J_m = 1 \rightarrow J_n = 0$. We shall distinguish between the two definitions for R^2_{mn} and C^{rot}_{mn} by using the subscript o as indicated. S_{mn} is of course the same for both, that is:

$$\left(S_{mn}\right)_{rot} = C^{rot}_{mn} \, R^2_{\substack{mn \\ rot}} = C^{rot}_{o_{mn}} \, R^2_{\substack{o_{mn} \\ rot}} \tag{3.114}$$

Note that in contrast to the vibrational transitions which depend on the vibrational constant ν_o , the "bare" transition elements R^2_{mn} and S_{mn} of rotational transitions are independent of the rotational constant B_e . Only the parameter d_o or μ_o is needed.

For symmetric diatomic molecules such as O_2 whose permanent electric dipole moment $\mu_o = 0$, the rotational quantum states (populated via collisions) might still radiate via the weaker second-order magnetic dipole interaction with the electromagnetic field, if the total electron angular momentum of the molecule including electron spin, $\Omega \neq 0$. The condition $\Omega \neq 0$ occurs for most diatomic molecules only in electronically-excited levels. There are a few exceptions however such as O_2 , whose ground electronic level is a $^3\Sigma$ level, for which $|\Omega| = 1$.*

Provided then that $\Omega \neq 0$, rotational transitions can take place via the magnetic dipole moment $\mu_{M.D.}$ or magnetic dipole length $d_{M.D.} = \mu_{M.D.}/e$ which is approximately giben by (Ref. 6):

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*Other molecules for which $\Omega \neq 0$ in the ground level are NO , NO_2 , and ClO_2 . However these molecules can radiate via the stronger electric dipole interaction of course.

$$d_{M.D.} \approx \left(\frac{\pi e^2}{hc}\right) r_e = \frac{r_e}{274.06} \quad , \text{ cm} \tag{3.115}$$

The transition parameters $\left(R^2_{mn}\right)_{rot}$ and $\left(S_{mn}\right)_{rot}$ for magnetic dipole transitions are then simply given by Eqs. (3.109) and (3.110) with d_o^2 replaced by $d^2_{M.D.}$. By comparing (3.115) with (3.101), note that a magnetic dipole transition acts like an electric dipole transition with an effective permanent dipole charge z_o of:

$$\left(z_o\right)_{\substack{M.D.\\ \text{effective}}} \approx \frac{\pi e^2}{hc} \approx 0.00365 \tag{3.116}$$

A magnetic dipole transition with the value (3.115) can take place for O_2 only for the isotopic combination $O^{16}O^{18}$ or $O^{16}O^{17}$. For a homonuclear diatomic molecule such as $O^{16}O^{16}$, a new selection rule arising from nuclear spin forbids transitions between two adjacent rotational levels (Ref. 2, pp. 130-139). We shall discuss this situation again in Chapter 4 in more detail.

3.4.2 Linear Polyatomic Molecules

Rotational transitions in linear polyatomic molecules are quite similar to those occurring in diatomic molecules, except for one additional complication called "ℓ-type doubling." This effect is caused by the fact that in a linear molecule, the doubly-degenerate bending vibration (usually denoted ν_2 for triatomic molecules) can vibrate either in a plane perpendicular to the molecular rotation axis (the rotation is end-over-end) or parallel to this axis. In the former case an effective Coriolis force exists if the molecule is rotating while in the latter case this Coriolis force is zero (see Ref. 16, p. 31-34). As a result, rotational transitions for a molecule that is vibrating in the bending mode are slightly different for the parallel and perpendicular cases and this lifting of the degeneracy causes the "ℓ-type doubling" of rotational transition frequencies.

Not only are rotational transition frequencies slightly shifted (doubled) when the bending vibration is present, but the transition rate relations and selection rules are also effected. If the bending vibration ν_b (usually $\nu_b = \nu_2$ for triatomic linear molecules) has quantum level v_b (where $v_b = 0\ ,\ 1\ ,\ 2\ ,\ldots.$), the effect of the Coriolis force is to introduce another set of quantum numbers ℓ , where:*

$$\ell = v_b\ ,\ v_b - 2\ ,\ v_b - 4\ ,\ \ldots\ldots\ ,\ -v_b \tag{3.117}$$

The transition parameters S_{mn} and R^2_{mn} for transitions with $\Delta J = |J_m - J_n| = 1$ are then (Ref. 16, p. 34):

$$\boxed{\underset{\substack{\text{linear mol.}\\ (J\,=\,\sup(J_m,J_n)\ ;\ \Delta J\,=\,1)}}{\left(S_{mn}\right)_{\text{rot}}} = \left(\frac{J^2 - \ell^2}{J}\right) d_o^2\ ,\ \text{cm}^2} \tag{3.118}$$

and:

---

*This quantum number ℓ should not be confused with the quantum number ℓ for the orbital momentum of an electron.

$$\boxed{\begin{array}{l}\left(R^2_{mn}\right)_{\substack{\text{rot}\\\text{linear mol.}}} = \left(\dfrac{J^2 - \ell^2}{J}\right) \dfrac{d_o^2}{(2J + 1)(2J - 1)} \ , \ \text{cm}^2 \\ (J = \sup(J_m, J_n) \ ; \ \Delta J = 1)\end{array}} \qquad (3.119)$$

while for ΔJ = 0 transitions which can also take place (see below) we have (Ref. 16, p. 34):

$$\boxed{\begin{array}{l}\left(S_{mn}\right)_{\substack{\text{rot}\\\text{linear mol.}}} = \left(\dfrac{\ell^2}{J}\right)\left(\dfrac{2J - 1}{J - 1}\right) d_o^2 \ , \ \text{cm}^2 \\ (J = \sup(J_m, J_n) \ ; \ \Delta J = 0)\end{array}} \qquad (3.120)$$

and:

$$\boxed{\begin{array}{l}\left(R^2_{mn}\right)_{\substack{\text{rot}\\\text{linear mol.}}} = \left(\dfrac{\ell^2}{J}\right) \dfrac{d_o^2}{(J - 1)(2J + 1)} \ , \ \text{cm}^2 \\ (J = \sup(J_m, J_n) \ ; \ \Delta J = 0)\end{array}} \qquad (3.121)$$

The weights of rotational levels m and n are the same as for diatomic molecules, that is:

$$\left({}^{w}r_k\right)_{\substack{\text{rot}\\\text{linear mol.}}} = 2J_k + 1 \qquad (3.122)$$

and also:

$$\left(C^{rot}_{mn}\right)_{\text{linear mol.}} = w_{r_m} w_{r_n} = (2J_m + 1)(2J_n + 1) \tag{3.123}$$

If we define parameters $\left(R^2_{o_{mn}}\right)$ and $C^{rot}_{o_{mn}}$ again (see Eq. (3.112), we have:

$$\boxed{\left(R^2_{o_{mn}}\right)_{\substack{\text{rot}\\ \text{linear mol.}}} = d_o^2 \quad , \quad \text{cm}^2 \quad ,} \tag{3.124}$$

and:

$$\boxed{\begin{gathered}\left(C^{rot}_{o_{mn}}\right)_{\text{linear mol.}} = \frac{J^2 - \ell^2}{J} \\ (J = \sup(J_m, J_n) \;\; ; \;\; \Delta J = 1)\end{gathered}} \tag{3.125}$$

$$\boxed{\begin{gathered}\left(C^{rot}_{o_{mn}}\right)_{\text{linear mol.}} = \frac{\ell^2(2J - 1)}{J(J - 1)} \\ (J = \sup(J_m, J_n) \;\; ; \;\; \Delta J = 0)\end{gathered}} \tag{3.126}$$

The selection rules for rotational transitions in linear molecules are (Ref. 10):

$$\boxed{\left\{\begin{array}{c} \Delta J = |J_m - J_n| = 1 \\ \ell = 0 \rightarrow \ell = 0 \end{array}\right\}} \qquad (3.127)$$

or:

$$\boxed{\left\{\begin{array}{c} \Delta J = J_m - J_n = 0\ ,\ \pm 1 \\ \Delta\ell = \pm 1\ ;\ (J_m = 0) \nleftrightarrow (J_n = 0) \end{array}\right\}} \qquad (3.128a)$$

$$\boxed{\left\{\begin{array}{c} \Delta J = J_m - J_n = \pm 1\ ;\ \Delta J = 0\ (\text{weak}) \\ \Delta\ell = 0\ ;\ \ell \neq 0 \end{array}\right\}} \qquad (3.128b)$$

In addition we have always that $J \geq \ell$. Note when $v_b = 0$, we have $\ell = 0$, and all transitional relations are identical to those for diatomic molecules.

The permanent dipole moment μ_o or length d_o of a linear molecule has been measured for a number of species. Values of some selected linear molecules taken from Refs. 15 and 20 are listed in Table 3-12. If values of μ_o or d_o are not available but the values of z_o and r_e are known for the diatomic components XY and YZ of a triatomic linear XYZ molecule, an estimate of d_o for the XYZ molecule may be obtained via the relation (see Appendix B):

$$d_o = (2\pi\nu_1 M_1)^{1/2} \left[\frac{\ell_{XY}(z_o)_{XY}}{(k_{11}M_{11})^{1/4}} - \frac{\ell_{YZ}(z_o)_{YZ}}{(k_{12}M_{12})^{1/4}} \right] =$$

$$= 0.0155786\ \underset{(\mathrm{cm}^{-1})(\mathrm{amu})}{(\nu_1 M_1)^{1/2}} \left[\frac{\ell_{XY}(z_o)_{XY}}{(k_1 M_{11})^{1/4}} - \frac{\ell_{YZ}(z_o)_{YZ}}{(k_3 M_{12})^{1/4}} \right]_{(\mathrm{dyne/cm})(\mathrm{amu})}\ ,\ \mathrm{cm}\ . \qquad (3.129)$$

TABLE 3-12. ROTATIONAL CONSTANTS, PERMANENT ELECTRIC DIPOLE MOMENTS μ_o, AND ELECTRIC DIPOLE LENGTHS d_o OF SELECTED LINEAR MOLECULES (Data from Refs. 15, 16, 20)

Molecule*	Rotational Constant B_e (cm^{-1})	Correction Constant from ν_1 Vibration, α_1 (10^{-4} cm^{-1})	Correction Constant from ν_2 Vibration, α_2 (10^{-4} cm^{-1})	Correction Constant from ν_3 Vibration, α_3 (10^{-4} cm^{-1})	ℓ-Doubling Energy Splitting q_ℓ (10^{-4} cm^{-1})	Dipole Length d_o (Angstroms = 10^{-8} cm)
OCO	0.39021	12.1	-7.2	30.9		0
SCS	0.10910	1.5	-2.6	7.11		0
OUO	0.21109					0
OCS	0.20286	6.8	-3.52	12.128	2.116	0.148
OCSe	0.1340	4.43	-3.46	(~10)	2.025	0.157
SCSe	0.0674					(0.08)
SCTe	0.0520		-1.08		0.220	0.035
HCN	1.47822	9.5	-3.6	10.4	7.49	0.625
CℓCN	0.19916		-5.47		2.50	0.583
BrCN	0.1374	5.18	-3.86		1.31	0.604
ICN	0.1076	3.11	-3.18		0.897	0.775
NNO	0.419011	17.9	-5.6	34.5	7.92	0.0346
HCCCℓ	0.1896					0.092
HCCCN	0.1517					0.75

*The most abundant isotopes are assumed for the atoms in the molecule.

where ℓ_{XY} and ℓ_{YZ} are the equilibrium separations of atoms X,Y and Y,Z in the molecule XYZ (in units of cm) and $(z_o)_{XY}$ and $(z_o)_{YZ}$ are the permanent dipole charges of the molecules or radicals XY and YZ, that is:

$$(z_o)_{XY} = e^{-1} \left(\mu_o / r_e\right)_{XY} , \qquad (3.130)$$

$$(z_o)_{YZ} = e^{-1} \left(\mu_o / r_e\right)_{YZ} , \qquad (3.131)$$

which are tabulated in Table B-3 of Appendix B for a large number of species. The parameters M_{11} and M_{12} in Eq. (3.129) are given by (see Appendix B):

$$M_{11} = \frac{2M_X M_Y}{(M_X + M_Y)(1 - \sqrt{1 - A})} , \text{ amu} , \qquad (3.132)$$

$$M_{12} = \frac{2M_Y M_Z}{(M_Y + M_Z)(1 - \sqrt{1 - A})} , \text{ amu} , \qquad (3.133)$$

where the constant A is given by:

$$A = \frac{4k_1 k_3 (M_X + M_Y + M_Z)\, M_X M_Y M_Z}{\left[k_1 (M_X + M_Y)\, M_Z + k_3 (M_Y + M_Z)\, M_X\right]^2} \qquad (3.134)$$

and M_X , M_Y , M_Z are the atomic masses (in amu) of the atoms X , Y , and Z. The force constants $k_{11} = k_1$ and $k_{12} = k_3$ (in dynes/cm) are tabulated in

Table B-4 of Appendix B for a number of linear molecules. Finally we have (see Appendix B):

$$M_1 = \left[M_{11}^{-1/2} + M_{12}^{-1/2}\right]^{-2} \qquad (3.135)$$

The reason why the $(z_o)_{XY}$ and $(z_o)_{YZ}$ have to be weighted with vibrational parameters is that the vibrational frequencies are much higher than the rotational frequencies, so that as far as rotational transitions is concerned, quantum-mechanically-calculated values of $(z_o)_{XY}$ and $(z_o)_{YZ}$ are needed which are averaged over the vibrations. That is in the quantum-mechanical expression for the transition matrix, we must write:

$$\left(R^2_{mn}\right)_{\substack{rot \\ (v_{1_m}=v_{1_n})}} = \left| \iint \Psi^{\dagger}_{v_{1_n}} \Psi^{\dagger}_{J_n} \vec{r}_{rot} \, z \, \Psi_{v_{1_m}} \Psi_{J_m} \, d\tau_v \, d\tau_J \right|^2 =$$

$$= \left| \left[\int_{(v_{1_n}=v_{1_m})} \Psi^{\dagger}_{v_{1_n}} z \, \Psi_{v_{1_m}} \, d\tau_v \right] \left[\int \Psi^{\dagger}_{J_n} \vec{r}_{rot} \Psi_{J_m} \, d\tau_J \right] \right|^2 , \qquad (3.136)$$

where v_1 refers to a vibrational level of the first normal vibration ν_1, the $\Psi_{v_{1_k}}$ are the vibrational eigenfunctions of the ν_1 vibration with the molecule in state k, and the Ψ_{J_k} are the rotational eigenfunctions of the molecule in state k.

In the last member of (3.136), the first factor involving the vibrational eigenfunctions and the dipole charge z introduces weight factors involving the vibrational parameters k_1 , k_3 , and the atomic masses M_X , M_Y , and M_Z , if one employs the composite dipole charge method as explained in Appendix B. Although in Appendix B, the composite dipole-charge method was developed primarily for the treatment of vibrational dipole transitions, the same techniques can be applied for the construction of the permanent dipole charge z_o needed in rotational dipole transition calculations. However whereas one needs to calculate three derivative dipole charges z_1 , z_2 , z_3 for the three normal vibrations of an XYZ molecule, for the rotational transitions we need only one constant z_o . For the XYZ molecule the calculation of this z_o value via the composite dipole method involves the same weighting constants as that involved in the calculation of z_1 for the vibrational derivative dipole charge of the first normal vibration ν_1 as was illustrated in Appendix B in the discussion on OCS.

Note from Table 3-12 that the permanent dipole moment of symmetric triatomic linear molecules such as CO_2 (OCO) and CS_2 (SCS) are zero as one would expect from Eq. (3.129). This means that these molecules cannot absorb or emit a photon (in the microwave region) in a pure rotational transition. Of course this does not prevent a photon from being emitted or absorbed (in the infrared) in a vibrational transition which is accompanied by a rotational transition of a symmetric triatomic molecule like CO_2 (see Chapter 4), since in general the vibrational first-order-derivative charge $z_1 \neq z_o$.

Though we shall have occasion to discuss rotational energy levels more fully in Chapter 4, we give here for completeness the expression for the rotational energy of a linear polyatomic molecule (Ref. 16) with quantum number J:

$$\left(E_J\right)^{\text{rot}}_{\substack{\text{linear}\\ \text{molecule}}} = hc\left[B_v\left\{J(J+1) - \ell^2\right\} - D_v\left\{J(J+1) - \ell^2\right\}^2\right] =$$

$$\approx hc\left[B_v\left\{J(J+1) - \ell^2\right\}\right] \text{, erg ,} \tag{3.137}$$

where:

$$B_v = B_e - \alpha_1\left(v_1 + \frac{1}{2}\right) - \alpha_2(v_2 + 1) - \alpha_3\left(v_3 + \frac{1}{2}\right) \text{ , } \quad \text{cm}^{-1} \tag{3.138}$$

The centrifugal stretching constant D_v for linear polyatomic molecules depends in a complicated manner on other molecular parameters (see Ref. 16), but fortunately it is small so that the second term in (3.137) can usually be ignored. We have also neglected the small "ℓ-doubling" energy level splitting of each rotational line, which equals (Ref. 16):

$$\left(\Delta E_J\right)_{\ell\text{-doubling}} \approx 1.3\,\frac{hcB_e^2}{\nu_2}\,(v_2 + 1)\,J(J+1) \text{ , ergs} \tag{3.139}$$

Here ν_2 and B_e are in units of cm^{-1} .

In Table 3-12, values for the rotational constants $B_e(\text{cm}^{-1})$ and α_1 , α_2 , α_3 (cm^{-1}) for selected linear polyatomic molecules are given, taken from Refs. 2 and 16. If measured values for α_1 , α_2 , and α_3 are not available, we may estimate these parameters by the equation:

$$\alpha_3 \simeq 6\left[\left(\frac{x_3 B_3^3}{\nu_3}\right)^{1/2} - \frac{B_e^2}{\nu_3}\right], \quad \text{cm}^{-1} \tag{3.140}$$

in analogy with (3.107) for diatomic molecules. Here we take values for x_β and ν_β from Table 3-2 in the previous section.

Note again that as for the diatomic case the "bare" rotational transition elements R^2_{mn} and S_{mn} for linear molecules are independent of the rotational constant B_v. Of course when we consider broadening and spacing of rotational lines in a vibrational band which we shall take up in Chapter 4, B_v does play an important role.

3.4.3 Symmetric-Top Molecules

Symmetric-top molecules are basically pyramidal in their structure and rotate about the pyramid height coordinate as axis. Typical molecules in this class are XY_3 molecules such as NH_3 and AsF_3 in which the Y's are in one plane at the corners of a triangle and the X atom is some distance above this plane equidistant from the Y atoms and thus at the top of the pyramid. Other symmetric tops are formed by XY_3Z such as CH_3F and $CF_3C\ell$ in which XY_3 is similar to NH_3 , and the Z atom is stationed above the X atom along the height coordinate of the pyramid formed by XY_3 . Reference 16 lists other molecules of more than five atoms which are symmetric tops as far as rotation is concerned.

Rotations of symmetric-top molecules are specified by two quantum numbers J and K (Ref. 16, p. 48 ff), J being the quantum number for the total rotational angular momentum of the molecule which is given by:

$$P^2 = J(J + 1)\ h^2/(4\pi^2) \tag{3.141}$$

and K quantizing the z-component of the angular momentum (taken to be along the molecular axis) given by:

$$P_z^2 = K^2h^2/(4\pi^2) \qquad (3.142)$$

Here:

$$P^2 = P_x^2 + P_y^2 + P_z^2 \qquad (3.143)$$

For a given total rotational angular momentum having quantum number J, the quantum number K can take on any one of the values:

$$K = J\ ,\ J - 1\ ,\ \ldots\ldots\ ,\ -J \qquad (3.144)$$

The rotational energy levels for the symmetric-top rotator with rotational quantum numbers J and K are to first-order (Refs. 10 and 16):

$$\left(E_{J,K}\right)^{\text{rot}}_{\substack{\text{Symm.-Top}\\ \text{Molecule}}} = hc\Big[B\ J(J + 1) + (A - B)\ K^2 +$$

$$- 2\ A|K| \sum_{\beta} (\pm \ell_{\beta_i}\ \zeta_\beta)\Big]\ ;\quad \text{ergs} \qquad (3.145)^*$$

where B and A are rotational constants defined by:

$$B = \frac{h}{8\pi^2 cI_B} - \sum_{\beta} \alpha_\beta^B \left(v_\beta + \frac{d_\beta}{2}\right),\ \text{cm}^{-1} \qquad (3.146)$$

---

*We follow Herzberg's nomenclature. Townes and Schawlow prefer C in place of A.

$$A = \frac{h}{8\pi^2 c I_A} - \sum_\beta \alpha_\beta^A \left(v_\beta + \frac{d_\beta}{2}\right) \text{ , cm}^{-1} \qquad (3.147)$$

Here I_B and I_A are the two principal moments of inertia of the symmetric-top, and the terms with α_β^B and α_β^A are corrections for changes in these moments of inertia if vibrations β of excitation level v_β and degeneracy d_β (d_β = 1 or 2 usually) are present.

The term with the parameter ζ_β in Eq. (3.145) arises only when a degenerate vibration β ($d_\beta \neq 1$) is also excited together with the rotational excitations. Such a degenerate vibration possesses a vibrational angular momentum which gives rise to a Coriolis force (see Ref. 10, p. 403 ff) and which interacts with the pure rotational angular momenta. For the most common symmetric-top molecules such as pyramidal XY_3 , only doubly-degenerate (species E) vibrations can occur. For XY_3 for example, the ν_3 and ν_4 vibrations are each doubly-degenerate, and it can be shown that (Ref. 10, p. 404):

$$\underset{\text{(Pyramidal } XY_3)}{\zeta_3 + \zeta_4} = \frac{B}{2A} - 1 \qquad (3.148)$$

For planar XY_3 with $I_A = 2\ I_B$, this yields:

$$\underset{\text{(Planar } XY_3)}{\zeta_3 + \zeta_4} = 0 \text{ , or } \zeta_3 = -\zeta_4 \qquad (3.149)$$

The other two normal vibrations of planar or pyramidal XY_3 , ν_1 and ν_2, are non-degenerate (see section 3.3), and therefore $\zeta_1 = \zeta_2 = 0$.

Similar analyses (Ref. 10, p. 402) show that for planar X_3 molecules (triangular) one has for the one degenerate ν_2 vibration that:

$$\zeta_2 = -1 \,, \qquad \text{(Planar } X_3\text{)} \tag{3.150}$$

while $\zeta_1 = \zeta_3 = 0$ for this molecule since the ν_1 and ν_3 vibrations are non-degenerate.

The parameter ℓ_{β_i} in Eq. (3.145) takes on the values:

$$\ell_{\beta_i} = \underset{(i=1)}{v_\beta} \,,\ \underset{(i=2)}{v_\beta - 2} \,,\ \underset{(i=3)}{v_\beta - 4} \,,\ \ldots\ldots\ \underset{(i=i)}{1 \,,\ \text{or } 0} \tag{3.151}$$

For a single excitation of a degenerate normal vibration, the sum $\Sigma\left(\pm\, \ell_{\beta_i}\zeta_\beta\right)$ is simply $\pm\, \zeta_\beta$, but if for example $2\nu_3$ is excited in XY_3, we have $\ell_{3_1} = 2$ and $\ell_{3_2} = 0$, and we get for the sum $\pm\, 2\zeta_3$ and 0. Thus the sum term yields three different values and therefore the energy given by (3.145) has three sublevels in this case.

If two degenerate normal vibrations are singly excited for example $\nu_3 + \nu_4$, the sum term in (3.145) has the values $\pm(\zeta_3 + \zeta_4)$ and $\pm(\zeta_3 - \zeta_4)$ resulting in four sublevels. At higher levels of excitation v_β of a degenerate normal vibration ν_3, the value of ζ_3 is expected to change somewhat, that is $\zeta_\beta = \zeta_3(v_3)$ (Ref. 10, p. 406). However this change should be of second-order and we shall not consider it here. Excitation of the higher levels of the non-degenerate vibrations do not influence the ζ values in any way.

Values for ζ_β are best obtained experimentally although they can be calculated in principle from the molecule's vibrational parameters (Ref. 10). For XY_3 and ZXY_3 molecules for example Ref. 23 gives:

$$\zeta_3(XY_3) = \zeta_4(ZXY_3) \approx \frac{(1 - \cos\alpha)\, M_Y}{M_X + (1 - \cos\alpha)\, M_Y} , \qquad (3.152)$$

where α is the angle YXY in the molecule (see section 3.3). Since $\zeta_4(XY_3)$ is related to ζ_3 via Eq. (3.148), ζ_4 can also readily be obtained from (3.152). One other condition that must always be satisfied by ζ_β is that $0 \leq |\zeta_\beta| \leq 1$.

The rotational energy levels and their splittings due to vibrational Coriolis forces do not directly effect the bare rotational transition elements R^2_{mn} . We will need the full energy level relations in Chapter 4 however and gave them here for completeness and future reference.

In Eqs. (3.146) and (3.147), $I_A = I_z$ is the moment of inertia about the molecular axis (pyramidal height coordinate), and $I_B = I_x = I_y$ is the moment of inertia about an axis perpendicular to this coordinate. Centrifugal stretching effects in Eq. (3.145) which may be expressed by a term $-D_J\, J^2(J + 1)^2 - D_{JK}\, J(J + 1)^2 - D_K K^4$ were neglected since this term is usually much smaller than the other vibrational correction terms.

The eigenfunctions for the symmetric-top rotator are given by modified hypergeometric functions (Ref. 16), and it is found that the selection rules for pure rotational radiative transitions in symmetric-top molecules are (Ref. 16):

Pure Rotational Transitions

$$\Delta J = 0 , \pm 1 \qquad (3.153a)$$

$$\Delta|K| = 0 \qquad (3.153b)$$

$$(+) \longleftrightarrow (-) \qquad (3.153c)$$

The selection rule $(+) \longleftrightarrow (-)$ states that only transitions between states whose wavefunctions have opposite parities are allowed. That is (+) refers to a state with an overall wavefunction for which $\Psi(-\vec{r}) = \Psi(\vec{r})$ while (-) refers to a state with an overall wavefunction for which $\Psi(-\vec{r}) = -\Psi(\vec{r})$, where $\vec{r}$ is the spatial position vector $\vec{r}$. The selection rule (3.153c) is only important for NH_3, which can oscillate between two mirror configurations in which N is "above" or "below" the H_3 plane. For most other molecules this so-called "inversion" is so slow (half-life $\approx$ years) that we may ignore it, and in this case the selection rules (3.153a) and (3.153b) automatically cause (3.153c) to be satisfied.

From (3.145) it is clear that all rotational energy levels (J,K) including states with K = 0 (see Ref. 10, p. 403) are doubly-degenerate since the states with quantum numbers +K and -K have the same energy. Since these two states have opposite parity (+) and (-), it is clear that each rotational energy level is composed of two states, one with (+) parity and the other with (-) parity. This means also that a radiative transition with $\Delta J = 0$ and $\Delta|K| = 0$ is allowed, in addition to $\Delta J = \pm 1$ (and $\Delta|K| = 0$) transitions.

For pure rotational transitions (i.e., no changes in vibrational levels), the (microwave) frequencies of the emitted or absorbed photons are according to (3.145) and (3.153) given by:

$$\left(\nu_{mn}\right)^{rot}_{\left(\substack{\Delta J = 1 \\ J = \sup(J_m, J_n)}\right)} = h^{-1}\left|\left(E_{J,K}\right)^{rot}_m - \left(E_{J,K}\right)^{rot}_n\right| = 2\,c\,BJ\ ,\ \mathrm{Hz}$$

$$= 2\,BJ\ ,\ \mathrm{cm}^{-1} \qquad (3.154a)$$

$$\underset{(\Delta J = 0)}{(\nu_{mn})^{rot} = 0} \tag{3.154b}$$

The degeneracy or weight of a rotational level m of given value $|K_m|$ is:

$$w_r(|K_m|, J_m) = (2J_m + 1)\{2 - \delta(K_m)\}\, H(J_m - |K_m|)\ , \tag{3.155}$$

since there are $(2J_m + 1)$ different values of K for each J. Here $\delta(x)$ is the Dirac delta function and $H(x)$ the Heaviside unit step function defined by:

$$\delta(x = 0) = 1\ ;\ \delta(x \neq 0) = 0 \tag{3.156a}$$

$$H(x \geq 0) = 1\ ;\ H(x < 0) = 0 \tag{3.156b}$$

The factor $\{2 - \delta(K_m)\}$ is 1 for $K_m = 0$ and equals 2 for $|K_m| \geq 1$ to account for the fact that each nonzero K value is doubly-degenerate. The factor $H(J_m - |K_m|)$ insures that for given $|K_m|$ only states with $J_m \geq |K_m|$ can exist.

The transition element R^2_{mn} for rotational transitions with $|J_m - J_n| = 1$, $\Delta|K| = 0$ is (Refs. 10 and 16)·

$$\boxed{\underset{\left(\begin{array}{l} |J_m - J_n| = 1 \\ J = \sup(J_m, J_n) \\ |K_m| = |K_n| = K \end{array}\right)}{(R^2_{mn})^{rot}} = d_o^2\ \frac{J^2 - K^2}{J(2J + 1)(2J - 1)}\ ,\ \mathrm{cm}^2\ ,} \tag{3.157a}$$

where d_o is the dipole length of the molecule in charge-cm as before. For transitions with $J_m = J_n = J$ and $\Delta|K| = 0$, which are also allowed according to (3.153), the matrix element is:

$$\boxed{\begin{array}{l} (R^2_{mn})^{rot} = d_o^2 \dfrac{K^2}{J(J+1)(2J+1)} \text{ , cm}^2 \\ \begin{pmatrix} \Delta J = 0 \\ \Delta|K| = 0 \end{pmatrix} \end{array}} \tag{3.157b}$$

This latter transition involves no emission or absorption of a photon however according to (3.154b) and only causes the molecule to change its value of K to -K.

The transition strength S^{rot}_{mn} and connection factor C_{mn} for $\Delta J = \pm 1$ are:

$$\begin{array}{ll} S^{rot}_{mn} & = d_o^2 \left(\dfrac{J^2 - K^2}{J}\right) \text{ , cm}^2 \\ J = \sup(J_m, J_n) & \\ \Delta J = \pm 1 \text{ ; } |K_m| = |K_n| = K & \end{array} \tag{3.158}$$

$$\begin{array}{ll} C_{mn} & = (2J_m + 1)(2J_n + 1) = (2J + 1)(2J - 1) \\ (J = \sup(J_m, J_n)) & \end{array} \tag{3.159}$$

Note that if we want to calculate the spontaneous rotational emission rate for example from state m to n, we must use the parameter $S^{rot}_{mn}/w_r(J_m)$ and <u>not</u> $S^{rot}_{mn}/w_r(J_m, K_m)$. If we consider each rotational level to be specified by (J,K) rather than J (with K as states, see Chapter 1, p. 13), then S^{rot}_{mn} must be defined by:

$$\begin{array}{ll} (S^{rot}_{mn})' & = 2 d_o^2 \left(\dfrac{J^2 - K^2}{J(2J+1)}\right) \text{ , cm}^2 \\ J = \sup(J_m, J_n) & \\ K = |K_m| = |K_n| & \end{array} \tag{3.160}$$

in order that $(S^{rot}_{mn})'/w_r(J_m, K_m) = (S^{rot}_{mn})'/2$ be the proper matrix parameter to be used in the expressions for cross-sections and rates for transitions m → n for example.

The emitted photon frequencies given by (3.154) and governed by the selection rules (3.153) only apply for pure rotational transitions. If the main transition is vibrational or electronic, and the rotational change accompanies it, the selection rules (3.153) are changed to (Ref. 10, p. 414):

a. (// Band)

$$\Delta|K| = 0 \ ; \ \Delta J = 0 \ , \ \pm 1 \ , \ \text{if } K \neq 0 \qquad (3.161a)$$

$$\Delta|K| = 0 \ ; \ \Delta J = \pm 1 \qquad , \ \text{if } K = 0 \ , \qquad (3.161b)$$

if the direction of the electronic or vibrational dipole vector $\vec{e}_\alpha$ (see section 3.3) is parallel to the symmetric-top axis, and:

b. (⊥ Band)

$$\Delta|K| = \pm 1 \ ; \ \Delta J = 0 \ , \ \pm 1 \ , \qquad (3.162)$$

if the electronic or vibrational dipole vector $\vec{e}_\alpha$ is perpendicular to the symmetric-top axis.

If the vibration vector $\vec{e}_\alpha$ (see section 3.3) has components along as well as perpendicular to the symmetric-top axis, vibrational/rotational transitions obeying both selection rules (3.161) and (3.162) can take place.

It is clear that for rotational transitions accompanying vibrational (and/or electronic) transition, the pure rotational energy difference between upper level m and lower level n will no longer be given by Eq. (3.154) because of (3.161) and (3.162), and the fact that the sum term in (3.145) has in general different values for a different upper and lower vibrational level. Thus we have for a transition with $\Delta v \neq 0$ and/or $\Delta\Lambda \neq 0$ according to Eqs. (3.145) and (3.161) for the parallel (//) and perpendicular (⊥) bands:

P (- sign) and R (+ sign) Branch ; $|\Delta J| = 1$; $J = \sup(J_m, J_n)$

$$\underset{(K = |K_m| = |K_n|)}{\left(\nu_{mn}^{rot}\right)^{//}} = \nu_{o_{mn}}^{vib/elc} \pm 2\bar{B}J - \Delta BJ^2 - (\Delta A - \Delta B)K^2 - 2\Delta A_\zeta\,|K| \text{ , cm}^{-1} \tag{3.163a}$$

$$\underset{(K = \sup(|K_m|, |K_n|))}{\left(\nu_{mn}^{rot}\right)^{\perp}} = \nu_{o_{mn}}^{vib/elc} \pm 2\bar{B}J - \Delta BJ^2 - (\Delta A - \Delta B)K^2 \pm 2\Delta A_\zeta\,|K| + $$

$$+ (A_n - B_n)(\pm 2|K| - 1) + 2A_n\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_n \text{ , cm}^{-1} \tag{3.163b}$$

Q-Branch ; $J = J_m = J_n$

$$\underset{(K \neq 0)}{\left(\nu_{mn}^{rot}\right)^{//}} = \nu_{o_{mn}}^{vib/elc} - \Delta BJ(J+1) - (\Delta A - \Delta B)K^2 - 2\Delta A_\zeta\,|K| \text{ , cm}^{-1} \tag{3.163c}$$

$$\underset{(K = \sup(|K_m|, |K_n|))}{\left(\nu_{mn}^{rot}\right)^{\perp}} = \nu_{o_{mn}}^{vib/elc} - \Delta BJ(J+1) - (\Delta A - \Delta B)K^2 + 2\Delta A_\zeta\,|K| + $$

$$+ (A_n - B_n)(\pm 2|K| - 1) + 2A_n\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_n \text{ , cm}^{-1} \tag{3.163d}$$

Here $\nu_{o_{mn}}^{vib/elc}$ is the frequency difference of the upper (m) vibrational/electronic level and the lower (n) vibrational/electronic level in the transition, and:

$$\Delta A = A(v_n,\Lambda_n) - A(v_m,\Lambda_m) \equiv A_n - A_m , \ cm^{-1} \qquad (3.164)$$

$$\Delta B = B(v_n,\Lambda_n) - B(v_m,\Lambda_m) \equiv B_n - B_m , \ cm^{-1} \qquad (3.165)$$

$$\bar{B} = \frac{1}{2}\left[B_m + B_n\right] \approx B_n \approx B_m \qquad (3.166)$$

$$\Delta A_\zeta = A_m\left(\sum_\beta \pm \ell_{\beta_i} \zeta_\beta\right)_m - A_n\left(\sum_\beta \pm \ell_{\beta_i} \zeta_\beta\right)_n , \ c,^{-1} \qquad (4.167)$$

We shall need Eq. (3.163) later in Chapter 4, and give them here for completeness. Note that usually $B_m \equiv B(v_m,\Lambda_m) \approx B_n \equiv B(v_n,\Lambda_n)$ and $A_m \equiv A(v_m,\Lambda_m) \approx \approx A_n \equiv A(v_n,\Lambda_n)$ so that the approximation $\bar{B} \approx B_n \approx B_m$ in (3.163) is usually good. However terms that contain the difference of B_m and B_n or A_m and A_n can of course not use this approximation. Also note that for transitions between non-degenerate vibrational levels, the last term in (1.163) with the summation over the Coriolis constants vanishes.

Table 3.13 lists rotational parameters B and A and Coriolis constants ζ_3 and ζ_4 for some selected XY_3 symmetric-top molecules.

The rotational dipole moment μ_o or dipole length $d_o = \mu_o/e$ for symmetric-top molecules are also listed in Table 3-13. If a value for μ_o and thus d_o is not available in the literature, one can calculate one via the composite-dipole method analogous to the illsutration given in the previous subsection for linear molecules, using the proper vibrational weighting parameters discussed in Appendix B. We shall not elaborate on this method further however, since for most molecules of interest a measured value for μ_o and thus d_o is available.

TABLE 3-13. ROTATIONAL PARAMETERS OF SOME SELECTED SYMMETRIC-TOP MOLECULES (Refs. 11, 14, 16)*

Molecule XY_3	Rotational Constant B ** (cm^{-1})	Rotational Constant A ** (cm^{-1})	Coriolis Constants ζ_3	ζ_4		Dipole Length d_o (Angstrom = 10^{-8} cm)
AsH_3	3.7232					0.0416
AsF_3	0.1961					0.5393
$AsC\ell_3$	0.0716					0.3311
$C\ell F_3$						0.1249
NH_3	9.9443	6.196	0.06	-0.26		0.3061
ND_3	5.1369	3.1555	0.20	-0.36		0.3061
NF_3	0.3563					0.0489
PH_3	4.4523	3.93	0.01	-0.43		0.1208
PF_3	0.2608					0.2145
$PC\ell_3$	0.0873					0.1624
PBr_3	0.0332					
SbH_3	2.9354		0.01	-0.48		0.0250
$SbC\ell_3$	0.0585					
			ζ_4	ζ_5	ζ_6	
CH_3F			0.099	(-0.31)	0.28	0.3852
$CH_3C\ell$	0.443401	5.087	0.100	-0.273	0.222	0.3894
CH_3B_r	0.319160	5.082	0.049	-0.229	0.169	0.3769
CH_3I	0.250217	5.109	0.059	-0.240	0.206	0.3373

*The molecules are assumed to be composed of the most abundant isotopic atoms.

**The rotational constants B and A listed are for the ground vibrational and electronic levels. For the higher levels, α_β^B and α_β^A values are needed (see Eqs. (3.146) and (3.147)) which may be found in Ref. 11 for some molecules.

3.4.4 Spherical-Top Molecules

Spherical-top molecules are similar to symmetric-top molecules except that the principal moments of inertia $I_B = I_A$ and therefore $B = A$ in all the relations that pertain to the symmetric-top. For the most general case we have for the rotational energy levels (Ref. 10):

$$\left(E_J\right)^{\text{rot}}_{\substack{\text{spher.-top}\\ \text{molecule}}} = hcBJ(J+1) + \left.\begin{array}{lll} \nearrow & +\,hcB(J+1)\,\zeta & (+) \\ \rightarrow & 0 & (0) \\ \searrow & -\,hcBJ\,\zeta & (-) \end{array}\right\} ,\ \text{cm}^{-1} , \qquad (3.168)$$

where:

$$B = \frac{h}{8\pi^2 c I_B} - \sum_\beta \alpha_\beta \left(v_\beta + \frac{d_\beta}{2} \right) , \qquad (3.169)$$

and where we have three sublevels for E_J designated by (+), (0), and (-). Here, as before, the α_β in Eq. (3.169) give corrections for the average moment of inertia I_B in the presence of vibrations β of level v_β and degeneracy d_β, while the splitting into three sublevels with the ζ factors arises from Coriolis interactions of the vibrations β on the rotations.

Spherical-top molecules are primarily represented by tetrahedral XY_4 and octahedral XY_6 molecules discussed in section 3.3, whose normal vibrations and degeneracies are as follows.

	XY_4				XY_6					
Normal Vibration ν_β	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Degeneracy d_β	1	2	3	3	1	2	3	3	3	3
Symmetry Type	A_1	E	F_2	F_2	A_{1_g}	E_g	F_{1_u}	F_{1_u}	F_{2_g}	F_{2_u}

Since the ν_1 vibration of both XY_4 and XY_6 is non-degenerate, we have $\zeta_1 = 0$, that is:

$$\zeta = \zeta_1 = 0 \text{ , for vibrations } \nu_v = v_1\nu_1 \tag{3.170}$$

Also for both XY_4 and XY_6 , we have for the combination bands $\nu_v = \nu_3 + v_1\nu_1$, $\nu_v = \nu_4 + v_1\nu_1$, $\nu_v = \nu_3 + v_2\nu_2$, and $\nu_v = \nu_4 + v_2\nu_2$ (Ref. 10):

$$\zeta = \zeta_3 \quad , \left\{ \begin{array}{ll} \text{exactly for } \nu_v = \nu_3 + v_1\nu_1 & (3.171a) \\ \text{approximately for } \nu_v = \nu_3 + v_2\nu_2 & (3.171b) \end{array} \right\}$$

and:

$$\zeta = \zeta_4 \quad , \left\{ \begin{array}{ll} \text{exactly for } \nu_v = \nu_4 + v_1\nu_1 & (3.172a) \\ \text{approximately for } \nu_v = \nu_4 + v_2\nu_2 & (3.172b) \end{array} \right\}$$

Here v_1 , v_2 = 0 , 1 , 2 ..... of course.

We have further (for both XY_4 and XY_6) the relations (Ref. 10):

$$\zeta_3 + \zeta_4 = \frac{1}{2} , \tag{3.173}$$

and:

$$\zeta = -\zeta_3 \text{ , approximately for } \nu_v = 2 \nu_3 \tag{3.174}$$

$$\zeta = -\zeta_4 \text{ , approximately for } \nu_v = 2 \nu_4 \tag{3.175}$$

$$\zeta = -\frac{1}{2} \left(\zeta_3 + \zeta_4\right) = -\frac{1}{4} \text{ , approximately for } \nu_v = \nu_3 + \nu_4 \tag{3.176}$$

There are additional [illegible]-vibrational Coriolis perturbations and energy shifts of the rotational levels when the vibrations ν_v indicated in Eqs. (3.171b), (3.172b), (3.174), (3.175), and (3.176) are present. These additional perturbations are discussed in Refs. 24, 25, and 26. For ζ values of other combination or overtone bands not listed above these same references should also be consulted.

For XY_4 , Jahn (Ref. 23) predicts for the Coriolis parameters ζ_3 and ζ_4 the approximate relations:

$$\underset{(XY_4)}{\zeta_3} = \frac{4M_Y}{3M_X + 4M_Y} \tag{3.177}$$

$$\underset{(XY_4)}{\zeta_4} = \frac{3M_X - 4M_Y}{2(3M_X + 4M_Y)} \tag{3.178}$$

where M_X and M_Y are the masses of atoms X and Y.

For XY_6 it appears that similarly:

$$\zeta_{3\,(XY_6)} = \frac{6M_Y}{2M_X + 6M_Y} \qquad (3.179)$$

and:

$$\zeta_{4\,(XY_6)} = \frac{2M_X - 6M_Y}{2(2M_X + 6M_Y)} , \qquad (3.180)$$

which seem to agree with Claassen's experimental results (Ref. 27) for $UF_6 \left((\zeta_3)_{expt} = 0.24 \pm 0.07 \; ; \; (\zeta_3)_{Eq.\ (3.179)} = 0.193\right)$, and with ζ_3 derivable from Hinkley's data (Ref. 28) on $SF_6 \left((\zeta_3)_{expt} = 0.673 \; ; \; (\zeta_3)_{Eq.\ (3.179)} = 0.640\right)$.

The selection rules for rotational transitions, with or without accompanying vibrational transitions, are (Ref. 10):

$$\Delta J = 0 \; , \; \pm 1 \qquad (3.181)$$

and:

$$(A_{tot}) \longleftrightarrow (A_{tot}) \qquad (3.182a)$$

$$(E_{tot}) \longleftrightarrow (E_{tot}) \qquad (3.182b)$$

$$(F_{tot}) \longleftrightarrow (F_{tot}) \qquad (3.182c)$$

The selection rule (3.182) states that in a transition, rotational levels of a molecule whose initial total symmetry is of type X (X = A,E,F) can only combine with those rotational levels in the final state of the molecule which cause the total symmetry to remain of the same type. By "total" symmetry type we mean here the symmetry type of the combined electronic, vibrational and rotational wave function.

For vibrational/rotational transitions between a triply-degenerate vibrational state $(F)_{vib}$ and the non-degenerate vibrational ground state $(A)_{vib}$, the combined restrictions (3.181) and (3.182) give the selection rule (Ref. 10):

$$J_{(F)_{vib}} - J_{(A)_{vib}} = +1 \quad , \quad (-) \longleftrightarrow (0) \quad , \tag{3.183a}$$

$$J_{(F)_{vib}} - J_{(A)_{vib}} = 0 \quad , \quad (0) \longleftrightarrow (0) \quad , \tag{3.183b}$$

$$J_{(F)_{vib}} - J_{(A)_{vib}} = -1 \quad , \quad (+) \longleftrightarrow (0) \quad , \tag{3.183c}$$

where (+), (0), and (-) refer to the sublevels of Eq. (3.168).

The selection rules (3.183) restrict the allowed photon frequencies to the values (Ref. 10):

(a) P-Branch $(J_m - J_n \equiv J_{(F)_{vib}} - J_{(A)_{vib}} = -1)$

$$\nu^{rot}_{mn} \atop {\begin{pmatrix} J = \sup(J_m, J_n) = \\ J = J_n = J_m + 1 \end{pmatrix}} = \nu^{vib/elc}_{o_{mn}} - (B_m + B_n - 2B_m\zeta_m)\, J - (B_n - B_m)\, J^2 \tag{3.184a}$$

(b) Q-Branch $(J_m \equiv J_{(F)_{vib}} = J_n \equiv J_{(A)_{vib}})$

$$\nu^{rot}_{mn} \atop {J = J_m = J_n} = \nu^{vib/elc}_{o_{mn}} - (B_n - B_m)\, J + (B_n - B_m)\, J^2 \tag{3.184b}$$

(c) R-Branch ($J_m - J_n = J_{(F)_{vib}} - J_{(A)_{vib}} = +1$)

$$\nu_{mn}^{rot} = \nu_{o_{mn}}^{vib/elc} + (B_m + B_n - 2B_m\zeta_m)J - (B_n - B_m)J^2$$

$$\begin{pmatrix} J = \sup(J_m, J_n) = \\ J = J_m = J_n + 1 \end{pmatrix} \qquad (3.184c)$$

Here $\nu_{o_{mn}}^{elc/vib}$ is the difference in the vibrational and/or electronic energy level of the molecule.

In Table 3-14, rotational constants (B values) and Coriolis parameters of some spherical-top XY_4 and XY_6 molecules are listed. The values for B can only be obtained from infrared vibration/rotation transitions, since for all spherical tops the permanent dipole moment $\mu_o = 0$, and thus pure rotational transitions (in the microwave region) do not occur. Thus radiative transitions of the rotational states of spherical-top molecules only occur when a vibrational or electronic/vibrational change also takes place.

As we saw in section 3.3, only the dipole charge for ν_3 and ν_4 vibrational transitions of XY_4 and XY_6 are non-vanishing and hence most radiative transitions of these molecules involve the ν_3 and ν_4 vibrations, or combination bands in which ν_3 and ν_4 participate. The transition strengths S_{mn} for such transitions are of course determined by the vibrational value $(R^2_{mn})_{vib}$. The effect of the simultaneous rotational changes in these vibrational transitions will appear only in the broadening function for the transition and will be taken up in Chapter 4.

The statistical weight of a rotational level of a spherical-top molecule is (Ref. 10):

TABLE 3-14. ROTATIONAL PARAMETERS OF SPHERICAL-TOP MOLECULES XY_4 AND XY_6

Molecule	Rotational Constant, B (cm^{-1}) *	Coriolis Parameters for the Single Excitation of Normal Vibration ν_β **					
		ζ_1	ζ_2	ζ_3	ζ_4	ζ_5	ζ_6
CH_4	5.2412	0	~ 0	0.0552	0.4448	Not Applicable	Not Applicable
CD_4	(2.6158)	0	~ 0	(0.1818)	(0.3182)		
SiH_4	(3.1552)	0	~ 0	(0.0455)	(0.4545)		
CF_4	(0.1895)	0	~ 0	(0.6786)	(-0.1786)		
SiF_4	(0.1467)	0	~ 0	(0.4750)	(0.0250)		
CCl_4	(0.0585)	0	~ 0	(0.7955)	(-0.2955)		
$SiCl_4$	(0.0513)	0	~ 0	(0.6250)	(-0.1250)		
$TiCl_4$	(0.0364)	0	~ 0	(0.4828)	(0.0172)		
$GeCl_4$	(0.0348)	0	~ 0	(0.3900)	(0.1100)		
$SnCl_4$	(0.0502)	0	~ 0	(0.2817)	(0.2183)		
CBr_4	(0.0208)	0	~ 0	(0.8989)	(-0.3989)		
$SiBr_4$	(0.0185)	0	~ 0	(0.7921)	(-0.2921)		
$GeBr_4$	(0.0130)	0	~ 0	(0.5937)	(-0.0937)		
$SnBr_4$	(0.0181)	0	~ 0	(0.4727)	(0.0273)		
UI_4	(0.00595)	0	~ 0	(0.4157)	(0.0843)		
OsO_4	0.114	0	~ 0	(0.1009)	(0.3991)		
SF_6	(0.084)	0	~ 0	(0.6405)	(-0.1405)		
SeF_6	(0.076)	0	~ 0	(0.4191)	(0.0800)		
TeF_6	(0.062)	0	~ 0	(0.3098)	(0.1902)		
MoF_6	(0.056)	0	~ 0	(0.3725)	(0.1275)		
WF_6	(0.056)	0	~ 0	(0.2365)	(0.2635)		
UF_6	(0.041)	0	~ 0	(0.1932)	(0.3068)		

*Values in parentheses are calculated; Values of B are for the ground vibrational state — for higher vibrational levels, one needs α_β parameters some of which are given in Ref. 11.

**For combination-band and overtone vibrational excitations see Refs. 24 and 26.

$$\boxed{\underset{\left(\begin{smallmatrix}\text{spher.-top}\\ \text{molecule}\end{smallmatrix}\right)}{w_{r_J}} = (2J + 1)^2} \qquad (3.185)$$

which is different from linear and symmetric-top molecules. The connection factor is:

$$\boxed{\underset{\text{spherical-top}}{C^{rot}_{mn}} = (2J_m + 1)^2(2J_n + 1)^2} \qquad (3.186)$$

Since μ_o and $d_o = 0$ for spherical-top molecules, we have:

$$\boxed{\underset{\text{spherical-top}}{S^{rot}_{mn}} = \left(R^2_{mn}\right)_{\substack{rot\\ \text{spherical-top}}} = 0} \qquad (3.187)$$

The statistical weight given by (3.185) is due to the fact that for a spherical-top, aside from the (2J + 1) orientations that the rotational angular momentum $\vec{J}$ can have with respect to a fixed direction in the molecule, $\vec{J}$ can also have (2J + 1) orientations with respect to a direction fixed in space. Thus the total degeneracy of a rotational level of given $\vec{J}$ is $(2J + 1)^2$.

3.4.5 Asymmetric-Top Molecules

For the asymmetric-top molecular rotor, there are three principal moments of inertia that are all different. That is the rotational energy is given by:

$$\left(E^{rot}_{J,W}\right)_{\substack{\text{asymm-top}\\ \text{molecule}}} = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z} = A\,\frac{4\pi^2 P_x^2}{h} + B\,\frac{4\pi^2 P_y^2}{h} + C\,\frac{4\pi^2 P_z^2}{h} \qquad (3.188)$$

where P_x , P_y , and P_z are the angular momenta along the three spatial coordinates x , y , and z , and:

$$A = \frac{h}{8\pi^2 c I_x} \; , \quad cm^{-1} \qquad (3.189)$$

$$B = \frac{h}{8\pi^2 c I_y} \; , \quad cm^{-1} \qquad (3.190)$$

$$C = \frac{h}{8\pi^2 c I_z} \; , \quad cm^{-1} \qquad (3.191)$$

are the rotational constants, with $A \neq B \neq C$ for the asymmetric-top. If $A = C$, we have a symmetric-top, while for $A = B = C$ we have a spherical-top. The three constants A , B , C are assigned to the three principal moments of inertia of the molecule such that $A > B > C$.

The rotational energy levels for an asymmetric-top molecule cannot be so easily calculated from a simple formula such as was given in the previous subsections for linear, symmetric-top, and spherical-top molecules. The exact expression for the levels is (Refs. 10 and 16):

$$\left(E^{rot}_{J,W}\right)_{\substack{\text{asymm-top}\\ \text{molecule}}} = hc\left[\frac{B + C}{2}\, J(J + 1) + \left(A - \frac{B + C}{2}\right) W\right] \qquad (3.192)$$

Here $W = W(J)$ is in general a non-integer pseudo-quantum-number (W reduces to $|K|^2$ for the symmetric-top) which has multiple values for each value of J (like K, which has the values J , $J - 1$, ... , $-J$). W is determined by the roots of the following equations (Refs. 10 and 16):

$$J = 0: \qquad W = 0 \tag{3.193a}$$

$$J = 1: \qquad \left.\begin{aligned} &W = 0 \\ &W - 1 - b = 0 \\ &W - 1 + b = 0 \end{aligned}\right\} \tag{3.193b}$$

$$J = 2: \qquad \left.\begin{aligned} &W - 4 = 0 \\ &W - 1 + 3b = 0 \\ &W - 1 - 3b = 0 \\ &W^2 - 4W - 12b^2 = 0 \end{aligned}\right\} \tag{3.193c}$$

$$J = 3: \qquad \left.\begin{aligned} &W - 4 = 0 \\ &W^2 - 4W - 60b^2 = 0 \\ &W^2 - (10 - 6b)W + (9 - 54b - 15b^2) = 0 \\ &W^2 - (10 + 6b)W + (9 + 54b - 15b^2) = 0 \end{aligned}\right\} \tag{3.193d}$$

$$J = 4: \qquad \left.\begin{aligned} &W^2 - 10(1 - b)W + (9 - 90b - 63b^2) = 0 \\ &W^2 - 10(1 + b)W + (9 + 90b - 63b^2) = 0 \\ &W^2 - 20W + (64 - 28b^2) = 0 \\ &W^3 - 20W^2 + (64 - 208b^2)W + 2880b^2 = 0 \end{aligned}\right\} \tag{3.193e}$$

$$
J = 5: \quad \left.\begin{aligned}
& W^2 - 20W + 64 - 108b^2 = 0 \\
& W^3 - 20W^2 + (64 - 528b^2)W + 6720b^2 = 0 \\
& W^3 - W^2(35 - 15b) + W(259 - 510b - 213b^2) \\
& \qquad - (225 - 3375b - 4245b^2 + 675b^3) = 0 \\
& W^3 - W^2(35 + 15b) + W(259 + 510b - 213b^2) \\
& \qquad - (225 + 3375b - 4245b^2 - 675b^3) = 0
\end{aligned}\right\} \quad (3.193f)
$$

$$
J = 6: \quad \left.\begin{aligned}
& W^3 - W^2(35 - 21b) + W(259 - 714b - 525b^2) \\
& \qquad - 225 + 4725b + 9165b^2 - 3465b^3 = 0 \\
& W^3 - W^2(35 + 21b) + W(259 + 714b - 525b^2) \\
& \qquad - 225 - 4725b + 9165b^2 + 3465b^3 = 0 \\
& W^3 - 56W^2 + W(784 - 336b^2) - 2304 + 9984b^2 = 0 \\
& W^4 - 56W^3 + W^2(784 - 1176b^2) \\
& \quad - W(2304 - 53{,}664b^2) - 483{,}840b^2 + 55{,}440b^4 = 0
\end{aligned}\right\} \quad (3.193g)
$$

where:

$$
b = \frac{C - B}{2\left[A - \frac{1}{2}(B + C)\right]} \qquad (3.194)
$$

Relations for $W(J)$ with J up to $J = 11$ are available, and various approximations for the set of relations (3.192) through (3.194) have been developed (Refs. 10 and 16). Note from (3.193) that there are $2J + 1$ values (roots of Eq. 3.193) of W for a given J.

The rotational constants A, B, and C are dependent on vibrational excitations if they are present and may be written, as before, in the form:

$$A = A_o - \sum_\beta \alpha_\beta^A \left(v_\beta + \frac{d_\beta}{2}\right) \tag{3.195}$$

$$B = B_o - \sum_\beta \alpha_\beta^B \left(v_\beta + \frac{d_\beta}{2}\right) \tag{3.196}$$

$$C = C_o - \sum_\beta \alpha_\beta^C \left(v_\beta + \frac{d_\beta}{2}\right) \tag{3.197}$$

where α_β^A, α_β^B, and α_β^C are correction constants, v_β is the excitation level of the normal vibration β and d_β is its degeneracy. For most asymmetric-top molecules $d_\beta = 1$ for all normal vibrations. Centrifugal stretching corrections (with correction constants D_v) can usually be neglected (Ref. 10), and it is customary to include the vibrational Coriolis and anharmonic effects on the rotational levels in the α_β terms by writing (Ref. 10):

$$\alpha_\beta^{A,\ B,\ \text{or}\ C} = \left[\alpha_\beta^{(\text{harm.})} + \alpha_\beta^{(\text{anharm.})} + \alpha_\beta^{(\text{Cor.})}\right]^{A,\ B,\ \text{or}\ C} \tag{3.198}$$

The average rotational energy of the $2J + 1$ sublevels with different values W(J) for a given J is:

$$\frac{\sum_W E_{J,W}^{\text{rot}}/hc}{2J + 1} = \frac{1}{3}\ (A + B + C)\ J(J + 1) \quad , \tag{3.199}$$

which follows from conservation of energy.

The selection rules for transitions between the rotational levels of the asymmetric-top rotor are similar to those for the symmetric-top rotor:

$$\Delta J = 0 \ , \ \pm 1 \tag{3.200a}$$

$$(+)_{tot} \longleftrightarrow (-)_{tot} \ ; \ (+)_{tot} \not\longleftrightarrow (+)_{tot} \ ; \ (-)_{tot} \not\longleftrightarrow (-)_{tot} \tag{3.200b*}$$

where $(+)_{tot}$ and $(-)_{tot}$ indicates the symmetry of the total wave function of the molecule (rotational plus electronic plus vibrational contributions) with (+) indicating a symmetric wavefunction and (-) an antisymmetric one (see the discussion after Eq. (153)). The selection rule (3.200b) can be reduced to combinations of pure rotational symmetry selection rules for 180° rotations about two of the principal moment-of-inertia axes (see Ref. 16, p. 92-95), but we shall not elaborate on them here.

In general, the permanent dipole moment μ_o of an asymmetric rotor can have components along each of the three principal moment of inertia axes, which are designated a, b, and c, for respectively the smallest, intermediate, and largest moment of inertia I_A , I_B , and I_C . We have then:

$$\mu_o \vec{e}_d = \mu_a \vec{e}_a + \mu_b \vec{e}_b + \mu_c \vec{e}_c = \left[\mu_o \cos(a,d)\right] \vec{e}_a + \left[\mu_o \cos(b,d)\right] \vec{e}_b + \left[\mu_o \cos(c,d)\right] \vec{e}_c \tag{3.201}$$

where $\vec{e}_a$, $\vec{e}_b$, $\vec{e}_c$, and $\vec{e}_d$ are unit vectors along the moment of inertia axes a , b , c , and the permanent dipole moment axis d. The cos(a,d), (cos(b,d), and cos(c,d) terms are the direction cosines of axes a, b, and c with the

---

* $\longleftrightarrow$ = allowed; $\not\longleftrightarrow$ = forbidden.

dipole moment axis d. In many real molecules, the dipole moment μ_o is along one of the axes a, b, or c and in that case the relations are simplified of course, since one of the direction cosines will be unity and the others usually zero.

The transition parameters for rotational transitions in asymmetric rotors are easiest expressed by using the J = 0 ⟷ J = 1 transition element $R^2_{o_{mn}}$ as the reference transition (see the discussion following Eqs. (3.112) and (3.113), and Eqs. (3.124) through (3.126)). We then have that:

$$\left({}^{g}R^{2}_{o_{mn}}\right)_{\substack{\text{rot.}\\ \text{asymm. rotor}}} = {}^{g}d^{2}_{o} \equiv d^{2}_{o}\cos^{2}(g,d)\ ,\ \text{cm}^{2} \tag{3.202}$$

where, as before of course, $d_o = \mu_o/e$. Then the connection factor which contains all dependencies on J and W(J) is:

$$\left({}^{g}C^{\text{rot}}_{o_{mn}}\right)_{\substack{\text{asymm. rotor}\\ (\Delta J = 0)}} = {}^{g}Q(J,W) \tag{3.203}$$

$$\left({}^{g}C^{\text{rot}}_{o_{mn}}\right)_{\substack{\text{asymm. rotor}\\ (J_m - J_n = +1)}} = {}^{g}P(J,W) \tag{3.204}$$

$$\left({}^{g}C^{\text{rot}}_{o_{mn}}\right)_{\substack{\text{asymm. rotor}\\ (J_m - J_n = -1)}} = {}^{g}R(J,W) \tag{3.205}$$

The superscript g = a, b, or c, that is there is in the most general case a value for the connection factor for each of the principal axes of the moments of inertia. Tabulations of values for the functions ${}^gQ(J,W)$, ${}^gP(J,W)$, and ${}^gR(J,W)$ and other asymmetric rotor parameters may be found in Ref. 16 (Appendix V), and Refs. 29 and 30. Reference 16 uses for the connection factor ${}^gC^{rot}_{o_{mn}}$ the notation ${}^xS_{JJ'}$ and calls it the (dimensionless) transition strength which agrees with our definition (except that we use g instead of x), since:

$$ {}^gS^{rot}_{o_{mn}} = \left(R^2_{o_{mn}}\right)_{rot} \; {}^gC^{rot}_{o_{mn}} = {}^gd^2_o \; {}^gC^{rot}_{o_{mn}} \tag{3.206} $$

If one non-dimensionalizes this expression by dividing by the constant factor ${}^gd^2_o$, we get that $\left({}^gS^{rot}_{o_{mn}}\right)' = \left({}^gS^{rot}_{mn}\right) / {}^gd^2_o = {}^gC^{rot}_{o_{mn}}$.

In the tabulations of the functions ${}^gP(J,W)$, etc., the so-called "Ray asymmetry parameter" κ is employed which is defined by:

$$ \kappa = \frac{2B - A - C}{A - C} \tag{3.207} $$

Note that κ is related to b by:

$$ b = \frac{\kappa + 1}{\kappa - 3} \quad , \tag{3.208} $$

For a prolate symmetric-top with $B = C$, the asymmetry parameter $\kappa = -1$, while for an oblate symmetric top with $B = A$, $\kappa = +1$.

Instead of labeling a rotational level of an asymmetric rotor (with $A \neq B \neq C$) by (J,W), one may label such a level also by $(J\,;\,K_{-1}\,,\,K_{+1})$ where K_{-1} is the value of the quantum number K that would result for the level (J,W) if $B = C$ for the molecule (and hence $\kappa = -1$), and where K_{+1} denotes the value of the quantum number K that the level (J,W) would have if $B = A$ in the molecule (and thus $\kappa = +1$). The functions ${}^{g}Q(J,W)$, ${}^{g}P(J,W)$ and ${}^{g}R(J,W)$ whose values are tabulated in Refs. 29 and 16 actually use this latter notation, that is:

$$\left({}^{g}C^{rot}_{o_{mn}}\right)_{\substack{\text{asymm. rotor}\\ \Delta J = 0}} = {}^{g}Q(J,W) \equiv {}^{g}Q(J\,;\,K_{-1}\,,\,K_{+1}) \tag{3.209}$$

$$\left({}^{g}C^{rot}_{o_{mn}}\right)_{\substack{\text{asymm. rotor}\\ J_m - J_n = +1}} = {}^{g}P(J,W) \equiv {}^{g}P(J\,;\,K_{-1}\,,\,K_{+1}) \tag{3.210}$$

$$\left({}^{g}C^{rot}_{o_{mm}}\right)_{\substack{\text{asymm. rotor}\\ J_m - J_n = -1}} = {}^{g}R(J,W) \equiv {}^{g}R(J\,;\,K_{-1}\,,\,K_{+1}) \tag{3.211}$$

For each fixed change in J, as expressed in any one of Eqs. (3.209) through (3.211), the change in W or corresponding change in $(K_{-1}\,,\,K_{+1})$ can have a number of different values. If a molecule is almost a symmetric-top, usually only K_{-1} or K_{+1} (not both) is specified depending on whether $B \sim C$ or $B \sim A$.

The statistical weight of a rotational level $k(J)$ with quantum number J is given by:

$$w_{r_k} = 2J_k + 1 \, , \tag{3.212}$$

and thus for example for the spontaneous emission rate A^{o}_{mn} :

$$\left(A_{mn}\right)^{o}_{\text{asymm. rotor}} = \frac{64\pi^4 e^2 \nu^3_{mn}}{3hc^3} \left|\vec{r}_{mn}\right|^2_{\text{asymm. rotor}} \, , \ \sec^{-1} \, , \tag{3.213}$$

we have:

$$\left|\vec{r}_{mn}\right|^2_{\text{asymm. rotor}} = \left(\frac{{}^{g}S^{rot}_{mn}}{w_{r_m}}\right)_{\text{asymm. rotor}} = \left(\frac{{}^{g}C^{rot}_{o_{mn}}}{2J_m + 1}\right) {}^{g}d^2_o \, , \ \text{cm}^2 \tag{3.214}$$

for a particular line.

The most studied asymmetric-top rotor is the H_2O molecule. Table 3-15 lists rotational parameters of H_2O and other asymmetric-top molecules.

TABLE 3-15. ROTATIONAL PARAMETERS OF SOME ASYMMETRIC-TOP MOLECULES (Ref. 16)

Molecule*	Rotational Constants (cm^{-1})**			Permanent Dipole Length and Orientation***			
	A	B	C	d_o (Angstrom = 10^{-8} cm)	$\|\vec{e}_d \cdot \vec{e}_a\|$	$\|\vec{e}_d \cdot \vec{e}_b\|$	$\|\vec{e}_d \cdot \vec{e}_c\|$
H_2O	27.7925	14.5000	9.9569	0.4039	1	0	0
HDO	23.4815	9.1263	6.3997	0.3831	~ 0.95	~ 0.1	0
D_2O	15.3936	7.2630	4.8520	0.3894	1	0	0
H_2S	10.5507	9.2234	4.9213	0.2124	1	0	0
HDS	9.6819	4.8439	3.1400	0.2124	~ 0.95	~ 0.1	0
O_3	3.5535	0.4453	0.3947	0.1104	1	0	0
SO_2	2.0274	0.3442	0.2935	0.3311	1	0	0
NOF	3.1752	0.3951	0.3505	0.3769	0.939	0.343	0
NO_2F	0.4404	0.3818	0.2041	0.0979	1	0	0
HN_3	20.342	B + C = 0.7944		0.1764	(~ 0.8)		
$C\ell F_3$	0.4586	0.1538	0.1150	(0.1832)	1	0	0
HCNO	30.6678	0.3667	0.3666	0.3311	(~ 0.3)		
CH_2O	9.4100	1.2954	1.1342	0.4872	1	0	0
$CH_2C\ell_2$	1.0675	0.1108	0.1022	0.3373	1	0	0
CH_2F_2	1.6391	0.3537	0.3085	0.4081	1	0	0

*The most abundant atomic isotopes are assumed to make up the molecule (except that D = H^2).

**Values of A, B, and C are for the ground state. For excited levels see Refs. 10 and 11.

***The dipole is along the unit vector $\vec{e}_d$, while $\vec{e}_a$, $\vec{e}_b$, and $\vec{e}_c$ are unit vectors along the principal axes with moments of inertia I_A, I_B and I_C respectively.

4. GENERALIZED THEORY OF TRANSITION BROADENING

4.1 SURVEY OF BROADENING PROCESSES AND THE LAW OF SPECTROSCOPIC STABILITY

The emission lines of gaseous atoms or the rotational lines of gaseous molecules are "broadened" by various perturbations which cause shifts in the effective energy levels of an atomic transition with respect to the rest frame of an observer. The most commonly occurring line-broadening processes are:

a. Natural or Homogeneous Broadening
b. Temperature or "Doppler" Broadening
c. Pressure, Collision, or "Lorentz" Broadening
d. Electric Field or "Stark" Broadening

We shall review these elementary line-broadening processes and give analytical expressions for them in subsequent sections.

In molecules, vibrational transititions exhibit broad emission/absorption bands instead of lines due to the rotational sublevels of each vibrational level. These bands do not show a continuous distribution of wavelengths as is the case for the broadened lines (a) through (d), but instead they exhibit a number of separated discrete (broadened) rotational lines. In many applications, it is advantageous to consider an equivalent continuous smeared-out band in which the rotational lines are no longer resolved but continuously distributed. The equivalent smeared-out band gives also the contour of the real band.

The reason why the radiation emitted in a vibrational transition is not sharp but distributed over a band of frequencies is of course due to the rotational perturbations. It is therefore appropriate to call this broadening of the vibrational transition energy:

e. "Rotational Broadening,"

and we shall show that the rotational broadening of the vibrational band contours can be treated in a manner similar to the broadening of an individual line such as in processes (a) through (d).

Similar to the rotationally-broadened vibrational transitions, each electronic transition spectrum of a molecule shows a system of bands due to the vibrational and rovibrational sublevels. Each electronic band-system shows discrete vibrational bands which in turn contain rotational lines. Again one may smear out the band-system of discrete bands and lines into an equivalent continuous band which gives the overall contour of the band system, and again one may call the broadening effect on an electronic transition by the vibrational rotational sublevels:

f. "Vibrational or Rovibrational Broadening"

Before reviewing analytical expressions for the broadening processes (a) through (f), we shall first state some general conservation laws which apply to all broadening effects. Imagine a gas containing N* atoms or molecules which are in a sharply defined excited state m of energy E_m which can relax to a sharply defined lower energy state E_n with the emission of a photon of frequency $\nu_{mn} = (E_m - E_n)/h$, at a spontaneous decay rate of A°_{mn} sec^{-1}. Then:

$$\frac{d(\text{photons of frequency } \nu_{mn})}{dt} = A^{o}_{mn} N^{*} \text{, photons} \cdot \text{sec}^{-1} \tag{4.1}$$

Now suppose that the state m of energy E_m and the state n at energy E_n are perturbed by interactions involving exchange energies small compared to E_m, E_n, and $E_{mn} = E_m - E_n$. For example, due to the random kinetic motions of the excited atoms N^*, some have effective energy levels $E_m - \Delta E_D$ and others $E_m + \Delta E_D$ with respect to an observer, depending on whether they are moving away or towards the observer. Here ΔE_D is the kinetic energy which is small compared to E_m. It is clear that the frequency of the emitted photons as observed by a stationary observer is no longer ν_{mn}, but that it will vary over a range of frequencies $\Delta\nu_{mn}$ about ν_{mn}. Equation (4.1) must therefore be changed and we may write:

$$\frac{d^2(\text{photons of frequency } \nu)}{d\nu\ dt} = A^{o}_{mn} N^{*} g(\nu,\nu_{mn},\Delta\nu_{mn}) \text{, photons} \cdot \text{sec}^{-1} \cdot \text{Hz}^{-1} \tag{4.2}$$

where ν is the general frequency in the range $\Delta\nu_{mn}$ about ν_{mn} and $g(\nu,\nu_{mn},\Delta\nu_{mn})$ is a function which describes the distribution of ν around the unperturbed frequency ν_{mn} per unit frequency range.

If the perturbations are small, $A^{o}_{mn}(\nu) \approx A^{o}_{mn}(\nu_{mn})$, that is A^{o}_{mn} is not affected by the perturbation, and we can write the important general relation:

$$\int_{\nu = \nu_{mn} - \epsilon}^{\nu = \nu_{mn} + \epsilon} \frac{d^2(\text{photons } \nu)}{d\nu\ dt} d\nu = \int_{\nu = \nu_{mn} - \epsilon}^{\nu_{mn} + \epsilon} A^{o}_{mn} N^{*} g(\nu,\nu_{mn},\Delta\nu_{mn})\ d\nu =$$

$$= A^{o}_{mn} N^{*} \text{, photons} \cdot \text{sec}^{-1}, \tag{4.3}$$

where $\epsilon >> \Delta\nu_{mn}$. That Eq. (4.3) holds, follows from the fact that regardless in what way the N^* excited species are perturbed (causing the emission of photons with frequencies differing somewhat from $\nu = \nu_{mn}$), as long as the integration in (4.3) covers all the emitted off-ν_{mn} frequencies, the total number of photons emitted per second must still equal the total number of excited species N^* multiplied by the decay rate A^o_{mn} (which was unaffected by the perturbation). This general principle, which applies to all the perturbing or broadening processes (a) through (f) listed above, is often referred to as the "Law of Spectroscopic Stability."

From Eq. (4.3) or the Law of Spectroscopic Stability, it follows at once that regardless of the general shape of the function $g(\nu,\nu_{mn},\Delta\nu_{mn})$, it must always be "normalized" so that:

$$\boxed{\int_{\nu=0}^{\nu=\infty} g(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = 1 \quad ,} \tag{4.4}$$

since we may set $\epsilon = \infty$, when integrating over $g(\nu,\nu_{mn},\Delta\nu_{mn})$. Of course $\nu \geq 0$.

We note from Eqs. (4.3) or (4.4) that the so-called "line-contour" or "line-profile function" $g(\nu,\nu_{mn},\Delta\nu_{mn})$ is not dimensionless. Since $g(\nu,\nu_{mn},\Delta\nu_{mn})$ is like a delta-function and differs only from zero for values of ν close to $\nu - \nu_{mn}$, in the general range $\Delta\nu_{mn}$ about ν_{mn} , it is conceptually and mathematically convenient to define a new dimensionless "line-shape function" $b(\nu,\nu_{mn},\Delta\nu_{mn})$ and a "width" or "spread" $\Delta\nu_{mn}$ of the broadened line as follows:

$$\boxed{g(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{b(\nu,\nu_{mn},\Delta\nu_{mn})}{\Delta\nu_{mn}} \ , \ \mathrm{Hz}^{-1} ,} \quad (4.5)$$

where because of (4.4):

$$\boxed{\Delta\nu_{mn} = \int_{\nu=0}^{\infty} b(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu \ , \ \mathrm{Hz}} \quad (4.6)$$

Since $b(\nu,\nu_{mn},\Delta\nu_{mn})$ usually peaks at or near ν_{mn} , it is convenient to set:

$$\boxed{b(\nu = \nu_{mn},\nu_{mn},\Delta\nu_{mn}) = 1 \ ,} \quad (4.7a)^*$$

from which it also follows according to (4.5) that:

$$\boxed{\Delta\nu_{mn} = \frac{1}{g(\nu = \nu_{mn},\nu_{mn},\Delta\nu_{mn})} \ , \ \mathrm{Hz}} \quad (4.7b)$$

We are free to choose condition (4.7) which is not in conflict with (4.5) and (4.6), since we can always multiply $b(\nu,\nu_{mn},\Delta\nu_{mn})$ by an arbitrary constant C to make C × $b(\nu,\nu_{mn},\Delta\nu_{mn})$ equal to 1 at $\nu = \nu_{mn}$. Then according to (4.6), $\Delta\nu_{mn}$ is also multiplied by C, leaving $g(\nu,\nu_{mn},\Delta\nu_{mn})$ in (4.5) unchanged.

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*We could for example also have specified that $b = 1$ for $\nu = \nu_{max}$, where ν_{max} corresponds to the frequency at which g or b has a maximum value. However, some band-contour functions may have several maxima and therefore we choose Eq. (4.7) to avoid complications.

Often in calculating say the total absorption of a certain transition we have to integrate some function $f(\nu)$ over a range of frequencies ν which include ν_{mn} and the line-shape distribution $b(\nu,\nu_{mn},\Delta\nu_{mn})$ or $g(\nu,\nu_{mn},\Delta\nu_{mn})$. If the function $f(\nu)$ does not vary rapidly in the region $(\nu_{mn} - \Delta\nu_{mn}) < \nu <$ $< (\nu_{mn} + \Delta\nu_{mn})$, we have that:

$$\boxed{\int_{\nu=0}^{\nu=+\infty} f(\nu)\ b(\nu,\nu_{mn},\Delta\nu_{mn})\ d\nu = f(\nu=\nu_{mn})\ \Delta\nu_{mn}} \tag{4.8}$$

or:

$$\boxed{\int_{\nu=0}^{\nu=+\infty} f(\nu)\ g(\nu,\nu_{mn},\Delta\nu_{mn})\ d\nu = f(\nu=\nu_{mn})} \tag{4.9}$$

Thus the integration of the function $f(\nu)$ over the line-shape can simply be replaced by the product of the "width" or "spread" $\Delta\nu_{mn}$ and the value of $f(\nu)$ at $\nu = \nu_{mn}$. Equation (4.8) shows why $\Delta\nu_{mn}$ as defined by (4.7) is conceptually the most logical choice for defining the "width" of a line or band.

Others have used the frequency-spread at half the height of the function $g(\nu,\nu_{mn},\Delta\nu_{mn})$ or $b(\nu,\nu_{mn},\Delta\nu_{mn})$ as a measure of the "spread" in the shape function, calling it the "half-width" or the "width-at-half-height" $\Delta\nu_{mn}$. In order not to confuse this earlier convention for the measure of the breadth of a line with the one defined by (4.7), we shall call $\Delta\nu_{mn}$ as defined by Eq. (4.7) the line "spread" although it is actually more deserving of the name "width." This nomenclature is even more necessary in view of the fact that many call the "width-at-half-height" or the "half-width" $\Delta\!\!\!\!-\nu_{mn}$ simply the "width."

Of course the two differently defined measures of the broadness of a line-shape function, $\Delta\!\!\!\!-\nu_{mn}$ and $\Delta\nu_{mn}$, are simply related by a constant factor as we shall show. However use of $\Delta\nu_{mn}$ has the advantage that a general equation such as Eq. (4.8) can be written which applies to all types of line-shape functions $b(\nu,\nu_{mn},\Delta\nu_{mn})$. If one works with $\Delta\!\!\!\!-\nu_{mn}$ and functions $b(\nu,\nu_{mn},\Delta\!\!\!\!-\nu_{mn})$, a different normalization constant is necessary for each type of function $b(\nu,\nu_{mn},\Delta\!\!\!\!-\nu_{mn})$ in order that Eq. (4.4) be satisfied.

For example, the two most common line-shape functions are the Gaussian line-shape function (applicable to temperature broadening):

$$b_G\left(\nu,\nu_{mn},\Delta\nu_{mn}\right) = \exp-\left\{\frac{\nu-\nu_{mn}}{\left(\frac{\Delta\nu_{mn}}{\sqrt{\pi}}\right)}\right\}^2 \qquad (4.10)$$

and the Lorentzian line-shape function (applicable to pressure-broadening):

$$b_L\left(\nu,\nu_{mn},\Delta\nu_{mn}\right) = \frac{\left(\frac{\Delta\nu_{mn}}{\pi}\right)^2}{(\nu-\nu_{mn})^2 + \left(\frac{\Delta\nu_{mn}}{\pi}\right)^2} \qquad (4.11)$$

We have namely that:

$$\int_{\nu-\nu_{mn}=-\infty}^{\nu-\nu_{mn}=+\infty} \exp-\left(\frac{\nu-\nu_{mn}}{\alpha'}\right)^2 d\nu = \sqrt{\pi}\,\alpha' \qquad (4.12)$$

and:

$$\int_{\nu - \nu_{mn} = -\infty}^{\nu - \nu_{mn} = +\infty} \frac{\alpha^2}{(\nu - \nu_{mn})^2 + \alpha^2}\, d\nu = \pi\,\alpha\,, \qquad (4.13)$$

so if we choose $\alpha' = \Delta\nu_{mn}/\sqrt{\pi}$ and $\alpha = \Delta\nu_{mn}/\pi$ in Eqs. (4.12) and (4.13), as we did in Eqs. (4.10) and (4.11), the integrations yield $\Delta\nu_{mn}$. Thus Eqs. (4.10) and (4.11) obey the "normalization" condition (4.7), and of course also (4.4).

The relations between the conventional "half-widths" $\Delta\!\!\!\!-\nu_{mn}$ and the "spreads" $\Delta\nu_{mn}$ for the Gaussian and Lorentzian line-contours are:

$$\left(\Delta\nu_{mn}\right)_G = \sqrt{\frac{\pi}{\ell n\ 2}}\,\left(\Delta\!\!\!\!-\nu_{mn}\right)_G \qquad (4.14)$$

and:

$$\left(\Delta\nu_{mn}\right)_L = \pi\left(\Delta\!\!\!\!-\nu_{mn}\right)_L \qquad (4.15)$$

The corresponding expressions for the line-shape functions in terms of $\Delta\!\!\!\!-\nu_{mn}$ are:

$$b_G\left(\nu, \nu_{mn}, \Delta\!\!\!\!-\nu_{mn}\right) = \exp-\left\{\frac{\nu - \nu_{mn}}{\left(\frac{\Delta\!\!\!\!-\nu_{mn}}{\sqrt{\ell n\ 2}}\right)}\right\}^2 \qquad (4.16)$$

$$b_L\left(\nu, \nu_{mn}, \Delta\!\!\!\!-\nu_{mn}\right) = \frac{\left(\Delta\!\!\!\!-\nu_{mn}\right)^2}{(\nu - \nu_{mn})^2 + \left(\Delta\!\!\!\!-\nu_{mn}\right)^2} \qquad (4.17)$$

which when integrated over the resonance ν_{mn} yield:

$$\int_0^\infty b_G\left(\nu,\nu_{mn},\not\Delta\nu_{mn}\right)\,d\nu = \sqrt{\frac{\pi}{\ell n\ 2}}\ \not\Delta\nu_{mn} \qquad (4.18)$$

and:

$$\int_0^\infty b_L\left(\nu,\nu_{mn},\not\Delta\nu_{mn}\right)\,d\nu = \pi\ \not\Delta\nu_{mn} \qquad (4.19)$$

The line-contour functions $g(\nu,\nu_{mn},\not\Delta\nu_{mn})$ and $g(\nu,\nu_{mn},\Delta\nu_{mn})$ for the two cases are:

$$g_G\left(\nu,\nu_{mn},\not\Delta\nu_{mn}\right) = \frac{\exp-\left\{\dfrac{\nu-\nu_{mn}}{\left(\dfrac{\not\Delta\nu_{mn}}{\sqrt{\ell n\ 2}}\right)}\right\}^2}{\sqrt{\dfrac{\pi}{\ell n\ 2}}\ \not\Delta\nu_{mn}} \qquad (4.20)$$

$$g_L\left(\nu,\nu_{mn},\not\Delta\nu_{mn}\right) = \frac{1}{\pi}\ \frac{\not\Delta\nu_{mn}}{(\nu-\nu_{mn})^2+(\not\Delta\nu_{mn})^2} \qquad (4.21)$$

$$g_G\left(\nu,\nu_{mn},\Delta\nu_{mn}\right) = \frac{\exp-\left\{\dfrac{\nu-\nu_{mn}}{\left(\dfrac{\Delta\nu_{mn}}{\sqrt{\pi}}\right)}\right\}^2}{\Delta\nu_{mn}} \qquad (4.22)$$

$$g_L\left(\nu,\nu_{mn},\Delta\nu_{mn}\right) = \frac{1}{\Delta\nu_{mn}} \frac{\left(\frac{\Delta\nu_{mn}}{\pi}\right)^2}{(\nu - \nu_{mn})^2 + \left(\frac{\Delta\nu_{mn}}{\pi}\right)^2} \tag{4.23}$$

Of course all these line-contour functions satisfy Eq. (4.4).

In the following we shall discuss specific line-shape functions $b(\nu,\nu_{mn},\Delta\nu_{mn})$ and line-spreads $\Delta\nu_{mn}$ for the six broadening processes discussed above.

4.2 NATURAL BROADENING

The energy levels E_m and E_n in an atom or molecule between which radiative transitions of frequency $\nu_{mn} = (E_m - E_n)/h$ can occur are actually not completely "sharp" but according to quantum mechanics are subject to uncertainties $h\gamma_m$ and $h\gamma_n$ which in turn cause emitted (or absorbed) photons to have a spread in frequencies ν about ν_{mn} in the interval:

$$(\nu_{mn} - \gamma_{mn}) \lesssim \nu \lesssim (\nu_{mn} + \gamma_{mn}) \qquad (4.24)$$

where:

$$\gamma_{mn} = \gamma_m + \gamma_n \qquad (4.25)$$

To first order (see Refs. 5 and 7), the uncertainties γ_m and γ_n are equal to the inverse lifetimes of states m and n, or:

$$\gamma_m = \sum_k A^o_{mk} \text{ , Hz ,} \qquad (4.26)$$

and:

$$\gamma_n = \sum_k A^o_{nk} \text{ , Hz} \qquad (4.27)$$

where A^o_{mk} was given by Eq. (2 8) of Chapter 2. If, as is often the case, the state n is the ground state with infinite lifetime, and if the transition m → n is the only possible one for level m, we have that:

$$\boxed{\gamma_{mn} = \gamma_m = A^o_{mn} \text{ , Hz ,}} \qquad (4.28)$$

and:

$$\gamma_n \approx 0 \tag{4.29}$$

The probability that the energy of state m lies in the range $E \pm \frac{1}{2} dE$ is given by (Ref. 7):

$$W(E)\ dE = \frac{\gamma_m}{h} \frac{dE}{\left(\frac{2\pi}{h}\right)^2 \left(E - E_m\right)^2 + \left(\frac{\gamma_m}{2}\right)^2} \tag{4.30}$$

and therefore the simultaneous probability that the upper state m is at energy $E \pm \frac{1}{2} dE$ and the lower state n is in the energy range $E' \pm \frac{1}{2} dE'$, is:

$$W(E)\ W(E')\ dE\ dE' = \frac{\gamma_m \gamma_n}{h^2} \frac{dE\ dE'}{\left\{\left(\frac{2\pi}{h}\right)^2 \left(E - E_m\right)^2 + \left(\frac{\gamma_m}{2}\right)^2\right\}\left\{\left(\frac{2\pi}{h}\right)^2 \left(E' - E_n\right)^2 + \left(\frac{\gamma_n}{2}\right)^2\right\}} \tag{4.31}$$

For the observation of photons with emission frequencies:

$$\nu = \frac{1}{h}(E - E') , \tag{4.32}$$

we obtain then that:

$$g_N(\nu, \nu_{mn}, \Delta\nu_{mn}) = \frac{b_N(\nu, \nu_{mn}, \Delta\nu_{mn})}{\left(\Delta\nu_{mn}\right)_N} = \frac{d}{d\nu} \int_{E' = -\infty}^{\infty} W(E)\ W(E')\ dE\ dE' \tag{4.33}$$

After carrying out the integration of Eq. (4.31), we find (Ref. 7) that:

$$\boxed{b_N(\nu, \nu_{mn}, \Delta\nu_{mn}) = \frac{\left\{\frac{(\Delta\nu_{mn})_N}{\pi}\right\}^2}{(\nu - \nu_{mn})^2 + \left\{\frac{(\Delta\nu_{mn})_N}{\pi}\right\}^2}} \tag{4.34}$$

$$\boxed{(\Delta\nu_{mn})_N = \frac{\gamma_{mn}}{4} , \quad \mathrm{Hz}} \tag{4.35}$$

Thus the natural line-contour is Lorentzian (see Eq. (4.11)).

For the special ground-state-connected case defined by (4.28) and (4.29), Eq. (4.35) reduces to:

$$\boxed{(\Delta\nu_{mn})_N = \frac{A^{\circ}_{mn}}{4} , \quad \mathrm{Hz}} \tag{4.36}$$

The half-width $\delta\nu_{mn}$ is then according to Eq. (4.15):

$$\boxed{(\delta\nu_{mn})_N = \frac{(\Delta\nu_{mn})_N}{\pi} = \frac{\gamma_{mn}}{4\pi} = \frac{A^{\circ}_{mn}}{4\pi} , \quad \mathrm{Hz}} \tag{4.37}$$

where the last part of Eq. (4.37) applies only to the ground-state-connected transition discussed above.

4.3 DOPPLER BROADENING

The so-called "Doppler" or "temperature" broadening of spectral lines emitted by atomic and molecular gases is essentially caused by the Doppler shift in the emitted photon wave due to the random thermal motion of the gaseous atoms or molecules. The Doppler shifted frequency ν of the emitted photons produced by atoms deexciting from state m to state n and moving at thermal velocity v_x along the line-of-sight or x-direction away from the observer is given by:

$$\nu = \nu_{mn}\left(1 - \frac{v_x}{c}\right) \tag{4.38}$$

where c is the velocity of light.

The number of molecules moving with linear velocities between v_x and $v_x + dv_x$ in a gas at thermal equilibrium is given by:

$$\frac{dN}{N_o} = \left(\frac{M}{2\pi\ kT}\right)^{1/2} \left\{\exp-\left(\frac{M\ v_x^2}{2\ kT}\right)\right\} dv_x \tag{4.39}$$

where M is the mass of the emitting atom or molecule, N_o equals the total number of emitters, and the other parameters have the usual meanings.

With Eq. (4.38), Eq. (4.39) can be rewritten in the form:

$$\frac{dN}{N_o} = \frac{1}{\nu_{mn}}\left(\frac{M\ c^2}{2\pi\ kT}\right)^{1/2} \left[\exp-\left\{\frac{M\ c^2\ (\nu - \nu_{mn})^2}{2\ kT\ \nu_{mn}^2}\right\}\right] d\nu \tag{4.40}$$

Since the probability of observing a photon with a frequency between $|\nu - \nu_{mn}|$ and $|\nu - \nu_{mn}| + d\nu$ is equal to $(1/N_o)\, dN/d\nu$, we can write:

$$g_D(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{b_D(\nu,\nu_{mn},\Delta\nu_{mn})}{\left(\Delta\nu_{mn}\right)_D} = \frac{1}{N_o}\,\frac{dN}{d\nu} \quad , \; Hz^{-1} \tag{4.41}$$

in which according to Eq. (4.40):

$$\boxed{\left(\Delta\nu_{mn}\right)_D = \frac{\nu_{mn}}{c}\sqrt{\frac{2\pi\, kT}{M}} \quad , \quad Hz} \tag{4.42}$$

$$\boxed{b_D(\nu,\nu_{mn},\Delta\nu_{mn}) = \exp-\left[\frac{\nu - \nu_{mn}}{\left\{\dfrac{\left(\Delta\nu_{mn}\right)_D}{\sqrt{\pi}}\right\}}\right]^2} \tag{4.43}$$

We see that the Doppler line-shape function is Gaussian (Eq. (4.10)). According to Eq. (4.14), the "half-width" $\cancel{\Delta}\nu_{mn}$ is then given by:

$$\boxed{\left(\cancel{\Delta}\nu_{mn}\right)_D = \sqrt{\frac{\ell n\ 2}{\pi}}\left(\Delta\nu_{mn}\right)_D = \frac{\nu_{mn}}{c}\sqrt{\frac{2(\ell n\ 2)\ kT}{M}} \quad , \; Hz} \tag{4.44}$$

4.4 COLLISION BROADENING

Collision or pressure broadening of emission lines, as the name indicates, arises from atomic or molecular collisions. Lorentz first considered this type of broadening effect, hence it is also called "Lorentz" broadening. The effect of collisions on a large number of oscillating atoms or molecules is to produce a random distribution of abrupt stops to the oscillations. If τ_c is the mean time between collisions, the number of molecules oscillating freely for time t is $N_t = N_o \exp - (t/\tau_c)$. The Lorentz theory of collision broadening assumes that after a collision during which the oscillation was briefly stopped, an atom or molecule oscillates again with a phase having no relationship to the phase before the collision.

A detailed analysis of the effect of such collisional oscillation perturbations on the emission frequency (Ref. 7) shows that the center-line frequency of a transition ν_{mn} is broadened in the same way as in natural broadening, except that now $\Delta\nu_{mn} = 1/(2\tau_c)$, that is:

$$\boxed{b_C(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{\left\{\dfrac{\left(\Delta\nu_{mn}\right)_C}{\pi}\right\}^2}{(\nu - \nu_{mn})^2 + \left\{\dfrac{\left(\Delta\nu_{mn}\right)_C}{\pi}\right\}^2}} \qquad (4.45)$$

Here:

$$\left(\Delta\nu_{mn}\right)_C = \frac{1}{2\,\tau_c} = \frac{z_c}{2}\ , \ \mathrm{Hz}\ , \qquad (4.46a)$$

where the collision rate $z_c = 1/\tau_c$ according to kinetic theory is given by:

$$z_c = 6.7682 \times 10^{26} \frac{\sigma_{1-2}\, p}{\sqrt{\mu_{1-2}\, T}} \text{ , Hz} \qquad (4.46b)$$

so that:

$$\boxed{\left(\Delta\nu_{mn}\right)_C = 3.3841 \times 10^{26} \frac{\sigma_{1-2}\, p}{\sqrt{\mu_{1-2}\, T}} \text{, Hz}} \qquad (4.47)$$

where:

σ_{1-2} = Collision cross-section for oscillation-stopping collisions between atoms 1 and 2 , cm^2

p = Pressure of gas, atm

T = Temperature of gas, °K

and the reduced mass μ_{1-2} is given by:

$$\mu_{1-2} = \frac{M_1 M_2}{M_1 + M_2} \text{ , a.m.u. ,} \qquad (4.48)$$

in which:

M_1, M_2 = Mass of colliding atoms 1 and 2 respectively, a.m.u.

Measured values of typical collisional broadening cross-sections σ_{1-2} are listed in Table 4-1.

The half-width $\left(\Delta\nu_{mn}\right)_C$ is according to Eq. (4.15) given by:

TABLE 4-1. MEASURED ATOM-MOLECULE OSCILLATION-STOPPING CROSS-SECTIONS, σ_{1-2} (10^{-16} cm²) (Refs. 7 and 9)

First Atom	Second Atom or Molecule	Cross-Section, $\sigma(10^{-16}\ \text{cm}^2)$		
		Füchtbauer, Joos and Dinkelacker	Zemansky	Kunze
Hg	He	–	15.0	21.4
Hg	H_2	27.8	24.5	–
Hg	Ne	–	–	35.7
Hg	CO	–	44.5	–
Hg	N_2	64.8	51.0	–
Hg	O_2	65.1	–	–
Hg	CH_4	–	42.8	–
Hg	H_2O	68.5	–	–
Hg	Ar	88.9	61.5	62.0
Hg	CO_2	125	(98.4)*	–
Hg	NH_3	–	71.2	–
Hg	C_3H_8	–	73.5	–
			Penner & Webber	Schütz
Na	He	–	–	31.4
Na	Ne	–	–	37.8
Na	H_2	–	–	33.6
Na	N_2	–	–	68.9
Na	Ar	–	–	81.0
CO	CO	–	40.4	–
CO	He	–	1.94	–
CO	Ar	–	12.8	–
CO	H_2	–	6.37	–

*Extrapolated by comparison with FJD data, whose values are consistently 20% higher than Zemansky's.

$$\boxed{\left(\cancel{\Delta}\nu_{mn}\right)_C = \frac{\left(\Delta\nu_{mn}\right)_C}{\pi} = 1.0772 \times 10^{26} \, \frac{\sigma_{1-2}\, p}{\sqrt{\mu_{1-2}\, T}} \, , \ \mathrm{Hz}} \qquad (4.49)$$

For completeness we write out the expression for the line-contour function $g_C(\nu,\nu_{mn},\Delta\nu_{mn})$, which in accordance with (4.45) is:

$$g_C(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{1}{\left(\Delta\nu_{mn}\right)_C}\left[\frac{\left\{\dfrac{\left(\Delta\nu_{mn}\right)_C}{\pi}\right\}^2}{(\nu-\nu_{mn})^2 + \left\{\dfrac{\left(\Delta\nu_{mn}\right)_C}{\pi}\right\}^2}\right], \ \mathrm{Hz}^{-1} \, ; \qquad (4.50)$$

where $\left(\Delta\nu_{mn}\right)_C$ is given by Eq. (4.47).

4.5 COMBINED NATURAL, COLLISIONAL AND DOPPLER BROADENING

Usually the broadening of a line near the center frequency is determined by either natural, collisional or doppler effects since under a particular set of densities, pressures and temperatures, one of these broadening processes dominates over the others. In this case one can neglect the contour functions and line-spreads of all but the dominating processes. However, because doppler broadening drops off exponentially with increasing values of $(\nu - \nu_{mn})^2$ while pressure and natural broadening drop off only inversely with $(\nu - \nu_{mn})^2$, one finds at frequencies ν sufficiently far from the center frequency $\nu = \nu_{mn}$ that the pressure and/or natural broadening term dominates over the doppler term, as illustrated in Figure 4-1, even if doppler broadening is dominating for ν close to ν_{mn} .

The simplest case is the one in which collisional broadening dominates over doppler broadening at all frequencies. In this case, ignoring doppler effects, total line-shape and line-spread are given by respectively:

$$\boxed{b_{C,N}(\nu, \nu_{mn}, \Delta\nu_{mn}) = \frac{\left\{\frac{\left(\Delta\nu_{mn}\right)_{N,C}}{\pi}\right\}^2}{(\nu - \nu_{mn})^2 + \left\{\frac{\left(\Delta\nu_{mn}\right)_{N,C}}{\pi}\right\}^2}} \qquad (4.51)$$

and:

$$\boxed{\left(\Delta\nu_{mn}\right)_{N,C} = \left(\Delta\nu_{mn}\right)_C + \left(\Delta\nu_{mn}\right)_N \text{ , Hz ,}} \qquad (4.52)$$

where $\left(\Delta\nu_{mn}\right)_C$ and $\left(\Delta\nu_{mn}\right)_N$ are given by Eqs. (4.35) or (4.36) and (4.48).

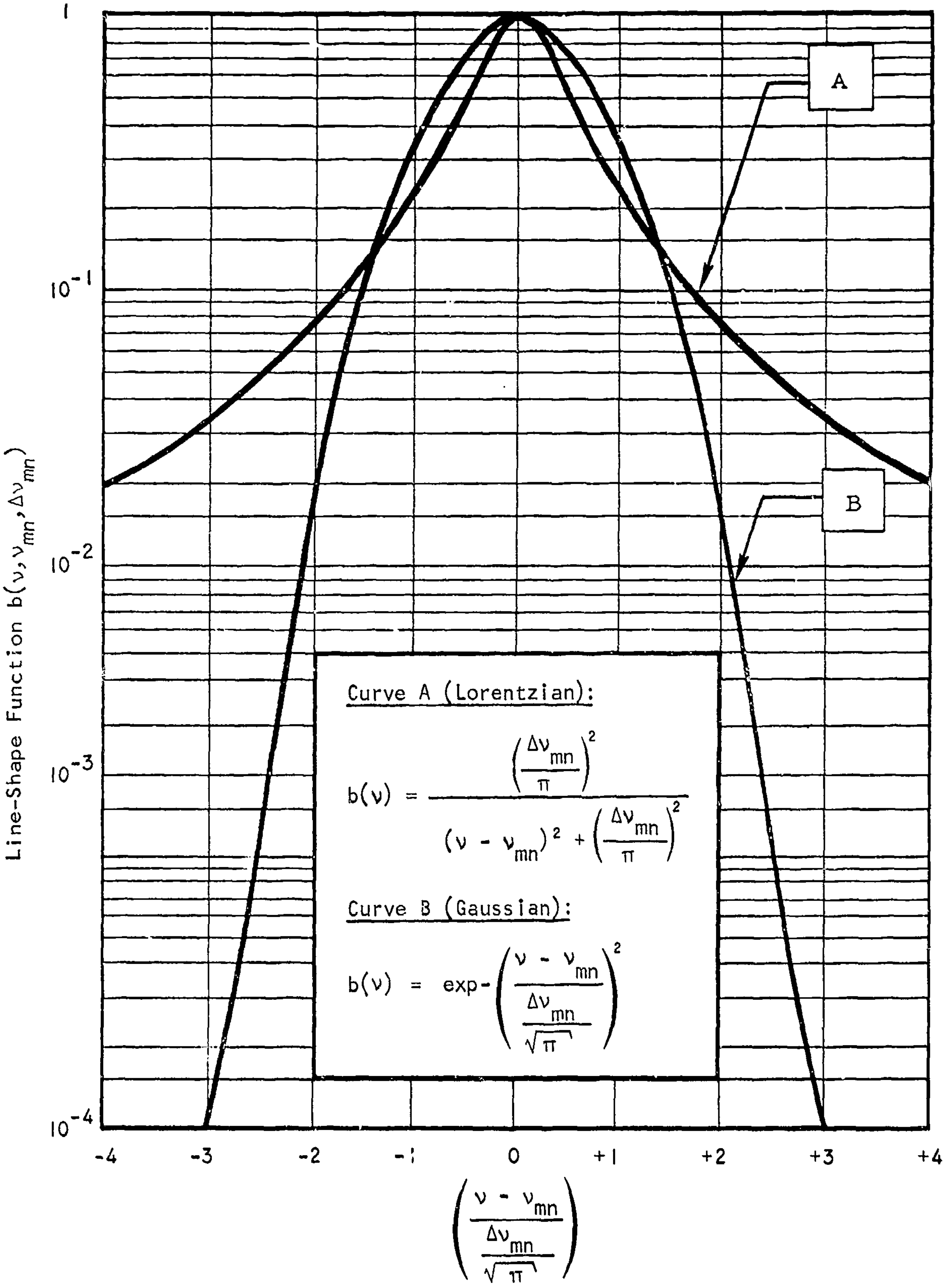

FIGURE 4-1. GAUSSIAN AND LORENTZIAN LINE-SHAPE FUNCTIONS

If all three broadening processes are important however, it can be shown (see for example Ref. 7 or 9) that:

$$g_{C,N,D}(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{\left(\Delta\nu_{mn}\right)_N + \left(\Delta\nu_{mn}\right)_C}{\left(\Delta\nu_{mn}\right)_D} \cdot$$

$$\cdot \int_{-\infty}^{+\infty} \frac{\left(\exp - \left[\dfrac{\nu' - \nu_{mn}}{\left\{\dfrac{\left(\Delta\nu_{mn}\right)_D}{\sqrt{\pi}}\right\}}\right]^2\right) d(\nu' - \nu_{mn})}{\left\{\left(\Delta\nu_{mn}\right)_N + \left(\Delta\nu_{mn}\right)_C\right\}^2 + \pi^2 \left\{(\nu - \nu_{mn}) - (\nu' - \nu_{mn})\right\}^2} =$$

$$= \alpha \int_{-\infty}^{+\infty} \frac{\exp - \left\{\dfrac{\pi\, y^2}{\left(\Delta\nu_{mn}\right)_D^2}\right\}}{\left(\Delta\nu_{mn}\right)_{N,C}^2 + \pi^2 \left\{(\nu - \nu_{mn}) - y\right\}^2}\, dy \ , \quad \mathrm{Hz}^{-1} \qquad (4.53)$$

where $\left(\Delta\nu_{mn}\right)_{N,C}$ is given by (4.52), $\left(\Delta\nu_{mn}\right)_D$ is given by (4.42), and:

$$\alpha = \frac{\left(\Delta\nu_{mn}\right)_N + \left(\Delta\nu_{mn}\right)_C}{\left(\Delta\nu_{mn}\right)_D} \qquad (4.54)$$

$$y = \nu' - \nu_{mn} \quad , \quad \mathrm{Hz} \qquad (4.55)$$

To find $\left(\Delta\nu_{mn}\right)_{N,C,D}$, we recall from Eqs. (4.5) and (4.6) that:

$$g(\nu = \nu_{mn}, \nu_{mn}, \Delta\nu_{mn}) = \frac{b(\nu = \nu_{mn}, \nu_{mn}, \Delta\nu_{mn})}{\Delta\nu_{mn}} = \frac{1}{\Delta\nu_{mn}}, \qquad (4.56)$$

since the line-shape function $b(\nu, \nu_{mn}, \Delta\nu_{mn})$ is unity at $\nu = \nu_{mn}$. Thus applying (4.56) to Eq. (4.53) we find:

$$\boxed{\begin{aligned}\left(\Delta\nu_{mn}\right)_{N,C,D} &= \frac{1}{\alpha}\left[\int_{-\infty}^{+\infty} \frac{\exp-\left\{\dfrac{\pi\, y^2}{\left[\left(\Delta\nu_{mn}\right)_D^2\right]}\right\}}{\left(\Delta\nu_{mn}\right)_{N,C}^2 + \pi^2\, y^2}\, dy\right]^{-1} = \\ &= \left(\Delta\nu_{mn}\right)_D \left(\frac{a}{\pi}\int_{-\infty}^{+\infty} \frac{\exp(-z^2)}{a^2 + z^2}\, dz\right)^{-1} \equiv \frac{\left(\Delta\nu_{mn}\right)_D}{I(a,o)}, \text{ Hz}\end{aligned}} \qquad (4.57)$$

where:

$$a = \frac{\alpha}{\sqrt{\pi}} = \frac{1}{\sqrt{\pi}}\left\{\frac{\left(\Delta\nu_{mn}\right)_N + \left(\Delta\nu_{mn}\right)_C}{\left(\Delta\nu_{mn}\right)_D}\right\} \qquad (4.58)$$

Then from (4.53) and (4.57) we get for $b_{N,C,D}(\nu, \nu_{mn}, \Delta\nu_{mn})$:

$$\boxed{\begin{aligned} b_{N,C,D}(\nu,\nu_{mn},\Delta\nu_{mn}) &= \left(\Delta\nu_{mn}\right)_D \left(\frac{\pi^{1/2}\, a}{I(a,o)}\right) \cdot \\ &\cdot \int_{-\infty}^{+\infty} \frac{\exp -\left\{\pi\, y^2 / \left(\Delta\nu_{mn}\right)_D^2\right\}}{\left(\Delta\nu_{mn}\right)_{N,C}^2 + \pi^2\,(\nu - \nu_{mn} - y)^2}\, dy = \frac{I(a,\xi)}{I(a,o)}\ , \end{aligned}} \qquad (4.59)$$

where:

$$\boxed{\xi = \frac{\pi^{1/2}\,(\nu - \nu_{mn})}{\left(\Delta\nu_{mn}\right)_D}} \qquad (4.60)$$

and the integral in Eq. (4.59):

$$\boxed{I(a,\xi) = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-z^2)}{a^2 + (\xi - z)^2}\, dz} \qquad (4.61)$$

The integral $I(a,\xi)$ cannot be solved analytically, but many approximations have been made for small and large values of a/ξ (see Ref. 7, section 4.4). Some values of $I(a,\xi)$ are listed in Table 4-2 (after Ref. 7), while Figure 4-2 shows plots of these tabulated values.

Note that with the definition (4.61), Eq. (4.53) can be written more compactly:

$$\boxed{g_{C,N,D}(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{I(a,\xi)}{\left(\Delta\nu_{mn}\right)_D}\ ,\ \mathrm{Hz}^{-1}} \qquad (4.62)$$

TABLE 4-2. NUMERICAL VALUES OF $I(a, \xi)$ AS A FUNCTION OF ξ FOR DIFFERENT VALUES OF a. (After Ref. 7)

ξ	$I(a, \xi)$ for $a = 0$	$I(a, \xi)$ for $a = 0.5$	$I(a, \xi)$ for $a = 1$	$I(a, \xi)$ for $a = 1.5$	$I(a, \xi)$ for $a = 2$	$I(a, \xi)$ for $a = 10$
0.0	1.0000	0.6157	0.4276	0.3216	0.257	0.0561
0.2	0.9608	0.6015	0.4215	0.3186		
0.4	0.8521	0.5613	0.4038	0.3097	0.252	
0.6	0.6977	0.5011	0.3766	0.2958		
0.8	0.5273	0.4294	0.3425	0.2779	0.236	
1.0	0.3679	0.3540	0.3047	0.2571		
1.2	0.2369	0.2846	0.2662	0.2349	0.212	
1.4	0.1409	0.2233	0.2292	0.2123		
1.6	0.0773	0.1728	0.1954	0.1902	0.178	
1.8	0.0392	0.1333	0.1657	0.1695		
2.0	0.0183	0.1034	0.1402	0.1504	0.148	0.0541
2.2	0.0079		0.120			
2.4	0.0032		0.102		0.123	
2.6	0.0012		0.088			
2.8	0.0004		0.078		0.101	
3.0	0.0001		0.066			
3.2			0.057		0.0850	
3.4			0.051			
3.6			0.045		0.0708	
3.8			0.041			
4.0		0.0183	0.037	0.0487	0.0598	0.0486
4.4					0.0505	
4.8					0.0440	
5.2					0.0378	
5.6					0.0330	
6.0		0.0081	0.016	0.0228	0.0291	0.0414
6.4					0.0259	
6.8					0.0231	
7.2					0.0208	
7.6					0.0186	
8.0		0.004	0.009	0.0131	0.0169	0.0344
10		0.003	0.005	0.0083		0.0283
12						0.0232
14						0.0191
16						0.0159
18						0.0134
20						0.0114
22						0.00965
24						0.00835
26						0.00728
28						0.00637
30						0.00564
32						0.00502
34						0.00451
36						0.00406
38						0.00366
40						0.00333

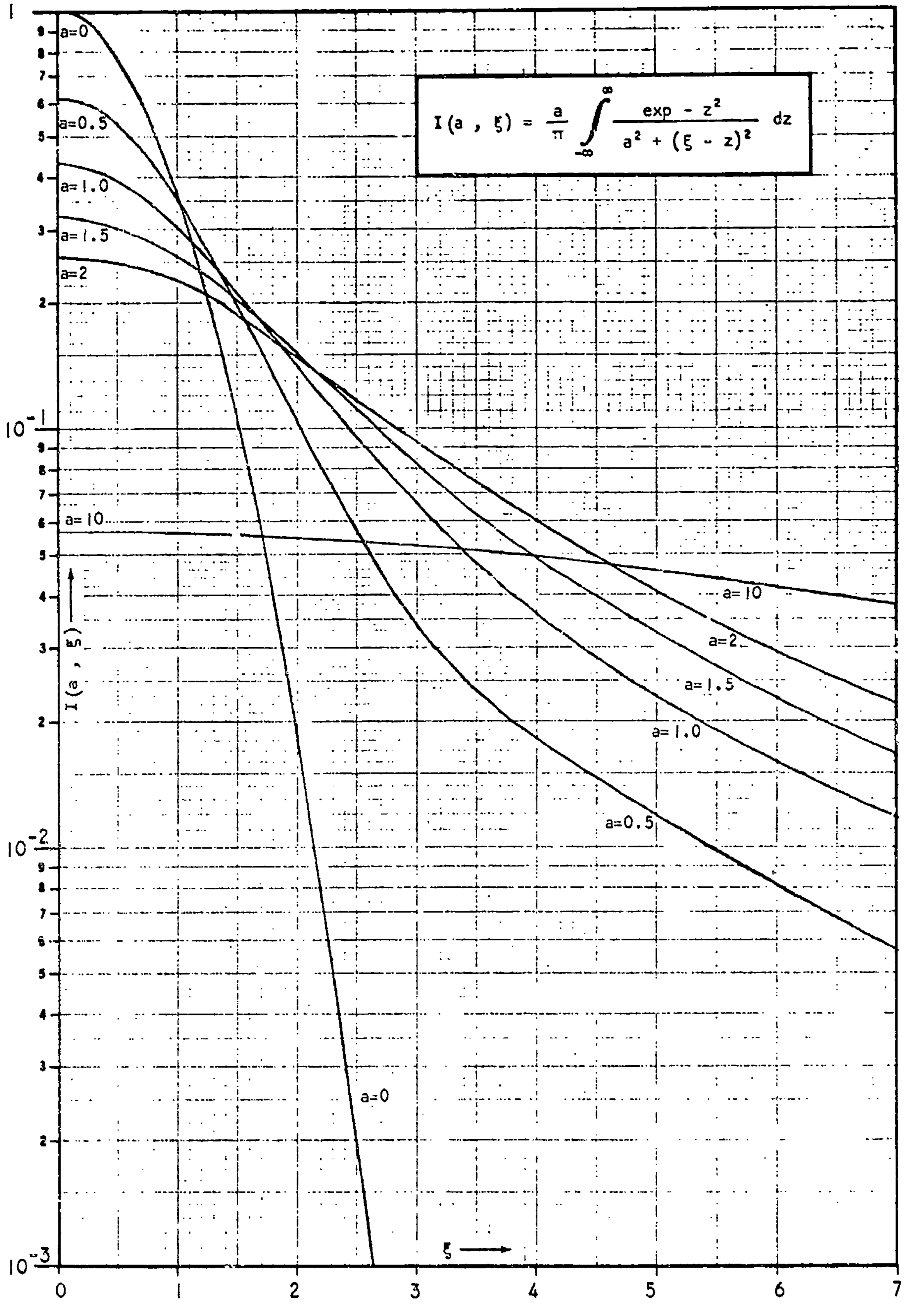

FIGURE 4-2. PLOT OF THE FUNCTION I(a , ξ)

4.6 STARK BROADENING

Stark or electric-field broadening of emission lines arises in highly-ionized gases or plasmas due to the Stark-Effect displacements of the emission wavelength by the surrounding positive ions that act on an atom (molecule) or ion which is emitting. Although the free electrons also cause some Stark broadening, their effect may usually be assumed to be small.

The most commonly used expressions for Stark broadening were originally developed by Holtzmark whose results are very closely approximated by a simpler theory of Russell and Stewart, and of Penner (Refs. 7 and 9). According to the simpler theory by the latter authors, the probability than an atom or ion experiences a Stark-broadening electric field E or nondimensionalized field $\beta = E/E_o$, is given by (Ref. 7):

$$p(\beta)\, d\beta = g_S(\nu, \nu_{mn}, \Delta\nu_{mn})\, d\nu = \frac{3}{2}\, \beta^{-(5/2)}\, d\beta \qquad (4.63)$$

where:

$$\beta \equiv \frac{E}{E_o} \qquad (4.64)$$

$$E_o \simeq \frac{z_i\, e}{r_o^2} = \left(\frac{4}{3}\pi\right)^{2/3} z_i\, e\, n_i^{2/3} \simeq 2.60\, z_i\, e\, n_i^{2/3} = 4.16 \times 10^{-19}\, z_i\, n_i^{2/3}\, , \ \frac{\text{Volts}}{\text{m}} \qquad (4.65)$$

z_i = Degree of ionization of ions (usually $z_i \approx 1$)

e = Electron charge = 1.6021×10^{-19} Coulombs

n_i = Density of ions, ions/m^3

r_o = Radius of sphere containing on the average one positive ion

The value of r_o used in (4.65) follows from the definition of r_o which requires that:

$$\frac{4}{3}\pi r_o^3 n_i = 1 , \tag{4.66}$$

while Eq. (4.63) is obtained from the probability of finding an ion at a distance r which is given by:

$$p(r)\,dr = 3\left(\frac{r}{r_o}\right)^2 \frac{dr}{r_o} \tag{4.67}$$

Equation (4.63) has been criticized in Ref. 31 as being inadequate. This is immediately clear if one applies the law of spectroscopic stability to it, which demands that:

$$\int_0^\infty p(\beta)\,d\beta = \int_0^\infty g_S(\nu,\nu_{mn},\Delta\nu_{mn})\,d\nu = 1 \tag{4.68}$$

Obviously $p(\beta)\,d\beta = \frac{3}{2}\beta^{-(5/2)}\,d\beta$ as given by (4.63) becomes infinite when integrated from 0 to ∞. The problem can be corrected however if one assumes that for small β values $\beta \rightarrow \beta' = \beta_o + E/E_o \approx 1 + E/E_o$. A corrected expression which can satisfy (4.68) is therefore:

$$p(\beta)\, d\beta = \frac{3}{2}\, (1 + \beta)^{-(5/2)}\, d\beta \qquad (4.69)$$

Now the deviation of the Stark-broadened emission frequency $(\nu - \nu_{mn})$ from the center frequency ν_{mn} is to first order directly proportional to E:

$$(\nu - \nu_{mn}) = C_m\, E\ ,\ \mathrm{Hz}\ , \qquad (4.70)$$

where C_m is the Stark coefficient in Hz · m/Volts. Then from (4.69) and (4.70), we obtain:

$$g_S(\nu,\nu_{mn},\Delta\nu_{mn}) = 1.50\ (1 + \beta)^{-(5/2)}\ \frac{d\beta}{d\nu} =$$

$$= 1.50 \left(1 + \frac{\nu - \nu_{mn}}{C_m\, E_o}\right)^{-(5/2)} \left(\frac{1}{C_m\, E_o}\right) = \frac{1.50\ (C_m\, E_o)^{3/2}}{(C_m\, E_o + \nu - \nu_{mn})^{5/2}}\ ,\ \mathrm{Hz}^{-1} \qquad (4.71)$$

The field E_o is obtained from Eq. (4.65), while C_m can be either calculated from quantum theory or measured experimentally. Table 4-3 lists some measured Stark coefficients C_m .

To obtain $\Delta\nu_{mn}$ and $b(\nu,\nu_{mn},\Delta\nu_{mn})$, we use Eqs. (4.5) and (4.6) or (4.56) again and obtain:

$$\boxed{\left(\Delta\nu_{mn}\right)_S = 0.667\ C_m\, E_o = 2.78 \times 10^{-19}\ z_i\, n_i^{2/3}\ C_m\ ,\ \mathrm{Hz}\ ,} \qquad (4.72)$$

and:

TABLE 4-3. STARK COEFFICIENTS*

Emission Line	Center Wavelength of Emission Line (nm)	C_m (Hz · m/Volt)
Hydrogen		
Balmer – α	656.279	3.15×10^2
Balmer – β	486.133	0.887×10^2
Balmer – γ	434.047	0.446×10^2
Balmer – δ	410.174	0.322×10^2
Sodium		
D_2-Line	588.996	1.034×10^2
Mercury	253.7	0.158×10^2

*Data are partially from Refs. 7 and 31.

$$\boxed{\begin{aligned} b_S(\nu,\nu_{mn},\Delta\nu_{mn}) &= \frac{(C_m\,E_o)^{5/2}}{\left\{C_m\,E_o + (\nu - \nu_{mn})\right\}^{5/2}} = \frac{(1.5\,\Delta\nu_{mn})^{5/2}}{\left\{1.5\,\Delta\nu_{mn} + (\nu - \nu_{mn})\right\}^{5/2}} = \\ &= \frac{4.08 \times 10^{-47}\,z_i^{5/2}\,n_i^{5/3}\,C_m^{5/2}}{\left\{4.16 \times 10^{-19}\,z_i\,n_i^{2/3}\,C_m + (\nu - \nu_{mn})\right\}^{5/2}} \end{aligned}}$$

(4.73)

From the values of C_m listed in Table 4-3 and Eq. (4.72), it is clear that a high degree of ionization will be required (large n_i) for $\left(\Delta\nu_{mn}\right)_{Stark}$ to be appreciable. Only in stellar interiors, nuclear explosions, and high-energy plasmas is this usually the case.

4.7 ROTATIONAL BROADENING OF VIBRATIONAL TRANSITIONS

In the following we shall develop expressions for the average band contour of the photon emission or absorption frequencies of a vibrational transition (at a fixed electronic level) which is broadened by rotational substructure. The technique we shall use is similar to that employed by S. S. Penner, J. A. L. Thomson, and W. J. Hooker (Ref. 7), and by B. Kivel, et al (Refs. 32 and 33), although the derivation of our expressions and the form in which they are cast are somewhat different.

For pure rovibrational transitions, we have for the rotational levels always $\Delta J = \pm 1$ or 0, while for a vibrational level change, $\Delta v_\beta = \pm 1$ is most allowed but overtone transitions with $\Delta v_\beta = \pm 2, \pm 3$, and combination-band transitions with Δv_α, Δv_β, Δv_γ, ... = ±0, ±1, ±2, ±3, ... are also possible. This is in contrast with vibronic transitions in which only two or more specific vibrational level changes Δv can occur that are determined by the Franck-Condon principle (see section 4.8). The selection rule $\Delta J = \pm 1$ or $\Delta J = 0$ is absolute however in both vibrational and electronic transitions.

Because different types of rotors (namely linear, symmetric-top, spherical-top, and asymmetric-top) have different energy distributions, we shall have to consider each of them separately in what follows.

4.7.1 Linear Rotors

All diatomic molecules and linear polyatomic molecules are linear rotors whose quantized rotational energy levels can be expressed by the expression (see Eqs. (3.105) and (3.137)):

$$(E)^{\text{rot}}_{\begin{pmatrix}\text{linear}\\ \text{rotor}\end{pmatrix}} = hc\, B_v\left[J(J+1) - \ell^2\right] = h\nu_B\left[J(J+1) - \ell^2\right] , \qquad (4.74)$$

where we neglected anharmonicities and centrifugal stretching, and where for convenience we define:

$$\nu_B = c\,B_v = c\left[B_e - \sum_\beta \alpha_\beta\left(v_\beta + \frac{d_\beta}{2}\right)\right] , \text{ Hz} \qquad (4.75)$$

The quantum number ℓ equals v_β , $v_\beta - 2$, ..., $- v_\beta$ (see Eq. (3.117)), and we have always $J \geq \ell$ (Ref. 10). If we ignore the splitting of the rotational levels by ℓ^2, and refer all rotational energies to the $J = 0$ level, we may write:

$$E^{\text{rot}} = E^{\text{rot}}(J) - E^{\text{rot}}(J=0) = h\nu_B\, J(J+1) \qquad (4.76)$$

For the vibrational energy levels we have similarly to first approximation (harmonic oscillator):

$$(E)^{\text{vib}}_{\substack{\text{linear}\\ \text{molecules}}} = \sum_\beta \left(v_\beta + \frac{d_\beta}{2}\right) h\nu_\beta \quad , \qquad (4.77)$$

where anharmonic effects are again neglected. In all of the above equations $v_\beta = 0, 1, 2, \ldots$. are the vibrational quantum numbers of the normal vibration β of frequency ν_β and degeneracy d_β (see section 3.3), and the J are the rotational quantum numbers ($J = 0, 1, 2, \ldots$.). The constants α_β in (4.75) give the effects on the moment of inertia I_B and therefore on $B_e = h/(8\pi^2 I_B)$ due to vibration (see Eqs. (3.105), (3.108), and (3.138)). Of course for diatomic molecules the summation over vibrations β is not necessary since there is only one normal vibration. If we refer all vibrational energies to the ground state $v_o = (v_\alpha=0, v_\beta=0, \ldots.)$, then the energy of a particular vibration is:

$$E_o^{vib}(v_\alpha, v_\beta, \ldots.) = E^{vib}(v_\alpha, v_\beta, \ldots.) - E^{vib}(v_\alpha=0, v_\beta=0, \ldots.) = \sum_\alpha v_\alpha \, h\nu_\alpha \tag{4.78}$$

According to Boltzmann statistics we have for a gas in thermodynamic equilibrium at temperature T that the fraction of molecules in a vibrational level $(v_\alpha, v_\beta, \ldots.)$ and rotational state J is given by:

$$N_{v,J} = N_o \, f_v \, f_J = N_v \, f_J \tag{4.79}$$

where N_o is the total number of molecules, and:

$$f_v = \frac{w_v \exp-\left(E_o^{vib}/(kT)\right)}{Z_v} = \frac{w_v}{Z_v} \exp\left[-\sum_\alpha (v_\alpha \; h\nu_\alpha)/(kT)\right] \tag{4.80}$$

$$f_J = \frac{w_r \exp-\left(E_o^{rot}/(kT)\right)}{Z_r} = \left(\frac{2J+1}{Z_r}\right) \exp-\left\{J(J+1)\frac{h\nu_B}{kT}\right\} \tag{4.81}$$

The total vibration weight w_v is given by the general expression (see Eq. (3.91)):

$$w_v = \sum_\alpha w_\alpha = \sum_\alpha \left[\delta(d_\alpha - 1) + (v_\alpha + 1)\,\delta(d_\alpha - 2) + \frac{1}{2}(v_\alpha + 1)(v_\alpha + 2)\,\delta(d_\alpha - 3)\right] \tag{4.82}$$

where $\delta(x)$ is the Dirac delta function. Practically all linear molecules have a maximum degeneracy of $d_\alpha = 2$ in one of their normal vibrations so that the third term in the bracket of (4.82) vanishes. For diatomic molecules we have of course simply $w_v = 1$.

The vibrational and rotational partition functions Z_v and Z_r are summations over the fractional populations of all possible vibrational and rotational energy levels. Taking proper account of the degeneracies, these sums are (Refs. 10 and 16):

$$\begin{aligned} Z_v = \sum_{v_\alpha, v_\beta, \ldots} w_v \exp\text{-}\left(E_o^{vib}/(kT)\right) &= \left[\sum_{v_\alpha=0}^{\infty} \exp\text{-}\left\{v_\alpha\, h\nu_\alpha/(kT)\right\}\right]^{d_\alpha} \cdot \\ &\cdot \left[\sum_{v_\beta=0}^{\infty} \exp\text{-}\left\{v_\beta\, h\nu_\beta/(kT)\right\}\right]^{d_\beta} \cdots\cdots\cdots\cdots \approx \\ &\approx \left[1 - \exp\text{-}\left\{h\nu_\alpha/(kT)\right\}\right]^{-d_\alpha} \cdot \left[1 - \exp\text{-}\left\{h\nu_\beta/(kT)\right\}\right]^{-d_\beta} \cdots\cdots\cdots \\ &= \prod_\alpha \left[1 - \exp\text{-}\left\{h\nu_\alpha/(kT)\right\}\right]^{-d_\alpha} \end{aligned} \tag{4.83}$$

$$Z_r = \sum_{J=0}^{\infty} w_r \exp-(E^{rot}/(kT) = \sum_{J=0}^{\infty} (2\,J + 1) \exp-\left\{J(J + 1)\,\frac{h\nu_B}{kT}\right\} =$$

$$= \frac{kT}{h\nu_r} + \frac{1}{3} + \frac{1}{15}\left(\frac{h\nu_B}{kT}\right) + \frac{4}{315}\left(\frac{h\nu_B}{kT}\right)^2 + \frac{1}{315}\left(\frac{h\nu_B}{kT}\right)^3 + \ldots\ldots \qquad (4.84)$$

The frequencies of the allowed photon-active vibrational transitions between a level m and n in linear molecules are of course (to first-order) given by $\nu = h^{-1}\left[\left\{E_o^{vib} + E_o^{rot}\right|_m - \left\{E_o^{vib} + E_o^{rot}\right|_n\right]$. When the selection rules (3.127) and (3.128) are taken into account, this yields in general three groups of emission/absorption frequencies which are called the P-Branch ($J_m - J_n = -1$), Q-Branch ($J_m = J_n$), and the R-Branch ($J_m - J_n = +1$):

P-Branch ($J_m - J_n = -1$; $J_m > \ell_m = \ell_n$)

$$\nu = \nu_J = \nu_{mn} - \left(\nu_{B_m} + \nu_{B_n}\right) J_n - \left(\nu_{B_n} - \nu_{B_m}\right) J_n^2 =$$

$$= \nu_{mn} - 2\,\nu_{B_n} - \left(3\,\nu_{B_n} - \nu_{B_m}\right) J_m - \left(\nu_{B_n} - \nu_{B_m}\right) J_m^2 \qquad (4.85)$$

Q-Branch ($J_m = J_n \neq 0$; $J_m \geq \sup(\ell_m, \ell_n)$; $\Delta\ell = \pm 1$, or weakly for $\Delta\ell = 0$, $\ell \neq 0$)

$$\nu = \nu_J^Q = \nu_{mn} - J(J+1)\,\left(\nu_{B_n} - \nu_{B_m}\right) - \left(\ell_m^2\,\nu_{B_m} - \ell_n^2\,\nu_{B_n}\right) \qquad (4.86)$$

$$(J = J_m = J_n)$$

R-Branch $(J_m - J_n = +1\ ;\ J_m \geq \ell_m + 1 = \ell_n + 1)$

$$\nu = \nu_J = \nu_{mn} + \left(\nu_{B_m} + \nu_{B_n}\right) J_m - \left(\nu_{B_n} - \nu_{B_m}\right) J_m^2 = \nu_{mn} +$$

$$+ 2\nu_{B_m} + \left(3\nu_{B_m} - \nu_{B_n}\right) J_n - \left(\nu_{B_n} - \nu_{B_m}\right) J_n^2 \qquad (4.87)$$

Here the pure vibrational transition frequency ν_{mn} is given by:

$$\nu_{mn} = \sum_{\alpha} \left(v_{\alpha_m} - v_{\alpha_n}\right) \nu_{\alpha} \qquad (4.88)$$

For a diatomic molecule ν_{mn} is of course simply $\nu_{mn} = (v_m - v_n)\ \nu_e$.

If $\nu_{B_m} \approx \nu_{B_n} = \nu_B$ as is usually the case, Eqs. (4.86) through (4.88) simplify to:

P-Branch $(J_m - J_n = -1\ ;\ J_m \geq \ell_m)$

$$\nu = \nu_J = \nu_{mn} - 2\nu_B J_n - \Delta\nu_B J_n^2 = \nu_{mn} - 2\nu_B - 2\nu_B J_m - \Delta\nu_B J_m^2 \approx$$

$$\approx \nu_{mn} - 2\nu_B J_n = \nu_{mn} - 2\nu_B - 2\nu_B J_m \qquad (4.89)$$

Q-Branch $(J_m = J_n \neq 0\ ;\ J_m \geq \sup(\ell_m , \ell_n))$

$$\nu = \nu_J^Q = \nu_{mn} - \nu_B^Q - \Delta\nu_B J_m(J_m + 1) = \nu_{mn} - \nu_B^Q - \Delta\nu_B J_n(J_n + 1) \qquad (4.90)$$

R-Branch $(J_m - J_n = +1\ ;\ J_m \geq \ell_m + 1)$

$$\nu = \nu_J = \nu_{mn} + 2\nu_B J_m - \Delta\nu_B J_m^2 = \nu_{mn} + 2\nu_B + 2\nu_B J_n - \Delta\nu_B J_n^2 \approx$$

$$\approx \nu_{mn} + 2\nu_B J_m = \nu_{mn} + 2\nu_B + 2\nu_B J_n \qquad (4.91)$$

where in (4.90):

$$\nu_B^Q = (\ell_m^2 - \ell_n^2)\ \nu_B \qquad (4.92)$$

and:

$$\Delta\nu_B = \nu_{B_n} - \nu_{B_m} = c\left(B_{v_n} - B_{v_m}\right) \equiv c\ \Delta B_v = c\sum_\beta \alpha_\beta \left(v_{\beta_m} - v_{\beta_n}\right) \qquad (4.93)$$

The last expression in (4.93) follows from Eq. (4.75). Of course $\Delta\nu_B \ll \nu_B$.

For the purpose of calculating average band-contour functions, the approximate relations (4.89), (4.90), and (4.91) are more than adequate. When considering individual rotational lines on the other hand, Eqs. (4.85) through (4.87) are usually required.

In Figure 4-3, typical rovibrational emission bands are shown of some commonly-occurring linear molecules. The rotational lines in the P- and R-Branches are clearly resolved and spread out (line spacing = $2\nu_B$), but because the lines in the Q-Branch are so close (line spacing = $2J_m\Delta\nu_B$), the latter, if present, appears as one very broad and intense line centered around the frequency ν_{mn}. Note that the diatomic molecules $HC\ell$ and CO have no Q-Branch, nor does the non-deganerate ν_1 vibration of N_2O show such a branch since for the ν_1 vibration $\ell_m = \ell_n = 0$. Only for the degenerate ν_2 vibrational transition $(\Delta\ell = \pm 1)$ of CO_2 and for the ν_5 transition of C_2H_2, is there a Q-Branch present.

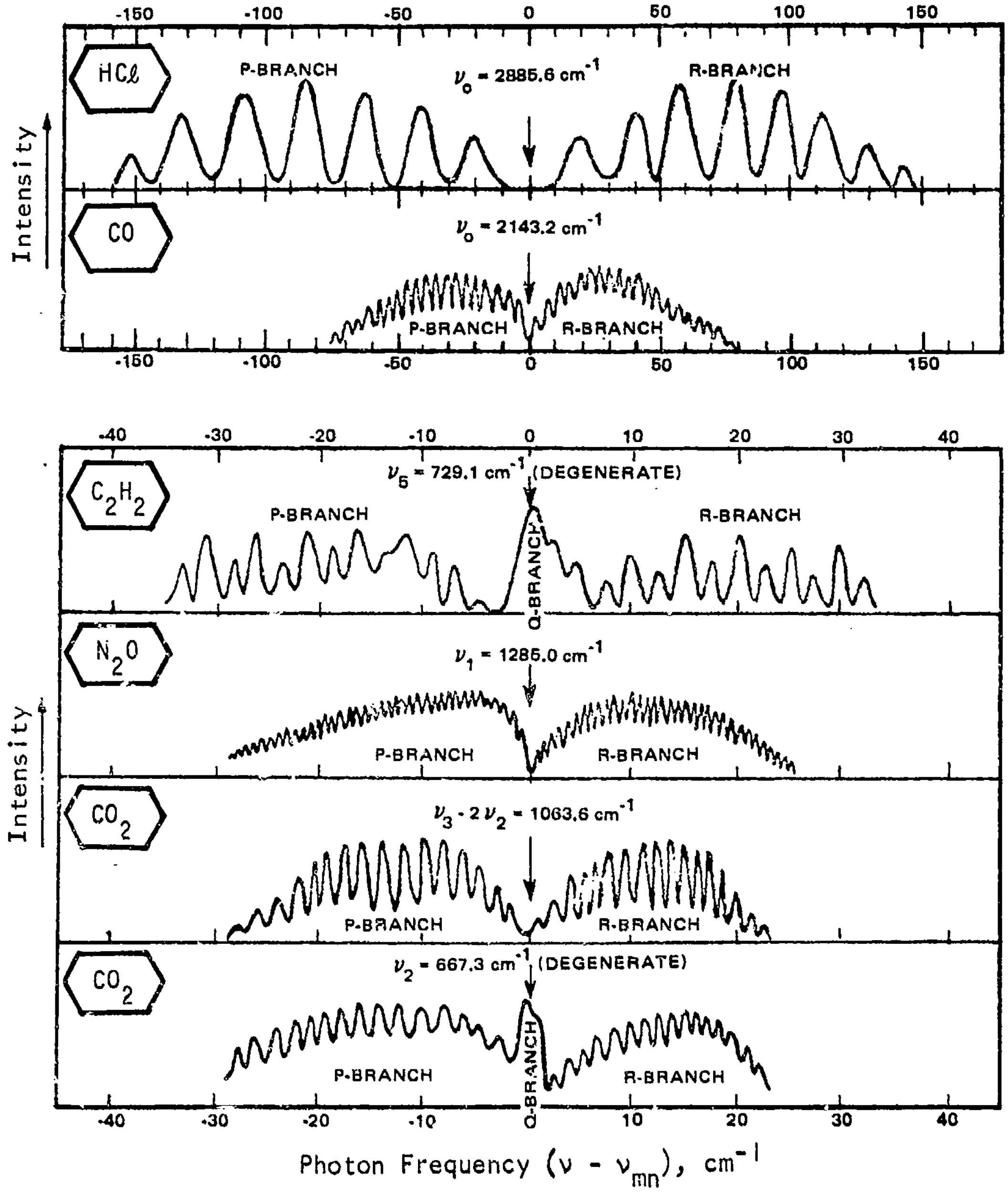

FIGURE 4-3. TYPICAL VIBRATIONAL EMISSION/ABSORPTION BANDS OF THE LINEAR MOLECULES HCℓ, CO, C_2H_2, N_2O, AND CO_2 AT T = 300°K (Ref. 10)

Now if there are $N_m = N_{v_m}$ vibrationally-excited molecules in the gas at one particular vibrational level v_m, then the probability of finding a v_m vibrationally-excited molecule in the J_m rotational sublevel equals f_{J_m}, that is of the N_m molecules, $f_{J_m} N_m$ are at level (v_m, J_m). The internal energy of the $f_{J_m} N_m$ molecules is given by:

$$h\nu'_m = h\nu_m + J_m(J + 1)\, h\nu_B , \tag{4.94}$$

where the rotational contribution $J_m(J_m + 1)\, h\nu_B$ is always small compared to the vibrational energy $h\nu_m$ and may be considered a perturbation of the basic vibrational energy $h\nu_m$ or frequency ν_m which is given by:

$$\nu_m = \sum_\alpha v_{\alpha_m} \nu_\alpha \tag{4.95}$$

The notation v_m in the above and below is short for $(v_{\alpha_m}, v_{\beta_m}, \ldots.)$.

Now according to Eq. (1.25), which was derived from quantum mechanics, we have that the rate dN_φ/dt of photons emitted by the N_m molecules already excited to the vibrational level v_m is:

$$\left(\frac{dN_\varphi}{dt}\right)_{\begin{pmatrix} v_m \to v_n \\ J_m \to J_n \end{pmatrix}} = N_m A^o_{mn} G^{vib}_{nm} = N_m A^o_{mn} F^{rot}_{nm} f_{J_m} = N_m A^o_{mn} F^{rot}_{nm} \cdot$$

$$\cdot \left(\frac{2J_m + 1}{Z_r}\right) \exp - \left\{\frac{J_m(J_m + 1)\, h\nu_B}{kT}\right\} , \; \frac{\text{photons/sec}}{\text{level } J_m} \tag{4.96}$$

Here F^{rot}_{mn}, which was defined by (1.27), gives the probability that the $J_m \rightarrow J_n$ transition occurs when the molecule deexcites vibrationally from level $v_m \rightarrow v_n$.

Because the total number of photons emitted per second must equal the total number of molecular deexcitations per second, we must have that:

$$N_m A^{\circ}_{mn} = \sum_{J_m=0}^{\infty} \frac{dN_{\varphi}(J_m)}{dt} = \sum_{J_m=0}^{\infty} N_m A^{\circ}_{mn} F^{rot}_{mn} f_{J_m} , \tag{4.97}$$

and since for any temperature T, we have always:

$$\sum_{J_m=0}^{\infty} f_{J_m} = 1 , \tag{4.98}$$

it follows that we must have:

$$F^{rot}_{mn} = \frac{{}^{\circ}C^{rot}_{mn}}{w_{r_m}} = 1 , \tag{4.99}$$

or:

$${}^{\circ}C^{rot}_{mn} = w_{r_m} , \tag{4.100}$$

because (4.97) holds for any temperature T, while F^{rot}_{mn} does not depend on T.

The result given by Eq. (4.99) or (4.100) means that the general summation over states i and k indicated in Eq. (1.12) must be a single summation over initial states i only, there being always one final state k available for each i. In the case of a pure rotational transition on the other hand for which the connection factor C_{mn}^{rot} given by (1.18) applies, the indicated general summation sign is a double summation, over all initial and final states, that is first we sum over all k for a given i and then over all i. Thus ${}^{o}C_{mn}^{rot} \neq C_{mn}^{rot} = w_{r_m} w_{r_n}$.

Now the probability p_P that the molecule makes a P-Branch transition from J_m to $J_n = J_m + 1$ is somewhat larger than the probability p_R that it makes an R-Branch transition from J_m to $J_n = J_m - 1$ by factors proportional to $(2J_m+3)$ and $(2J_m-1)$ respectively since the "availability" of quantum space at level J_n is equal to $2J_n+1$. If only P- and R-Branch transitions are allowed, we must have then that:

(P+R) Case

$$p_P(J_m, J_n=J_m+1) = \frac{p_R}{p_P + p_R} = \frac{2J_m+3}{2(2J_m+1)} , \tag{4.101}$$

$$p_R(J_m, J_n=J_m-1) = \frac{p_R}{p_P + p_R} = \frac{2J_m-1}{2(2J_m+1)} , \tag{4.102}$$

since according to (4.99) we must have for J_m that:

$$F_{mn}^{rot}(J_m, J_n) = p_P(J_m; J_n=J_m+1) + p_R(J_m; J_n=J_m-1) = 1 \tag{4.103}$$

Similarly we find for the case that transitions in the P- , Q- , and R-Branch are equally allowed:

(P+Q+R) Case

$$p_P(J_m, J_n = J_m + 1) = \frac{p_P}{p_P + p_Q + p_R} = \frac{2J_m + 3}{3(2J_m + 1)} , \qquad (4.104)$$

$$p_Q(J_m, J_n = J_m) = \frac{p_Q}{p_P + p_Q + p_R} = \frac{2J_m + 1}{3(2J_m + 1)} = \frac{1}{3} , \qquad (4.105)$$

$$p_R(J_m, J_n = J_m - 1) = \frac{p_R}{p_P + p_Q + p_R} = \frac{2J_m - 1}{3(2J_m + 1)} , \qquad (4.106)$$

and:

$$F_{mn}^{rot}(J_m, J_n) = p_P(J_m, J_n = J_n + 1) + p_Q(J_m, J_n = J_m) + p_R(J_m, J_n = J_m - 1) = 1 \qquad (4.107)$$

Returning to (4.96) then, dividing both sides by the constant factor $N_m \; A^o_{mn}$, and using (4.103) or (4.107), we can write:

$$G^{vib}_{mn_P}(J_m) = f_d \left(\frac{2J_m + 3}{Z_r} \right) \exp - \left\{ \frac{J_m(J_m + 1) \; h\nu_B}{kT} \right\} \qquad (4.108)$$

$$G^{vib}_{mn_Q}(J_m) = f_d \left(\frac{2J_m + 1}{Z_r} \right) \exp - \left\{ \frac{J_m(J_m + 1) \; h\nu_B}{kT} \right\} \qquad (4.109)$$

$$G^{vib}_{mn_R}(J_m) = f_d\left(\frac{2J_m - 1}{Z_r}\right)\exp-\left\{\frac{J_m(J_m+1)\ h\nu_B}{kT}\right\} \tag{4.110}$$

Here we have in the case of no vibrational degeneracy, that is in the P+R case, that f_d is given by:

$$f_d = 1/2 \quad \text{(P+R Branches only)} \quad , \tag{4.111}$$

while in the presence of degeneracy, that is for the P+Q+R case, f_d is:

$$f_d = 1/3 \quad \text{(P+Q+R Branches)} \tag{4.112}$$

The functions $G^{vib}_{mn_P}$, $G^{vib}_{mn_Q}$, and $G^{vib}_{mn_R}$ give essentially the fractional strength of an emission line J_m in each of the three possible branches and has values only for the discrete numbers $J_m=1,2,3,\ldots.$ (and $J_m=0$ for the P-Branch only). Now for reasons which will become clear below, when we go over from the discontinuous distribution function G^{vib}_{mn} to a continuous one, it is convenient to express G^{vib}_{mn} as the fractional strength per unit range of emitted photon frequency as defined by Eq. (1.30). Equations (4.89) through (4.91) show that in the P- and R-Branches the emitted photon frequencies are spaced at constant intervals $\Delta\nu_J = 2\nu_B$ for successive J_m values:*

$$\left|\frac{dJ_m}{d\nu}\right|_{\begin{pmatrix}\text{P-Branch}\\ \text{and}\\ \text{R-Branch}\end{pmatrix}} = (2\nu_B)^{-1}\ , \quad \frac{\text{Lines}}{\text{Hz}} \tag{4.113}$$

while for the Q-Branch:

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*We shall use only absolute values of $dJ_m/d\nu$ since we want to keep the functions g positive (see Eqs. (4.115) through (4.117)). For linear symmetric molecules such as CO_2 , the effective spacing between lines is $\Delta\nu_J = 4\nu_B$ instead of $2\nu_B$, so that $d\nu/dJ = 4\nu_B$, Hz/line (see factor f_I on p. 203, ff).

$$\left|\frac{dJ_m}{d\nu}\right|_{(Q\text{-Branch}} = \left\{2(J_m+1)\ \Delta\nu_B\right\}^{-1}, \quad \frac{\text{Lines}}{\text{Hz}} \tag{4.114}$$

Using (4.113) and (4.114), we may then rewrite Eqs. (4.108) through (4.110) in the form:

$$g_v^P(J_m) \equiv G_{mn_P}^{vib}(J_m)\ \left|\frac{dJ_m}{d\nu}\right| = f_d\,\frac{2J_m+3}{2\nu_B Z_r}\,\exp-\left\{\frac{J_m(J_m+1)h\nu_B}{kT}\right\}, \quad \text{Hz}^{-1} \tag{4.115}$$

$$g_v^Q(J_m) \equiv G_{mn_Q}^{vib}(J_m)\ \left|\frac{dJ_m}{d\nu}\right| = f_d\,\frac{2J_m+1}{2(J_m+1)\left|\Delta\nu_B\right| Z_r}\,\exp-\left\{\frac{J_m(J_m+1)h\nu_B}{kT}\right\}, \quad \text{Hz}^{-1} \tag{4.116}$$

$$g_v^R(J_m) \equiv G_{mn_R}^{vib}(J_m)\ \left|\frac{dJ_m}{d\nu}\right| = f_d\,\frac{2J_m-1}{2\nu_B Z_r}\,\exp-\left\{\frac{J_m(J_m+1)h\nu_B}{kT}\right\}, \quad \text{Hz}^{-1} \tag{4.117}$$

Before prceeding further, we have to consider one additional complication we avoided so far, and that is the effect of nuclear spin on the probabilities p_P , p_R , p_Q given in Eqs. (4.101) through (4.106). For nonsymmetric linear molecules such as HCℓ, CO, NNO, and HCN, these probabilities remain as given by Eqs. (4.101) through (4.106). However for symmetric linear molecules such as OCO(CO_2), OUO(UO_2), and HCCH(C_2H_2), these factors are modified by nuclear spin angular momentum effects.

For triatomic symmetric linear molecules, the statistical weights $w_m = 2J_m+1$ of the rotational sublevels J_m must be multiplied by the factor (Ref. 10, p. 16ff):

$$f_I(J_m, s_m)_{\left(\substack{\text{triatomic}\\ \text{symmetric}}\right)} = \left[\left(\frac{I}{2I+1}\right)\delta\left\{1 + (-1)^{(J_m+s_m)}\right\} + \left(\frac{I+1}{2I+1}\right)\delta\left\{1 + (-1)^{(J_m+s_m+1)}\right\}\right] \tag{4.118}$$

Here $\delta(x)$ is the Dirac delta function, that is $\delta(x=0) = 1$ and $\delta(x \neq 0) = 0$; therefore only one of the two terms in Eq. (4.118) is nonzero for a given J_m value. The parameter I in Eq. (4.118) is the nuclear spin quantum number of each of the two identical atoms that caused the linear triatomic molecule to be symmetrical, such as the Oxygen atom O in CO_2. The parameters s_m in (4.118) gives the total symmetry of the combined nuclear spin wave function ψ_I, the electronic wave function ψ_e, and the vibrational wave function ψ_v, that is of the wave function $\psi_s = \psi_I \psi_e \psi_v$. We define for convenience:

$$s_m = \frac{1}{2}\left(1 - s_I s_e s_v\right) \tag{4.119}$$

where the factors s_I, s_e, s_v are the parities ($s = +1$, or -1) of the wave function ψ_I, ψ_e, and ψ_v, respectively. Then we see that we can only have $s_m = 0$, or $s_m = 1$ for the case that $s_I s_e s_v = +1$ and $= -1$, respectively.

For triatomic symmetric molecules with two identical and symmetric nuclei each having nuclear spin quantum number I, the spin function ψ_I is fermionic with parity $s_I = -1$ if $I = (k + 1/2)$, and bosonic with parity $s_I = +1$ if $I = k$, where $k = 0, 1, 2, 3, \ldots$. Mathematically we can express this result in the simple form:

$$s_{I\,\left(\substack{\text{triatomic}\\ \text{symmetric}}\right)} \quad (-1)^{2I} \tag{4.120}$$

The parity s_v of the vibrational wavefunction at level m may be expressed by:

$$s_v = \prod_{\beta} s_{v_\beta} = \prod_{\beta} (-1)^{v_{\beta_m}} , \tag{4.121}$$

since the vibrational wavefunctions are even ($s_{v_\beta} = +1$) for even v_{β_m} and odd ($s_{v_\beta} = -1$) for odd values of v_{β_m} . Here the v_{β_m} are the vibrational quantum numbers of the normal vibrations β at level m.

The electronic wavefunction for nearly all rovibrational bands of interest is that of the electronic ground state and for nearly all photon-active* linear molecules $s_e = +1$ in this case.

For symmetric linear molecules with groups of symmetric atoms such as HC-CH(C_2H_2), CN-NC(C_2N_2), and DC-CD(C_2D_2), Eq. (4.118) is modified to (Ref. 10, p. 17):

$$\underset{\text{(symmetric)}}{f_I(J_m, s_m)} = \left[\left(\frac{g_I^a}{g_I^s + g_I^a} \right) \delta \left\{ 1 + (-1)^{(J_m + s_m)} \right\} + \left(\frac{g_I^s}{g_I^s + g_I^a} \right) \delta \left\{ 1 + (-1)^{(J_m + s_m + 1)} \right\} \right] \tag{4.122}$$

where:

$$g_I^s = \frac{1}{2} \left[\prod_X (2I_X + 1)^2 + \prod_X (2I_X + 1) \right] \tag{4.123}$$

---

*One usually uses the term "infrared-active" instead of "photon-active" meaning that the dipole moment for a vibrational transition is not zero. Because the photon is not always in the infrared we prefer the term "photon active."

and:

$$g_I^a = \frac{1}{2}\left[\prod_X (2I_X + 1)^2 - \prod_X (2I_X + 1)\right] \quad , \tag{4.124}$$

Here the subscript X takes on the values X = A, B, C.... in which A, B, C,.... are the nuclei in the group of atoms that cause the symmetry, that is X = H, C for C_2H_2 for example. The parameter s_m in (4.122) is again given by (4.119). The parity s_I in this case is however instead of (4.120) given by:

$$s_I = \prod_X (-1)^{2I_X} \tag{4.125}$$

Note that Eqs. (4.122) and (4.125) reduce to (4.118) and (4.120) if the two symmetric atomic groups contains only one atom each.

The result of the nuclear-spin weighting modifications just described will of course also change the probabilities (4.101) through (4.106) to:

(P+R) Case

$$p_P(J_m, J_n = J_m + 1) = \left(\frac{2J_m + 3}{2(2J_m + 1)}\right) f_I(J_m + 1, s_n) \tag{4.126}$$

$$p_R(J_m, J_n = J_m - 1) = \left(\frac{2J_m - 1}{2(2J_m + 1)}\right) f_I(J_m - 1, s_n) \tag{4.127}$$

(P+Q+R) Case

$$p_P(J_m, J_n = J_m + 1) = \left(\frac{2J_m + 3}{3(2J_m + 1)}\right) f_I(J_m + 1, s_n) \tag{4.128}$$

$$p_Q(J_m, J_n{=}J_m) = \frac{1}{3} f_I(J_m, s_n) \tag{4.129}$$

$$p_R(J_m, J_n{=}J_m-1) = \left(\frac{2J_m - 1}{3(2J_m+1)}\right) f_I(J_m-1, s_n) \tag{4.130}$$

From (4.122) it follows that $f_I(J_m+1) = f_I(J_m-1)$. Then using Eqs. (4.122) through (4.124) and defining:

$$f_I^{PR} = f_I(J_m-1, s_n) = f_I(J_m+1, s_n) = \frac{1}{2}\Big[(1 - \theta_I)\,\delta\Big\{1 + (-1)^{(J_m+s_n+1)}\Big\} + (1 + \theta_I)\,\delta\Big\{1 + (-1)^{(J_m+s_n)}\Big\}\Big] \,. \tag{4.131}$$

$$f_I^{Q} = f_I(J_n, s_n) = f_I(J_m, s_n) = \frac{1}{2}\Big[(1 - \theta_I)\,\delta\Big\{1 + (-1)^{(J_m+s_n)}\Big\} + (1 + \theta_I)\,\delta\Big\{1 + (-1)^{(J_m+s_n+1)}\Big\}\Big] \,, \tag{4.132}$$

where:

$$\theta_I = \Big\{\prod_X (2I_X + 1)\Big\} \Big/ \Big\{\prod_X (2I_X + 1)^2\Big\} \,, \tag{4.133}$$

it is clear that for symmetric molecules the factors f_d in Eqs. (4.115) through (4.117) must be multiplied by f_I^{PR} for the P- and R-Branches and by f_I^{Q} for the Q-Branch.

Note from the above relations that for molecules such as CO_2 where $I = I(0) = 0$, the parameter $\theta_I = 1$ so that the factor $f_I(J_m = \text{odd}, s_n = 0) = 0$ as well as $f_I(J_m = \text{even}, s_n = 1) = 0$. Thus alternate rotational lines are completely missing in these cases. For C_2H_2 on the other hand $I = 1/2$ and $\theta_I = 1/2$, so that alternate lines have "nuclear weights" $f_I = \frac{1}{4}$ and $f_I = \frac{3}{4}$ which is confirmed experimentally in Figure 4-3. In general the nuclear spin effect causes an intensity fluctuation of alternate lines. It is clear from this that for smeared-out bands which will be discussed below we may set the average f_I factor equal to $\frac{1}{2}$ for symmetric molecules, since always:

$$\bar{f}_I = \left[\frac{1}{2}(1-\theta_I) + \frac{1}{2}(1+\theta_I)\right]\Big/2 = \frac{1}{2} \tag{4.134a}$$

For nonsymmetric linear molecules on the other hand:

$$\bar{f}_I = 1 \tag{4.134b}$$

It should be emphasized that the f_I factors only apply to completely isotopically-symmetric molecules. Thus for the molecules $O^{16}CO^{18}$, $O^{16}CO^{17}$, DCCH, all rotational levels are equally probable as far as nuclear spin statistics is concerned. Only molecules such as $O^{16}CO^{16}$, $O^{18}CO^{18}$, $O^{17}CO^{17}$, HCCH, and DCCD have variations in weight of alternate rotational levels due to nuclear statistics effects.

For all diatomic molecules, and for all polyatomic linear molecules in which no degenerate vibration is actively participating (i.e., $\ell_m = \ell_n = 0$), only the P- and R-Branch emission can occur in vibrational transitions. We shall therefore first limit our further discussion to this (P+R) case, returning to the (P+Q+R) case in subsection 4.1.7.2.

4.7.1.1 Bands With Only P- and R-Branches

For the (P+R) case, we have according to (4.111) that $f_d = \frac{1}{2}$ in Eqs. (4.115) and (4.117), while the factor f_I^{PR} must be added for symmetric molecules. We shall add this factor in what follows for completeness with the understanding that it equals unity in all cases except when symmetric molecules are considered. Setting for simplicity $J = J_m$ in (4.115) and (4.117), these equations then read:

$$\underset{(J=0,1,2,3,\ldots)}{g_v^P(J)} = \left(\frac{J + 3/2}{2\nu_B Z_r}\right) f_I^{PR} \exp-\left\{\frac{J(J+1)\, h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1} \qquad (4.135)$$

$$\underset{(J=1,2,3,4,\ldots)}{g_v^R(J)} = \left(\frac{J - 1/2}{2\nu_B Z_r}\right) f_I^{PR} \exp-\left\{\frac{J(J+1)\, h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1}, \qquad (4.136)$$

where $J = 1,2,3,4,\ldots$ for both branches and in addition $J = 0$ for the P-Branch.

Inspection of the vibrational bands displayed in Figure 4-3 clearly show the near-symmetry but distinct difference between the P- and R-Branch line intensities as indicated by Eqs. (4.135) and (4.136). If we assume typical values of $\nu_B = 1\ \mathrm{cm}^{-1}$, $T = 300\ ^\circ\mathrm{K}$, and $Z_r \approx 1$, we get for the intensities in the P- and R-Branches the values shown in Table 4-4, according to these equations.

TABLE 4-4. TYPICAL P- AND R-BRANCH INTENSITIES

(ν_B = 1 cm^{-1} ; T = 300 °K ; Z_r = 1)

J_m	P-Branch Line	R-Branch Line	g_{ν_P} $(\mathrm{cm}^{-1})^{-1}$	g_{ν_R} $(\mathrm{cm}^{-1})^{-1}$
0	P-1	–	0.75	–
1	P-2	R-1	1.24	0.25
2	P-3	R-2	1.70	0.73
3	P-4	R-3	2.12	1.18
4	P-5	R-4	2.50	1.59

A comparison of the relative intensities of for example the CO (ν_B = 1.93 cm^{-1}) and N_2O (ν_B = 0.42 cm^{-1}) lines in Figure 4-3 with the values listed in Table 4-4 shows good agreement.

If one wishes to determine the band contour and its width or spread, or if one desires to calculate the average absorption or emission in applications where the lines cannot be resolved, it is convenient to assume that the lines are smeared-out continuously over the bands. To do this we let J become a continuous variable, so that the functions $g_\nu^P(J)$ and $g_\nu^R(J)$ become continuous. Of course ν is also continuous now according to Eqs. (4.89) and (4.91). J will run here from 0 to ∞ for the P-Branch and from 1 to ∞ for the R-Branch.

In the smearing-out process we also have that $f_I^{PR} \rightarrow \bar{f}_I$ given by Eq. (4.134), and we shall let $Z_r \rightarrow Z_r'$ since in changing from a discontinuous population density per state J to a continuous one, the normalizing constant Z_r given by Eq. (4.84) may change.

Now in what follows we want to express ν in terms of J and thus we have to invert Eqs. (4.89) through (4.91). For the P- and R-Branches, we have:

P-Branch

$$J = J_m = -\frac{1}{2}\left(\frac{\nu - \nu_{mn} + 2\nu_B}{\nu_B}\right) = -\frac{1}{2}\left(\frac{\nu - \nu_{mn}}{\nu_B}\right) - 1 \qquad (4.137)^*$$

R-Branch

$$J = J_m = \frac{1}{2}\left(\frac{\nu - \nu_{mn}}{\nu_B}\right) \qquad (4.138)^*$$

According to these relations a differential change in the continuously-varying photon frequency ν is related to a differential change in the (continuous) parameter J by:

P-Branch

$$\frac{d\nu}{dJ} = -2\nu_B \text{ Hz/Line} \qquad (4.139)^*$$

R-Branch

$$\frac{d\nu}{dJ} = +2\nu_B \text{ Hz/Line} \qquad (4.140)^*$$

---

*For linear symmetric molecules such as CO_2 and CS_2, $J = 0,2,4,6,\ldots \rightarrow J^{eff} = 0,1,2,\ldots$, and $\nu_B \rightarrow \nu_B^{eff} = 2\nu_B$, so that $d\nu/dJ^{eff} = \pm 4\nu_B$ Hz/line.

Using Eqs. (4.4), (4.135), (4.136), (4.139), and (4.140), we can now calculate the constant Z'_r:

$$Z'_r = \int_{\nu=0}^{\infty} Z'_r \left\{ g_\nu^P(J) + g_\nu^R(J) \right\} d\nu = -\int_{J=\infty}^{0} \bar{f}_I \left(J + \frac{3}{2}\right) \left[\exp - \left\{ \frac{J(J+1)\ h\nu_B}{kT} \right\} \right] dJ \; +$$

$$+ \int_{J=1}^{\infty} \bar{f}_I \left(J - \frac{1}{2}\right) \left[\exp - \left\{ \frac{J(J+1)\ h\nu_B}{kT} \right\} \right] dJ =$$

$$= \frac{1}{2} \bar{f}_I \left[\frac{kT}{h\nu_B} + \left\{ \exp\left(\frac{h\nu_B}{4kT} \right) \right\} \left\{ \left(\frac{\pi kT}{h\nu_B} \right)^{1/2} - 1 \right\} \right] +$$

$$+ \frac{1}{2} \bar{f}_I \left[\frac{kT}{h\nu_B} \left\{ \exp - \left(\frac{2\ h\nu_B}{kT} \right) \right\} + \sqrt{2} - \frac{1}{2} \left(\frac{\pi kT}{h\nu_B} \right)^{1/2} \right] \approx$$

$$Z'_r = \bar{f}_I \left[\frac{kT}{h\nu_B} + \frac{1}{2} \left(\frac{\pi kT}{h\nu_B} \right)^{1/2} + 0.4142 \right] = \bar{f}_I \left[\frac{kT}{h\nu_B} \left\{ 1 + \left(\frac{\pi h\nu_B}{4kT} \right)^{1/2} \right\} + 0.4142 \right] \tag{4.141}$$

where, as is almost always the case, we assumed that $\exp-(h\nu_B/kT) \approx 1$ because $h\nu_B << kT$. Often this also means that we can further approximate Z'_r by ignoring the last two terms in (4.141), setting:

$$Z'_r \approx \bar{f}_I \left(\frac{kT}{h\nu_B} \right) \tag{4.142}$$

This expression (except for the factor $\bar{f}_I$) is identical to the first-order approximation to (4.84) and thus approximately:

$$Z_r' \approx Z_r \tag{4.143}$$

With Eq. (4.142), Eqs. (4.135) and (4.136) which are now continuous (with $f_I^{PR} \to \bar{f}_I$ and $Z_r \to Z_r'$) become:

$$g_v^P(J) = \left(\frac{J + 3/2}{2\ kT/h}\right) \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1} \qquad (0 \le J < \infty) \tag{4.144}$$

$$g_v^R(J) = \left(\frac{J - 1/2}{2\ kT/h}\right) \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1}, \qquad (1 \le J < \infty) \tag{4.145}$$

or in terms of the photon frequency ν, using Eqs. (4.137) and (4.138):

$$g_v^P(\nu) = \left(\frac{\nu_{mn} + \nu_B - \nu}{4\nu_B\ kT/h}\right) \exp-\left\{\frac{(\nu_{mn} - \nu)(\nu_{mn} - 2\nu_B - \nu)}{4\nu_B\ kT/h}\right\}, \ \mathrm{Hz}^{-1} \qquad 0 < \nu \le (\nu_{mn} - 2\nu_B) \tag{4.146*}$$

$$g_v^R(\nu) = \left(\frac{\nu - \nu_{mn} - \nu_B}{4\nu_B\ kT/h}\right) \exp-\left\{\frac{(\nu - \nu_{mn})(\nu - \nu_{mn} + 2\nu_B)}{4\nu_B\ kT/h}\right\}, \mathrm{Hz}^{-1} \qquad (\nu_{mn} + 2\nu_B) \le \nu < \infty \tag{4.147*}$$

Note that we can conveniently combine Eqs. (4.146) and (4.147) into the one expression:

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*For linear symmetric molecules such as CO_2 and CS_2, $\frac{1}{2}(\nu - \nu_{mn})$ should be substituted for $(\nu - \nu_{mn})$ in these continuous expressions (see footnote on p. 211).

$$\boxed{\begin{aligned} & \underset{0<\nu<\infty}{g_\nu^{PR}(\nu)} = \left(\frac{|\nu - \nu_{mn} - \nu_B|}{4\nu_B\ kT/h}\right) \exp-\left\{\frac{(\nu - \nu_{mn})(\nu - \nu_{mn} + 2\nu_B)}{4\nu_B\ kT/h}\right\} \cdot \\ & \qquad \cdot H\left(\left|\ |\nu - \nu_{mn}| - 2\nu_B\ \right|\right)\ ,\ \mathrm{Hz}^{-1} \end{aligned}} \qquad (4.148)^*$$

Here H(x) is the unit step function, the integral of the delta function $\delta(x)$:

$$H(x \geq 0) = 1 \quad ; \quad H(x < 0) = 0 \qquad (4.149a)$$

$$\delta(x = 0) = \left(\frac{dH(x)}{dx}\right)_{x=0} = 1 \ ; \ \delta(x \neq 0) = 0 \qquad (4.149b)$$

Equation (4.148) has thus a "symmetric hole" in the region $(\nu_{mn} - 2\nu_B) < \nu < (\nu_{mn} + 2\nu_B)$ where no photons are emitted.

Now in the smearing-out process, we should actually have "smeared" the first lines of the P- and R-Branches also over the frequency regions $(\nu_{mn} - 2\nu_B) < \nu < \nu_{mn}$ and $\nu_{mn} < \nu < (\nu_{mn} + 2\nu_B)$ instead of assuming that all radiation stops abruptly at the $(\nu_{mn} - 2\nu_B)$ and $(\nu_{mn} + 2\nu_B)$ points. To correct this, we must therefore change (4.148) (which is symmetric about $\nu = \nu_{mn}$), and rewrite it as:

$$\boxed{\underset{0<\nu<\infty}{g_\nu^{PR}(\nu)} = \left(\frac{|\nu - \nu_{mn}|}{4\nu_B\ kT/h}\right) \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B\ kT/h}\right\}\ ,\ \mathrm{Hz}^{-1}} \qquad (4.150)^*$$

Equation (4.150) still drops to 0 at $\nu = \nu_{mn}$, but is now correctly "smeared" over the frequency spectrum in the vicinity of $\nu = \nu_{mn}$. The small adjustment

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*See footnote on previous page.

$(\nu_B << \nu_{mn})$ we made has virtually no effect on the normalization constant Z_r' .

We next want to determine the spread $\Delta\nu_{mn}$ and line-shape function $b(\nu,\nu_{mn},\Delta\nu_{mn})$ by using Eqs. (4.5) through (4.7). However if we use (4.7) we run into a problem since $g(\nu = \nu_{mn}) = 0$. We therefore shall use a slightly different definition than (4.7) to avoid that $\Delta\nu_{mn} \to \infty$. We can do this as long as Eq. (4.6) is obeyed (see the footnote and discussion following Eq. (4.7)).

The linear factor $|\nu - \nu_{mn}|$ is on the order of $J\nu_B$ in (4.150) and except in the vicinity $\nu = \nu_{mn}$, it has only a secondary influence on the function $g_v^{PR}(\nu)$, the exponential term giving a much larger change for a given change in ν . We shall therefore ignore the linear term and define the band-spread to be:

$$\Delta\nu_{mn} \equiv \left[\frac{\exp-\left\{\dfrac{(\nu_{mn} - \nu_{mn})^2}{4\nu_B \; kT/h}\right\}}{\sqrt{4\nu_B \; kT/h}}\right]^{-1} =$$

$$\boxed{\begin{aligned}\Delta\nu_{mn} &= \sqrt{\frac{4\nu_B \; kT}{h}} = 2.89 \times 10^5 \underset{(Hz)(^\circ K)}{(\nu_B \quad T)}^{1/2} , \text{ Hz} = \\ &= 5.006 \times 10^{10} \underset{(cm^{-1})(^\circ K)}{(\nu_B \quad T)}^{1/2} , \quad \text{Hz}\end{aligned}} \qquad (4.151)^*$$

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*For linear symmetric CO_2 and CS_2 , this expression must be multiplied by $\sqrt{2}$; see footnote on p. 213.

Then since $g(\nu) = b(\nu)/\Delta\nu_{mn}$, we have from (4.150) that:

$$\boxed{b_v^{PR}(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{|\nu - \nu_{mn}|}{\Delta\nu_{mn}} \exp-\left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}}\right)^2} \qquad (4.152)^*$$

Also we have then, rewriting (4.150):

$$\boxed{g_v^{PR}(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{|\nu - \nu_{mn}|}{(\Delta\nu_{mn})^2} \exp-\left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}}\right)^2, \ \mathrm{Hz}^{-1}} \qquad (4.153)^*$$

Note also that Eqs. (4.8) and (4.9) still hold, even though we defined $\Delta\nu_{mn}$ differently from Eq. (4.7).

Equations (4.151) through (4.153) are in the desired form that we set out to get. We can use these equations now also to obtain expressions for the individual pressure- or temperature-broadened lines in the bands. We get for the detailed rovibrational spectral profile:

$$g_{rov}^{PR}(\nu,\nu_{mn},\Delta\nu_{mn}) = g_v^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\ g_J(\nu,\nu_J,\Delta\nu_J)\ \delta\nu_J =$$

$$= \frac{b_v^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\ b_J(\nu,\nu_J,\Delta\nu_J)}{\Delta\nu_{mn}\ \Delta\nu_J}\ \delta\nu_J\ ,\ \mathrm{Hz}^{-1}\ , \qquad (4.154)$$

Here the band-shape function $b_v^{PR}(\nu{=}\nu_J,\nu_{mn},\Delta\nu_{mn})$ is given by (4.152) and ν_J is the center frequency of each rotational line, given by (4.85) and (4.87), that is for respectively the P-Branch and R-Branch:

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*See footnote on p. 215.

$$\nu_J = \left(\nu_J\right)_P = \nu_{mn} - \left(\nu_{B_m} + \nu_{B_n}\right)(J+1) - \left(\nu_{B_n} - \nu_{B_m}\right)(J+1)^2, \quad (J=0,1,2,\ldots.) \qquad (4.155a)^*$$

$$\nu_J = \left(\nu_J\right)_R = \nu_{mn} + \left(\nu_{B_m} + \nu_{B_n}\right) J - \left(\nu_{B_n} - \nu_{B_m}\right) J^2, \quad (J=1,2,3,\ldots.) \qquad (4.155b)^*$$

If the lines do not overlap, the parameter $\delta\nu_J$ is the spacing between lines:

$$\delta\nu_J = \delta\nu_J' = \nu_{J+1} - \nu_J = \nu_{B_m} + \nu_{B_n} \approx 2\nu_B, \quad (\delta\nu_J' > \Delta\nu_J) \qquad (4.155c)^*$$

If on the other hand adjacent lines do overlap considerably:

$$\delta\nu_J = 2\nu_B \left[\int_{\nu=\nu_J - \frac{1}{2}\delta\nu_J'}^{\nu_J + \frac{1}{2}\delta\nu_J'} g_J(\nu,\nu_J,\Delta\nu_J)\, d\nu \right]^{-1}, \quad (\delta\nu_J' < \Delta\nu_J) \qquad (4.155d)^*$$

The line-broadening function $g_J(\nu,\nu_J,\Delta\nu_J)$ in (4.154) is in most applications either the collision- or doppler-broadening function given in sections 4.3 and 4.4, and $\Delta\nu_J$ is the corresponding line-spread for collision- or doppler-broadening. That is $g_J(\nu,\nu_J,\Delta\nu_J) = g_C(\nu,\nu_J,\Delta\nu_C)$ and $\Delta\nu_J = \Delta\nu_C$ given by Eqs. (4.50) and (4.47) or $g_J(\nu,\nu_J,\Delta\nu_J) = g_D(\nu,\nu_J,\Delta\nu_D)$ and $\Delta\nu_J = \Delta\nu_D$ given by (4.41) through (4.43).

To prove that (4.154) is correct, we first integrate over one line:

$$\int_{\nu=\nu_J - \frac{1}{2}\Delta\nu_J}^{\nu_J + \frac{1}{2}\Delta\nu_J} \left\{ g_J(\nu,\nu_J,\Delta\nu_J)\, d\nu \right\} \left\{ g_V^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\,\delta\nu_J \right\} = g_V^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\,\delta\nu_J$$

(4.156a)

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*For symmetric linear molecules like CO_2, $J = 2, 4, 6, \ldots..$ only, and $2\nu_B \rightarrow 4\nu_B$ in the expressions for $\delta\nu_J$ and $\delta\nu_J'$.

Summing next over all lines J, we get:

$$\sum_{J=0}^{\infty} g_v^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\,\delta\nu_J \rightarrow \int_{\nu=0}^{\infty} g_v^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})\,d\nu = 1 \qquad (4.156b)$$

Instead of using Eq. (4.152) in Eq. (4.154), we can improve the accuracy of the latter relation by using the original expressions (4.135) and (4.136) from which (4.152) was derived together with (4.142), (4.143), and (4.151):

$$b_v^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn}) = \Delta\nu_{mn}\, g_v^{PR}(\nu_J,\nu_{mn},\Delta\nu_{mn}) =$$

$$= \Delta\nu_{mn}\left\{g_v^{P}(J) + g_v^{R}(J)\right\} = b_v^{PR}(J,\nu_{mn},\Delta\nu_{mn}) =$$

$$= w_I^{PR}(J)\left(\frac{4\nu_B\ kT}{h}\right)^{1/2}\left[\left(\frac{J+3/2}{2\ kT/h}\right)\left\{\exp-\left(\frac{J(J+1)\ h\nu_B}{kT}\right)\right\} H(\nu_{mn}-\nu_J)\cdot H(J) +\right.$$

$$\left. + \left(\frac{J-1/2}{2\ kT/h}\right)\left\{\exp-\left(\frac{J(J+1)\ h\nu_B}{kT}\right)\right\} H(\nu_J-\nu_{mn})\cdot H(J-1)\right] =$$

$$\boxed{\begin{aligned} b_v^{PR}(J,\nu_{mn},\Delta\nu_{mn}) &= w_I^{PR}(J)\left(\frac{h\nu_B}{kT}\right)^{1/2}\left\{\exp-\left(\frac{J(J+1)\ h\nu_B}{kT}\right)\right\}\cdot \\ &\cdot\left[\left(J+\frac{3}{2}\right)H(\nu_{mn}-\nu_J)\ H(J) + \left(J-\frac{1}{2}\right)H(\nu_J-\nu_{mn})\ H(J-1)\right]\end{aligned}} \qquad (4.157)$$

Here the nuclear-spin-effect factor w_I^{PR} is defined by:

$$w_I^{PR}(J) = \frac{f_I^{PR}}{\bar{f}_I} = \left[(1 - \theta_I)\, \delta \left\{ 1 + (-1)^{(J+S_n+1)} \right\} + \right.$$

$$\left. + (1 + \theta_I)\, \delta \left\{ 1 + (-1)^{(J+S_n)} \right\} \right], \text{ for}$$

$$\text{symmetric linear molecules} \qquad (4.158a)$$

$$w_I^{PR}(J) = 1 \text{ , for nonsymmetric linear molecules} \qquad (4.158b)$$

In Eq. (4.158), $\delta(x)$ is the Dirac delta function, while $H(x)$ in (4.157) is the Heaviside unit step function defined by (4.149). The factors $H(\nu_{mn} - \nu)\, H(J)$ and $H(\nu - \nu_{mn})\, H(J+1)$ in Eq. (4.157) insure that either the P-Branch factor $(J + \frac{3}{2})$ applies with $J = 0,1,2,\ldots,$ or the R-Branch factor $(J - \frac{1}{2})$ with $J = 1,2,3, \ldots,$ but not both simultaneously.

We shall distinguish between the approximate expression $b_v^{PR}(\nu_J, \nu_{mn}, \Delta\nu_{mn})$ given by Eq. (4.152) with ν_J substituted for ν , and the more exact expression (4.157) by writing the latter as $b_v^{PR}(J, \nu_{mn}, \Delta\nu_{mn})$, that is with J shown as a parameter instead of ν_J . Then the exact contour function for the rovibrational band lines is instead of (4.154) expressed by the formal relation:

$$\boxed{g_{rov}(\nu, \nu_{mn}, \Delta\nu_{mn}) = g_v^{PR}(J, \nu_{mn}, \Delta\nu_{mn})\, g_J(\nu, \nu_J, \Delta\nu_J)\, \delta\nu_J \text{ , Hz}^{-1}} \qquad (4.159)$$

Equation (4.159) is very useful in applied work and gives a continuous expression for the actual line intensities in a vibrational band as a function of the continuously-varying photon frequency ν . It follows the spectral profiles shown in Figure 4-3 rather well.

4.7.1.2 Bands With P-, Q-, and R-Branches

In case all three branches are allowed, we have from (4.115) through (4.117) and (4.112), that:

$$g_\nu^P(J) = \frac{J + 3/2}{3\nu_B Z_r} f_I^{PR} \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\} , \text{ Hz}^{-1} \tag{4.160}$$

$$g_\nu^Q(J) = \frac{(J + 1/2)\ f_I^Q}{3(J+1)|\Delta\nu_B|Z_r} \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\} , \text{ Hz}^{-1} \tag{4.161}$$

$$g_\nu^R(J) = \frac{J - 1/2}{3\nu_B Z_r} f_I^{PR} \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\} , \text{ Hz}^{-1} \tag{4.162}$$

where again $J = J_m = 1,2,3,\ldots.$ for all branches and in addition $J = 0$ for the P-Branch, and where the f_I factors are equal to 1 unless a symmetry exists. If we now let J become continuous, we must let as before f_I^{PR} and $f_I^Q \rightarrow \bar{f}_I$ and $Z_r \rightarrow Z_r'$. Further we need in addition to Eqs. (4.137) through (4.140) similar relations for the Q-Branch. Thus inverting Eq. (4.90), we have the relations:

Q-Branch

$$J = J_m = J_n = \frac{1}{2}\left[\sqrt{1 + 4\left\{\frac{\nu_{mn} - \nu - \nu_B^Q}{\Delta\nu_B}\right\}} - 1\right] \qquad (4.163)^*$$

$$J(J+1) = J_m(J_m+1) = J_n(J_n+1) = \frac{\nu_{mn} - \nu - \nu_B^Q}{\Delta\nu_B} \qquad (4.164)^*$$

$$d\nu = \Delta\nu_B\,(2J+1)\,dJ \qquad (4.165)^*$$

Here $\Delta\nu_B$ and ν_B^Q were given by Eqs. (4.93) and (4.92), and ℓ_m by Eq. (3.117) (in most transitions of interest $\ell_m = 1$ and $\ell_n = 0$).

Calculating Z_r', we have as before:

$$Z_r' = \int_{\nu=0}^{\infty} Z_r'\left\{g_v^P(J) + g_v^Q(J) + g_v^R(J)\right\}d\nu = \frac{2}{3}\,\bar{f}_I\left[\frac{kT}{h\nu_B}\left\{1 + \left(\frac{\pi h\nu_B}{4kT}\right)^{1/2}\right\} + 0.4142\right] +$$

$$+ \frac{\bar{f}_I}{3}\int_{J=1}^{\infty}\left(\frac{2J+1}{2J+2}\right)(2J+1)\left[\exp-\left(\frac{J(J+1)}{kT/(h\nu_B)}\right)\right]dJ \approx \bar{f}_I\,\frac{kT}{h\nu_B} \qquad (4.166)$$

Here we set $(2J+1)/(2J+2) \approx 1$ for the integration over J from $J = 1$ to $J = \infty$ for the Q-Branch, and we set $\exp-\left(\frac{2h\nu}{kT}\right) \approx 1$ as before because $(h\nu_B) << kT$. The integration over $g_v^P(J)$ and $g_v^R(J)$ is the same as for Eq. (4.141) except for the factor 2/3. From (4.166) we see that again $Z_r' \approx Z_r$ as in the (P+R) case.

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*For linear symmetric molecules such as CO_2 and CS_2, $J = 0,2,4,\ldots \rightarrow J^{eff} = 0,1,2,\ldots$ and $\Delta\nu_B \rightarrow \Delta\nu_B^{eff} = 2\,\Delta\nu_B$.

With (4.166), Eqs. (4.160) through (4.162) become:

$$\underset{(0 \le J < \infty)}{g_v^P(J)} = \left(\frac{J + 3/2}{3kT/h}\right) \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1} \tag{4.167}$$

$$\underset{(1 \le J < \infty)}{g_v^Q(J)} = \left(\frac{J + 1/2}{3\xi_B(J+1)\ kT/h}\right) \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1} \tag{4.168}$$

$$\underset{(1 \le J < \infty)}{g_v^R(J)} = \left(\frac{J - 1/2}{3kT/h}\right) \exp-\left\{\frac{J(J+1)\ h\nu_B}{kT}\right\}, \ \mathrm{Hz}^{-1} \tag{4.169}$$

Here ξ_B is defined by:

$$\xi_B = |\Delta\nu_B|/\nu_B = \frac{\left|\nu_{B_n} - \nu_{B_m}\right|}{\frac{1}{2}\left(\nu_{B_m} + \nu_{\ n}\right)} = \frac{\left|\sum_\beta \alpha_\beta\left(\nu_{\beta_m} - \nu_{\beta_n}\right)\right|}{\frac{1}{2}\left(\nu_{B_m} + \nu_{B_n}\right)} \tag{4.170}$$

Substituting next for the frequency ν via Eqs. (4.137) and (4.138), and letting ν run to ν_{mn} as discussed in connection with Eq. (4.150), we get for the P- and R-Branch:

$$\boxed{\underset{0 < \nu < \infty}{g_v^{PR}(\nu)} = \left(\frac{|\nu - \nu_{mn}|}{6\nu_B kT/h}\right) \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B kT/h}\right\}, \ \mathrm{Hz}^{-1} \qquad (4.171)^*}$$

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*See footnote on p. 213.

Similarly using (4.164), we obtain for the Q-Branch:

$$\boxed{\begin{array}{l} g_v^Q(\nu) \quad = \left(\frac{h}{3\xi_B kT}\right) \exp-\left\{\frac{|\nu_{mn} - \nu - \nu_B^Q|}{\xi_B kT/h}\right\}, \mathrm{Hz}^{-1} \\ (\nu_{mn}-\nu_3^Q) \le \nu < \infty, \text{ if } \Delta\nu_B < 0 \\ 0 < \nu \le (\nu_{mn}-\nu_B^Q), \text{ if } \Delta\nu_B > 0 \end{array}} \qquad (4.172)^*$$

Here ν_B^Q was given by Eq. (4.92), and we use the absolute sign on $(\nu_{mn}-\nu-\nu_B^Q)$ because of our definition for ξ_B (see Eq. (4.170)).

Defining the band-spread $\Delta\nu_{mn}$ and shape-function $b_v(\nu,\nu_{mn},\Delta\nu_{mn})$ again as we did for the (P+R) case, we find that:

$$\boxed{\Delta\nu_{mn} = \sqrt{4\nu_B \, kT/h}\,, \quad \mathrm{Hz}} \qquad (4.173)^*$$

$$\boxed{\begin{array}{ll} b_v^{PR}(\nu) & = \left[\frac{|\nu - \nu_{mn}|}{3\sqrt{\nu_B \, kT/h}}\right] \exp-\left\{\frac{h(\nu - \nu_{mn})^2}{4\nu_B \, kT}\right\}, \\ (0 \le \nu < \infty) & \end{array}} \qquad (4.174)^*$$

$$\boxed{\begin{array}{l} b_v^Q(\nu) \quad = \frac{2}{3\xi_B}\left(\frac{h\nu_B}{kT}\right)^{1/2} \exp-\left\{\frac{h|\nu_{mn}-\nu-\nu_B^Q|}{\xi_B kT}\right\}, \\ 0 < \nu \le (\nu_{mn}-\nu_B^Q), \text{ if } \Delta\nu_B > 0 \\ (\nu_{mn}-\nu_B^Q) \le \nu < \infty, \text{ if } \Delta\nu_B < 0 \end{array}} \qquad (4.175)^*$$

or in terms of $\Delta\nu_{mn}$:

---

*For linear symmetric CO_2 and CS_2 , $|\nu - \nu_{mn}| \rightarrow \frac{1}{2} \, |\nu - \nu_{mn}|$ in (4.172), (4.174), and (4.175). Also $\Delta\nu_{mn} = \sqrt{8\nu_B kT/h}$ in (4.173) in this case (see footnote on p. 215).

$$\boxed{\begin{array}{ll} \underset{(0 \leq \nu < \infty)}{b_{\nu}^{PR}(\nu)} = \dfrac{2}{3}\left(\dfrac{|\nu-\nu_{mn}|}{\Delta\nu_{mn}}\right)\ \exp-\left(\dfrac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2 \end{array}} \qquad (4.176)^*$$

$$\boxed{\begin{array}{l} b_{\nu}^{Q}(\nu) = \left(\dfrac{4\nu_B}{3\xi_B\Delta\nu_{mn}}\right)\ \exp-\left\{\dfrac{4\nu_B|\nu_{mn}-\nu-\nu_B^Q|}{\xi_B\Delta\nu_{mn}^2}\right\} \\ (0 < \nu \leq (\nu_{mn}-\nu_B^Q),\ \text{if } \Delta\nu_B > 0) \\ ((\nu_{mn}-\nu_B^Q) \leq \nu < \infty,\ \text{if } \Delta\nu_B < 0) \end{array}} \qquad (4.177)^*$$

Note that in Eqs. (4.175) and (4.177), $\nu \geq \nu_{mn}-\nu_B^Q$ or $\nu \leq \nu_{mn}-\nu_B^Q$ depending on whether $\Delta\nu_B > 0$ or $\Delta\nu_B < 0$.

Again like in the (P+R) case, we can write for the detailed rovibrational structure:

$$g_{rov}^{PQR}(\nu,\nu_{mn},\Delta\nu_{mn}) = h_{\nu}^{PQR}(\nu_J,\nu_{mn},\Delta\nu_{mn})\ g_J(\nu,\nu_J,\Delta\nu_J)\ ,\ \text{Hz}^{-1}\ , \qquad (4.178)$$

where:

$$h_{\nu}^{PQR}(\nu_J,\nu_{mn},\Delta\nu_{mn}) = \frac{2}{3}\left(\frac{\nu_{mn}-\nu_J}{\Delta\nu_{mn}^2}\right)\left[\exp-\left(\frac{\nu_J-\nu_{mn}}{\Delta\nu_{mn}}\right)^2\right]\delta\nu_J\ H(\nu_{mn}-\nu_J)H(-\nu_J^Q)\ +$$

$$+\ \frac{2}{3}\left(\frac{\nu_J-\nu_{mn}}{\Delta\nu_{mn}^2}\right)\left[\exp-\left(\frac{\nu_J-\nu_{mn}}{\Delta\nu_{mn}}\right)^2\right]\delta\nu_J\ H(\nu_J-\nu_{mn})H(-\nu_J^Q)\ +$$

$$+\ \left(\frac{4\nu_B}{3\xi_B\Delta\nu_{mn}^2}\right)\left[\exp-\left\{\frac{4\nu_B|\nu_{mn}-\nu_J^Q-\nu_B^Q|}{\xi_B\ \Delta\nu_{mn}^2}\right\}\right]\delta\nu_J^Q\ H(-\nu_J) \qquad (4.179)$$

Here ν_J and $\delta\nu_J$ are given by Eqs. (4.155a) through (4.155d) and ν_J^Q and $\delta\nu_J^Q$ by:

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*For CS_2 , CO_2 we have that $\Delta\nu_{mn} = \sqrt{8\nu_B kT/h}$ (see previous footnote).

$$\nu_J^Q = \nu_{mn} - \nu_B^Q - \Delta\nu_B\, J_Q(J_Q+1) \qquad (J_Q = 1,2,3,\ldots) \tag{4.180a}$$

$$\delta\nu_J^Q = (J+1)\Delta\nu_B \left[\int_{\nu=\nu_J^Q - \frac{1}{2}(J+1)\Delta\nu_B}^{\nu_J^Q + \frac{1}{2}(J+1)\Delta\nu_B} g_J(\nu,\nu_J,\Delta\nu_J)\,d\nu \right]^{-1} \approx \Delta\nu_J \text{ , if } \Delta\nu_B < \Delta\nu_J \tag{4.180b}$$

Instead of employing (4.179) in (4.178), we can again improve by using the original relations (4.160) through (4.162), replacing (4.179) by:

$$\boxed{\begin{aligned} h_\nu^{PQR}(J,\nu_{mn},\Delta\nu_{mn}) = {} & \frac{2}{3}\left(\frac{h\nu_B}{kT}\right)^{1/2} \left\{\exp-\left(\frac{J(J+1)\ h\nu_B}{kT}\right)\right\} \cdot \Bigg[H(-\nu_J^Q) \cdot \\ & \cdot w_I^{PR}(J) \left\{ \left(J+\frac{3}{2}\right) H(\nu_{mn}-\nu_J)\,\frac{\delta\nu_J}{\Delta\nu_{mn}}\,H(J) + \left(J-\frac{1}{2}\right) H(\nu_J-\nu_{mn})\,\frac{\delta\nu_J}{\Delta\nu_{mn}} \right. \\ & \left. \cdot\, H(J-1) \right\} + H(-\nu_J)\ w_I^Q(J_Q) \left(\frac{J_Q + 1/2}{\xi_B(J_Q+1)}\right) \frac{\delta\nu_J^Q}{\Delta\nu_{mn}}\,H(J_Q-1) \Bigg] \end{aligned}} \tag{4.181}$$

and thus:

$$\boxed{g_{rov}^{PQR}(\nu,\nu_{mn},\Delta\nu_{mn}) = h_\nu^{PQR}(J,\nu_{mn},\Delta\nu_{mn})\ g_J(\nu,\nu_J,\Delta\nu_J) \text{ , Hz}^{-1}} \tag{4.182}$$

The parameter $w_I^{PR}(J)$ in (4.181) is given by (4.158) again, and $w_I^Q(J_Q)$ by:

$$w_I^Q(J_Q) = \frac{f_I^Q}{\bar{f}_I} = (1-\theta_I)\ \delta\left\{1 + (-1)^{(J_Q+s_n)}\right\} + (1+\theta_I)\ \delta\left\{1 + (-1)^{(J_Q+1+s_n)}\right\},$$

$$\text{for symmetric linear molecules ,} \tag{4.183a}$$

$$w_I^Q(J_Q) = 1 \quad , \quad \text{for nonsymmetric linear molecules} \qquad (4.183b)$$

Here the nuclear spin parameter θ_I was defined by Eq. (4.133).

4.7.2 Symmetric-Top Rotors

For symmetric-top rotors we shall follow exactly the same steps as for linear molecules. The main difference is that the rotational energy levels now possess two rotational constants instead of one, that is in a rovibrational transition the emitted photon frequencies and the line spacings are (see Eq. (3.163)):

P-Branch (- sign) and R-Branch (+ sign)

$$\underset{(J = \sup(J_m, J_n))}{\nu_{JK}} = \nu_{mn} + \Delta\nu_o \pm 2\nu_B J - \Delta\nu_B J^2 - 2\Delta\nu_{A\zeta}|K| - (\Delta\nu_A - \Delta\nu_B)K^2 \qquad (4.184a)$$

Q-Branch

$$\underset{(J = J_m = J_n)}{\nu^Q_{JK}} = \nu_{mn} + \Delta\nu_o - \Delta\nu_B J(J+1) - 2\Delta\nu_{A\zeta}|K| - (\Delta\nu_A - \Delta\nu_B)K^2 \qquad (4.184b)$$

$$\delta\nu'_K = |\nu_{J,K+1} - \nu_{J,K}| = 2\Delta\nu_{A\zeta} + (2K+1)(\Delta\nu_A - \Delta\nu_B) \qquad (4.185a)$$

$$\delta\nu_K = \left[\int_{\nu=\nu_{JK} - \frac{1}{2}\delta\nu'_K}^{\nu_{JK} + \frac{1}{2}\delta\nu'_K} g_{J,K}(\nu, \nu_{JK}, \Delta\nu_{JK})\, d\nu\right]^{-1} \cdot \delta\nu'_K \qquad (4.185b)$$

Equation (4.185) will be discussed later in connection with Eq. (4.223). The constants $\Delta\nu_o$ and $\Delta\nu_{A\zeta}$ differ for the ⊥ and // bands (see section 3.4.3),* and are given by:

---

*The // and ⊥ bands involve transitions for which the vibrational dipole moment is parallel or perpendicular to the axis of the top, respectively.

(a) Perpendicular (⊥) Bands

$$\Delta\nu_o = 2\nu_{A_n}\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_n - \left(\nu_{A_n} - \nu_{B_n}\right), \quad \text{Hz} \qquad (4.186)$$

$$\Delta\nu_{A\zeta} = \nu_{A_m}\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_m - \nu_{A_n}\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_n \pm \left(\nu_{A_n} - \nu_{B_n}\right), \quad \text{Hz} \qquad (4.187)$$

(b) Parallel (//) Bands

$$\Delta\nu_o = 0 \qquad (4.188)$$

$$\Delta\nu_{A\zeta} = \nu_{A_m}\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_m - \nu_{A_n}\left(\sum_\beta \pm \ell_{\beta_i}\zeta_\beta\right)_n, \quad \text{Hz} \qquad (4.189)$$

The frequency ν_{mn} is the pure vibrational frequency change given again by Eq. (4.88), while the quantum number $K = J, J-1, .., +1, 0, -1, ..-J$ (see Eq. (3.144)), except that $K \neq 0$ for the Q-Branch of //-bands. For the // band $K = |K_m| = |K_n|$ that is $\Delta K = 0$, whereas for the ⊥-bands $|\Delta K| = 1$, and $K = \sup(|K_m|, |K_n|)$. The parameters ν_A, ν_B, $\Delta\nu_A$, $\Delta\nu_B$ are given by (see Eqs. (3.146) and (3.147)):

$$\nu_A = \frac{1}{2}\left(\nu_{A_m} + \nu_{A_n}\right) = \frac{c}{2}\left(A_m + A_n\right), \quad \text{Hz} \qquad (4.190)$$

$$\nu_B = \frac{1}{2}\left(\nu_{B_m} + \nu_{B_n}\right) = \frac{c}{2}\left(B_m + B_n\right), \quad \text{Hz} \qquad (4.191)$$

$$\Delta\nu_A = \nu_{A_n} - \nu_{A_m} = c(A_n - A_m) = c \sum_{\beta} \alpha_{\beta}^{A} \left(v_{\beta_m} - v_{\beta_n}\right) \text{ , Hz} \qquad (4.192)$$

$$\Delta\nu_B = \nu_{B_n} - \nu_{B_m} = c(B_n - B_m) = c \sum_{\beta} \alpha_{\beta}^{B} \left(v_{\beta_m} - v_{\beta_n}\right) \text{ , Hz} \qquad (4.193)$$

For each fixed value of K, there is a P-Branch, Q-Branch, and R-Branch according to (4.184) and (4.185). However the values of J for each sub-band of given K start from $J = K$ upwards, that is $J \geq K$ as illustrated in Figures 4-4 and 4-5. Also for the // bands there is no Q-Branch in the $K = 0$ sub-band. Whereas for a linear molecule the weight (2J+1) for a given value of J gave the number of states of equal energy, for a symmetric-top molecule this weight gives the number of sublevels of given J with different energies. With this difference, we can still use Eqs. (4.115) to (4.117), however in the modified form:

$$g_v^P(J_m) = \frac{(2J_m+3)\ H(J_m-|K_m|)\left\{2 - \delta(K_m)\right\}}{6\nu_B Z_r'} \exp-\left\{\frac{J_m(J_m+1)\ \nu_B + K_m^2(\nu_A-\nu_B)}{kT/h}\right\} \text{ , Hz}^{-1} \qquad (4.194)$$

$$g_v^Q(J_m) = \frac{(2J_m+1)\ H(J_m-|K_m|)\left\{2 - \delta(K_m)\right\}}{6(J_m+1)\,|\Delta\nu_B|\ Z_r'} \exp-\left\{\frac{J_m(J_m+1)\ \nu_B + K_m^2(\nu_A-\nu_B)}{kT/h}\right\} \text{ , Hz}^{-1} \qquad (4.195)$$

$$g_v^R(J_m) = \frac{(2J_m-1)\ H(J_m-|K_m|)\left\{2 - \delta(K_m)\right\}}{6\nu_B Z_r'} \exp-\left\{\frac{J_m(J_m+1)\ \nu_B + K_m^2(\nu_A-\nu_B)}{kT/h}\right\} \text{ , Hz}^{-1} \qquad (4.196)$$

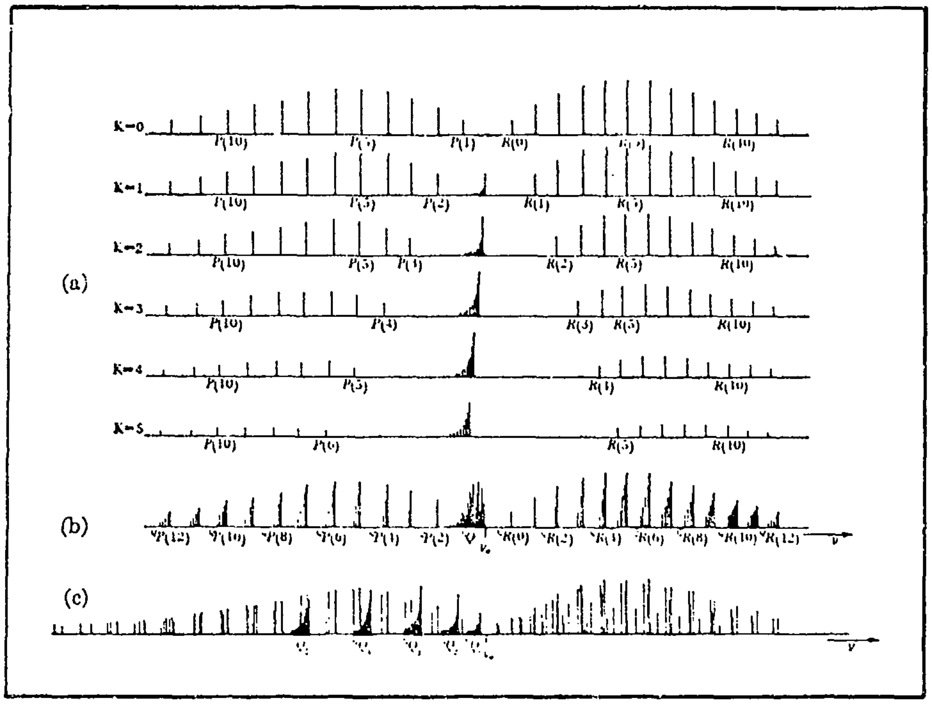

FIGURE 4-4. SUB-BANDS OF A // BAND AND COMPLETE // BAND OF A SYMMETRIC TOP. —— The sub-bands in (a) are directly superimposed in (b). In both (a) and (b) only a slight difference between $A_n - B_n$ and $A_m - B_m$ is assumed. In (c) the same sub-bands are superimposed but with shifts corresponding to a much larger difference between $A_n - B_n$ and $A_m - B_m$. Here also the lines of the Q branches have not been drawn separately. The heights of the lines indicate the intensities calculated on the basis of the assumption that $A_m = 5.25$, $B_m = 1.70\ \text{cm}^{-1}$, and $T = 144^\circ$ K. The intensities indicated for the sub-band K = 0 should be divided by 2. (After Ref. 10.)

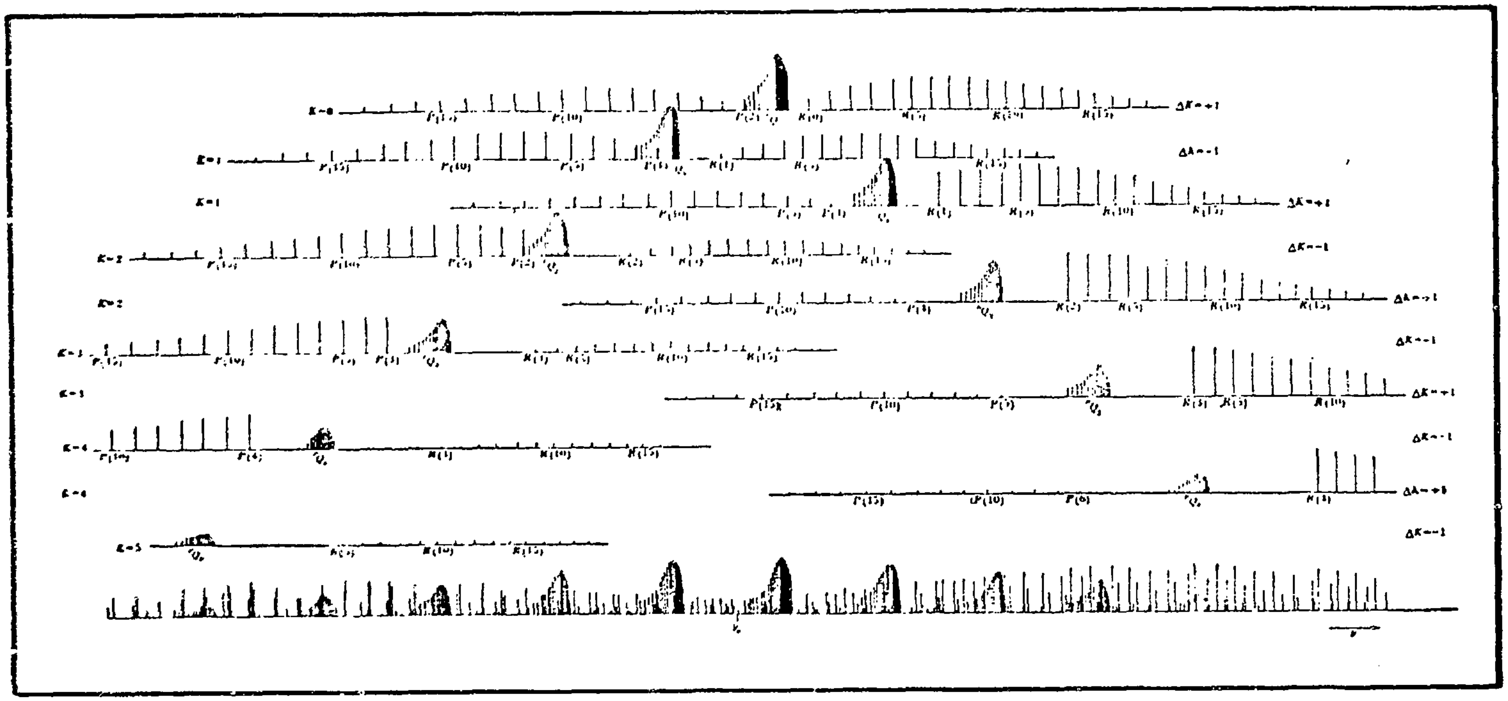

FIGURE 4-5. SUB-BANDS OF A ⊥ BAND OF A SYMMETRIC TOP. — The complete band is shown in the bottom strip. The spectrum is drawn under the assumption that $A' = 5.18$, $A'' = 5.25$, $B' = 0.84$, $B'' = 0.65$ cm^{-1} and $\zeta_i = 0$. The intensities were calculated for a temperature of 144° K. It should be realized that if the lines of an individual Q-Branch are not resolved the resulting "line" would stand out much more prominently than might appear from the spectrum given. (After Ref. 10)

Here we have primed Z_r since we shall assume that J_m (and thus K_m) can go over into a continuous variable as before, and we set the factor $f_d = 1/3$ since we always have three branches for a symmetric-top molecule.

Now like for linear molecules, there is for symmetric-top molecules such as pyramidal XY_3, XY_4, and XYZ_3 (where the Y or Z atoms are identical), also a nuclear-spin-statistics function $f_I(K,J)$ which will cause alternations in the intensity of rotational lines with different K belonging to a certain J. We shall not consider the functions $f_I(K,J)$ here however, since we are primarily interested in smeared-out bands for which the alternations in intensity when normalized by the "sum-over-states" factor Z_r' average out to 1. If individual (J,K) lines are of interest however, Eqs. (4.194) through (4.196) must be multiplied by $f_I(K,J)$ which may be obtained from Ref. 10, pp. 406-411, for particular molecules.

From Eqs. (4.184) and (4.185) we see that to first-order (ignoring second-order terms) and setting $J = J_m$ and $K = K_m$, we have for the P- and R-Branch that:

$$(d\nu)_{P,R} = \pm 2\nu_B \, dJ \, , \tag{4.197}$$

while for the Q-Branch:

$$(d\nu)_Q = - (2J+1) \, \Delta\nu_B \, dJ \tag{4.198}$$

To determine Z_r', we first integrate over J keeping $|K|$ fixed, remembering that for the P- and Q-Branches, increasing ν means decreasing J and for the R-Branch, increasing ν corresponds to increasing J:

$$Z_r'(|K|) = \int_{\nu = 0}^{\infty} Z_r' \left\{ g_\nu^P(J,K) + g_\nu^Q(J,K) + g_\nu^R(J,K) \right\} d\nu =$$

$$= \int_{J = |K|}^{\infty} \left\{ \frac{2J + 3}{3} + \frac{2J - 1}{3} + \frac{(2J+1)^2}{6(J+1)} \right\} \cdot$$

$$\cdot \left\{ \exp-\left(\frac{J(J+1)\, \nu_B + K^2\, (\nu_A - \nu_B)}{kT/h} \right) \right\} dJ =$$

$$= \left(\frac{kT}{h\nu_B} \right) \exp-\left(\frac{K^2\, \nu_A + |K|\, \nu_B}{kT/h} \right) \approx \left(\frac{kT}{h\nu_B} \right) \exp-\left(\frac{K^2\, \nu_A}{kT/h} \right) \qquad (4.199)$$

Here we set $\left[(2J+1)^2/6(J+1)\right] \approx (2J+1)/3$.

We next sum or integrate over all sub-bands K from $-\infty$ to $+\infty$:

$$Z_r' = \int_{|K| = -\infty}^{+\infty} Z_r'(|K|)\, dK = \int_{|K| = 0}^{\infty} 2\left(\frac{kT}{h\nu_B} \right) \left\{ \exp-\left(\frac{k^2\, \nu_A}{kT/h} \right) \right\} dK =$$

$$\boxed{Z_r' = \sqrt{\frac{\pi}{\nu_A\, \nu_B^2} \left(\frac{kT}{h} \right)^3}} \qquad (4.200)$$

The result (4.200) is the "classical partition function" for the symmetric-top rotor (Ref. 10), and is obtained if we approximate J(J+1) by J^2 in the exponential of (4.199). If we reverse the integrations of (4.199) and (4.200), and first integrate over $|K|$ and then over J, without the approximation $J(J+1) \approx J^2$ we get:

$$Z_r' = \int_{J=0}^{\infty} \int_{|K|=0}^{J} \left\{ \frac{2J+3}{3} + \frac{2J-1}{3} + \frac{2J+1}{3} \right\} \cdot$$

$$\cdot \left\{ \exp - \left(\frac{J(J+1)\ \nu_B + K^2\ (\nu_A - \nu_B)}{kT/h} \right) \right\} d\,|K|\ dJ =$$

$$= 2\int_{J=|K|}^{\infty} (2J+1)\ \exp - \left(\frac{J(J+1)\ \nu_B}{kT/h} \right) \cdot$$

$$\cdot \int_{|K|=0}^{J} \exp - \left(\frac{K^2\ (\nu_A - \nu_B)}{kT/h} \right) d|K|\ dJ = \left(\frac{\pi kT}{h(\nu_A - \nu_B)} \right)^{1/2} \cdot$$

$$\cdot \int_{J=0}^{\infty} \operatorname{erf} \left(\frac{J(\nu_A - \nu_B)^{1/2}}{(kT/h)^{1/2}} \right) (2J+1)\ \exp - \left(\frac{J(J+1)\ \nu_B}{kT/h} \right) dJ \approx$$

$$Z_r' = \sqrt{\frac{\pi}{\nu_B^2(\nu_A - \nu_B)} \left(\frac{kT}{h} \right)^3} \qquad (4.201)$$

Here we made the approximation that $\operatorname{erf}\left\{ J \sqrt{h(\nu_A - \nu_B)kT} \right\} \approx 1$ which is not bad, since erf (1) = 0.84 and erf (2) = 0.995, and the integration of J goes to infinity.

Comparing (4.201) with (4.200), we see that the two results differ by a factor $(\nu_A - \nu_B)^{1/2}$ versus $\nu_A^{1/2}$. If $\nu_A >> \nu_B$ as is usually the case, of course $(\nu_A - \nu_B)^{1/2} \approx \nu_A^{1/2}$ and the two calculations of Z_r' become equal.

It is not immediately obvious which of the two calculations is more accurate. In the "classical case" it is assumed that:

$$\exp-\left\{\frac{J(J+1)\ \nu_B}{kT/h}\right\} \underset{\sim}{\rightarrow} \exp-\left(\frac{J^2\ \nu_B}{kT/h}\right) \qquad (4.202)$$

while in the second case:

$$\mathrm{erf}\left(J\sqrt{\frac{\nu_A - \nu_B}{kT/h}}\right) \underset{\sim}{\rightarrow} 1 \qquad (4.203)$$

Both approximations are good for large values of J but for J → 0 , approximation (4.202) goes to 1 as it should, whereas approximation (4.203) is 1 while it should equal 0. We shall therefore assume that the "classical" result (4.200) is the more accurate value to be used for Z_r' .

With (4.200), Eqs. (4.194) through (4.196) become:

$$\underset{(0 \le J < \infty)}{g_v^P(J)} = \frac{(2J+3)\ \nu_A^{1/2}\ H(J-|K|)\left\{2 - \delta(K)\right\}}{6\pi^{1/2}\ (kT/h)^{3/2}} \exp-\left\{\frac{J(J+1)\ \nu_B + K^2(\nu_A-\nu_B)}{kT/h}\right\}, \ \mathrm{Hz}^{-1} \qquad (4.204)$$

$$\underset{(1 \le J < \infty)}{g_\nu^Q(J)} = \frac{(2J+1)\ \nu_A^{1/2}\ H(J-|K|)\left\{2 - \delta(K)\right\}}{6(J+1)\ \pi^{1/2}\ \xi_B (kT/h)^{3/2}}\ \exp-\left\{\frac{J(J+1)\ \nu_B + K^2(\nu_A-\nu_B)}{kT/h}\right\}, \ \mathrm{Hz}^{-1} \tag{4.205}$$

$$\underset{(1 \le J < \infty)}{g_\nu^R(J)} = \frac{(2J-1)\ \nu_A^{1/2}\ H(J-|K|)\left\{2 - \delta(K)\right\}}{6\pi^{1/2}\ (kT/h)^{3/2}}\ \exp-\left\{\frac{J(J+1)\ \nu_B + K^2(\nu_A-\nu_B)}{kT/h}\right\}, \ \mathrm{Hz}^{-1} \tag{4.206}$$

where:

$$\xi_B = \frac{|\Delta\nu_B|}{\nu_B} = \frac{\left|\sum_\beta \alpha_\beta^B \left(\nu_{\beta_m} - \nu_{\beta_n}\right)\right|}{\nu_B} \tag{4.207}$$

Converting (4.204) through (4.206) next to ν-dependent functions with the aid of Eqs. (4.184) and (4.185), we obtain for fixed values of $K = \pm\ |K|$, that is for each sub-band of given K:

$$\underset{\left(\substack{0 < \nu < \infty \\ K = \pm\ (0,1,2,3,\ldots.)}\right)}{g_\nu^{PR}(\nu,K)} = \frac{\left|\nu - \nu_{mn} + 2\ X_{AB}\ \nu_B\ K\right|\ \nu_A^{1/2}}{6\pi^{1/2}\ \nu_B (kT/h)^{3/2}}\ \cdot$$

$$\cdot\ H\left(\left|\frac{\nu - \nu_{mn} + 2\ X_{AB}\ \nu_B\ K}{2\ \nu_B}\right| - |K|\right)\ \cdot$$

$$\cdot\ \exp-\left\{\frac{(\nu-\nu_{mn} + 2\ \nu_B\ X_{AB}\ K)^2 + 4\ K^2\ (\nu_A-\nu_B)\ \nu_B}{4\ \nu_B\ kT/h}\right\}, \ \mathrm{Hz}^{-1} \tag{4.208}$$

$$g_{\nu}^{Q}(\nu,K) = \frac{\nu_A^{1/2}}{3\pi^{1/2}\,\xi_B (kT/h)^{3/2}}\; H\left(\frac{\nu_{mn} - \nu - 2\,x_{AB}\,\nu_B\,K}{\xi_B\,\nu_B} - K^2\right)\cdot$$

$$\begin{pmatrix} 0 < \nu < \nu_{mn} + 2\Delta\nu_{A\zeta}|K|, \text{ if } \Delta\nu_B > 0 \\ \nu_{mn} + 2\Delta\nu_{A\zeta}|K| < \nu < \infty, \text{ if } \Delta\nu_B < 0 \\ K = \pm\,(0,\ 1,\ 2,\ 3,\ \ldots\ldots) \end{pmatrix}$$

$$\cdot\ \exp-\left\{\frac{|\nu_{mn} - \nu - 2\,x_{AB}\,\nu_B\,K + K^2\,\xi_B(\nu_A - \nu_B)|}{\xi_B\,kT/h}\right\}\ ,\ \text{Hz}^{-1} \qquad (4.209)$$

The relations (4.208) and (4.209) do follow the contours of the curves shown in Figures 4-4 and 4-5 for the different K sub-bands.

We have neglected the constant term $\Delta\nu_o$ in the above relations which is zero for // bands but nonzero for ⊥ bands. In the latter case it can always be incorporated in ν_{mn} , that is we can always write $\nu_{mn} = \nu_{mn} + \Delta\nu_o \approx \nu_{mn} + \nu_A - \nu_B$ for the ⊥ bands. In Eqs. (4.208) and (4.209), K = 0 , ±1 , ±2 , ±3 , ... and:

$$\left(x_{AB}\right)_{\perp} = \frac{\nu_A - \nu_B}{\nu_B} \qquad (4.210a)$$

$$\left(x_{AB}\right)_{//} = 0 \qquad (4.210b)$$

In the approximations (4.210a) and (4.210b) we neglect some small terms in the expressions $\Delta\nu_{A\zeta}$ (see Eqs. (4.187) and (4.189).

The total value of $g_v(\nu)$ at a given ν for all values of K is obtained next by summing or integrating (4.208) and (4.209) from $K = -\infty$ to $K = +\infty$. Thus for // bands, with $\chi_{AB} = 0$, we get:

$$\underset{(0<\nu<\infty)}{g_{v_{//}}^{PR}(\nu)} = \int_{K=-\infty}^{+\infty} g_v^{PR}(\nu,K)\, dK = \left(\frac{|\nu - \nu_{mn}|}{6\nu_B\ kT/h}\right)\left(\frac{\nu_A}{\nu_A - \nu_B}\right)^{1/2} \cdot \mathrm{erf}\left(\frac{|\nu - \nu_{mn}|}{2\nu_B}\right) \cdot \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B\ kT/h}\right\}, \ \mathrm{Hz}^{-1} \qquad (4.211)$$

$$\underset{\substack{(0<\nu<\nu_{mn})\\ \text{or}\\ (\nu_{mn}<\nu<\infty)}}{g_{//}^{Q}(\nu)} = \int_{K=-\infty}^{+\infty} g_v^{Q}(\nu,K)\, dK = \left(\frac{h}{3\xi_B\ kT}\right) \cdot \left(\frac{\nu_A}{\nu_A - \nu_B}\right)^{1/2} \cdot \mathrm{erf}\left(\sqrt{\frac{\nu_{mn} - \nu}{\xi_B\ \nu_B}}\right) \cdot \exp-\left(\frac{|\nu_{mn} - \nu|}{\xi_B\ kT/h}\right), \ \mathrm{Hz}^{-1} \qquad (4.212)$$

The error function $\mathrm{erf}(x) = 0.8427$ for $x = 1$ and $\mathrm{erf}(x) = 0.99532$ for $x = 2$. Therefore, except for values of ν very close to ν_{mn}, no great error is made if we set the $\mathrm{erf}(x)$ functions in (4.211) and (4.212) equal to 1. Also in view of the discussion surrounding Eqs. (4.200) through (4.203), it appears that we should let the factor $\nu_A^{1/2}/(\nu_A - \nu_B)^{1/2} \approx 1$. Thus finally:

$$\boxed{\begin{array}{l} g^{PR}_{\nu_{//}}(\nu) \approx \dfrac{|\nu - \nu_{mn}|}{6\nu_B\ kT/h}\ \exp-\left\{\dfrac{(\nu - \nu_{mn})^2}{4\nu_B\ kT/h}\right\}\ ,\ \mathrm{Hz}^{-1} \\ (0 < \nu < \infty) \end{array}} \tag{4.213}$$

and:

$$\boxed{\begin{array}{l} g^{Q}_{\nu_{//}}(\nu) \approx \dfrac{h}{3\xi_B\ kT}\ \exp-\left(\dfrac{|\nu_{mn} - \nu|}{\xi_B\ kT/h}\right)\ ,\ \mathrm{Hz}^{-1} \\ (0 < \nu < \nu_{mn}\ \text{or} \\ \nu_{mn} < \nu < \infty) \end{array}} \tag{4.214}$$

For the ⊥ bands with $\chi_{AB} \approx (\nu_A - \nu_B)/\nu_B$, we get in the same way:

$$\begin{aligned} \underset{(0 < \nu < \infty)}{g^{PR}_{\nu_\perp}(\nu)} = {} & \frac{1}{3}\left(\frac{1}{\pi\nu_A\ kT/h}\right)^{1/2} \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B\ kT/h}\right\} + \\ & - \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_A\ kT/h}\left(\left(\frac{\nu_A}{|2\nu_B - \nu_A|} - 1\right)^2 + 1\right)\right\} + \\ & + \frac{|\nu - \nu_{mn}|}{3\nu_A\ kT/h}\left(\frac{\nu_B}{\nu_A - \nu_B}\right)^{1/2} \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_A\ kT/h}\right\} \cdot \\ & \cdot \left[\mathrm{erf}\left\{\left(\frac{\nu_A}{|2\nu_B - \nu_A|} - 1\right)\left(\frac{(\nu - \nu_{mn})^2\ \nu_B}{4\nu_A(\nu_A - \nu_B)\ kT/h}\right)^{1/2}\right\} + \right. \\ & \left. - \mathrm{erf}\left\{\frac{(\nu - \nu_{mn})^2\ (\nu_A - \nu_B)}{4\nu_A\nu_B\ kT/h}\right\}^{1/2}\right]\ ,\ \mathrm{Hz}^{-1} \end{aligned} \tag{4.215a*}$$

---

*Only the positive square root is to be taken throughout.

$$
\begin{aligned}
&\underset{\substack{(0 < \nu < \nu_{mn}+(\nu_A-\nu_B)/\xi_B,\ \text{or} \\ \nu_{mn}+\ (\nu_A-\nu_B/\xi_B < \nu < \infty)}}{g^{Q}_{\nu_\perp}(\nu)} = \left[\frac{1}{6\xi_B kT/h}\left(\frac{\nu_A}{\nu_A - \nu_B}\right)^{1/2} \exp-\left\{\frac{|\nu_{mn}-\nu|}{\xi_B\ kT/h} - \frac{\nu_A - \nu_B}{\xi_B^2\ kT/h}\right\}\right] \cdot \\
&\cdot \left[\mathrm{erf}\left\{\left(\frac{\nu_A - \nu_B}{\xi_B^2\ kT/h}\right)^{1/2}\left(\frac{\nu_A - \nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B\ |\nu_{mn} - \nu|}{(\nu_A - \nu_B)^2} + 1\right)^{1/2} - 1\right) - 1\right)\right\}\right. + \\
&\left. + \ \mathrm{erf}\left\{\left(\frac{\nu_A - \nu_B}{\xi_B^2\ kT/h}\right)^{1/2}\left(\frac{\nu_A - \nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B\ |\nu_{mn} - \nu|}{(\nu_A - \nu_B)^2} + 1\right)^{1/2} + 1\right) + 1\right)\right\}\right],\ \mathrm{Hz}^{-1}
\end{aligned}
$$

(4.215b)*

To be consistent, we shall set $(\nu_A - \nu_B)^{1/2} \rightarrow \nu_A^{1/2}$ as we did before. Then:

$$
\boxed{
\begin{aligned}
&\underset{(0 < \nu < \infty)}{g^{PR}_{\nu_\perp}(\nu)} = \frac{1}{3}\left(\frac{1}{4\pi\nu_A\ kT/h}\right)^{1/2}\left[\exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B\ kT/h}\right\}\right. + \\
&\left. - \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_A\ kT/h}\left(\left(\frac{\nu_A}{|2\nu_B - \nu_A|} - 1\right)^2 + 1\right)\right\}\right] + \\
&+ \frac{|\nu - \nu_{mn}|}{6\nu_A\ kT/h}\left(\frac{\nu_B}{\nu_A}\right)^{1/2} \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_A\ kT/h}\right\} \cdot \\
&\cdot \left[\mathrm{erf}\left\{\left(\frac{\nu_A}{|2\nu_B - \nu_A|} - 1\right)\left(\frac{(\nu - \nu_{mn})^2\ \nu_B}{4\nu_A(\nu_A - \nu_B)\ kT/h}\right)^{1/2}\right\}\right. + \\
&\left. - \ \mathrm{erf}\left\{\frac{(\nu - \nu_{mn})^2\ (\nu_A - \nu_B)}{4\nu_A\nu_B\ kT/h}\right\}^{1/2}\right],\ \mathrm{Hz}^{-1}
\end{aligned}
}
$$

(4.216a)*

---

*Only the positive square root is to be taken throughout.

$$\boxed{\begin{aligned}
g^{Q}_{\nu_\perp}(\nu) \quad &= \frac{1}{6\xi_B\ kT/h}\left[\exp-\left\{\frac{|\nu_{mn}-\nu|}{\xi_B\ kT/h}-\frac{\nu_A-\nu_B}{\xi_B^2\ kT/h}\right\}\right]\cdot \\
&(0<\nu<\nu_{mn}+(\nu_A-\nu_B)/\xi_B,\ \text{if } \Delta\nu_B>0; \\
&\nu_{mn}+(\nu_A-\nu_B)/\xi_B<\nu<\infty,\ \text{if } \Delta\nu_B<0) \\
&\cdot\left[\operatorname{erf}\left\{\left(\frac{\nu_A-\nu_B}{\xi_B^2\ kT/h}\right)^{1/2}\left(\frac{\nu_A-\nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B\,|\nu_{mn}-\nu|}{(\nu_A-\nu_B)^2}+1\right)^{1/2}-1\right)-1\right)\right\}\right. \\
&\left.+\operatorname{erf}\left\{\left(\frac{\nu_A-\nu_B}{\xi_B^2\ kT/h}\right)^{1/2}\left(\frac{\nu_A-\nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B\,|\nu_{mn}-\nu|}{(\nu_A-\nu_B)^2}+1\right)^{1/2}+1\right)+1\right)\right\}\right],\ \text{Hz}^{-1}
\end{aligned}} \tag{4.216b*}$$

A comparison of Eqs. (4.213) and (4.214) with (4.171) and (4.172) shows that the contour functions of the P- , Q- , and R-Branches of a // band of a symmetric-top rotor are the same as those of a linear molecule. However for a ⊥ band the spectrum is quite different. Figure 4-6 shows medium-resolution spectra of the vibrational emissions/absorptions of a // and a ⊥ band of NH_3 . The parallel ν_1 band of NH_3 shows a typical P-, Q-, and R-Branch structure like that of a linear molecule, except that there is a doubling of each line which is due to "inversion" (Refs. 10 and 16). That is each rotational energy level has two components, due to the fact that the N in NH_3 can be below or above the H_3 plane and oscillates between these two configurations. Except for the lightest symmetric-top rotors such as NH_3 , this oscillation is so slow however that the doubling is not noticeable and can be neglected (Refs. 10 and 16). The $(\nu_3 + \nu_4)$ perpendicular band of NH_3 shows a typical series of Q-Branches (due to the fact that $\Delta\nu_{A\zeta} \neq 0$) whose

---

*Only the positive square root is to be taken throughout.

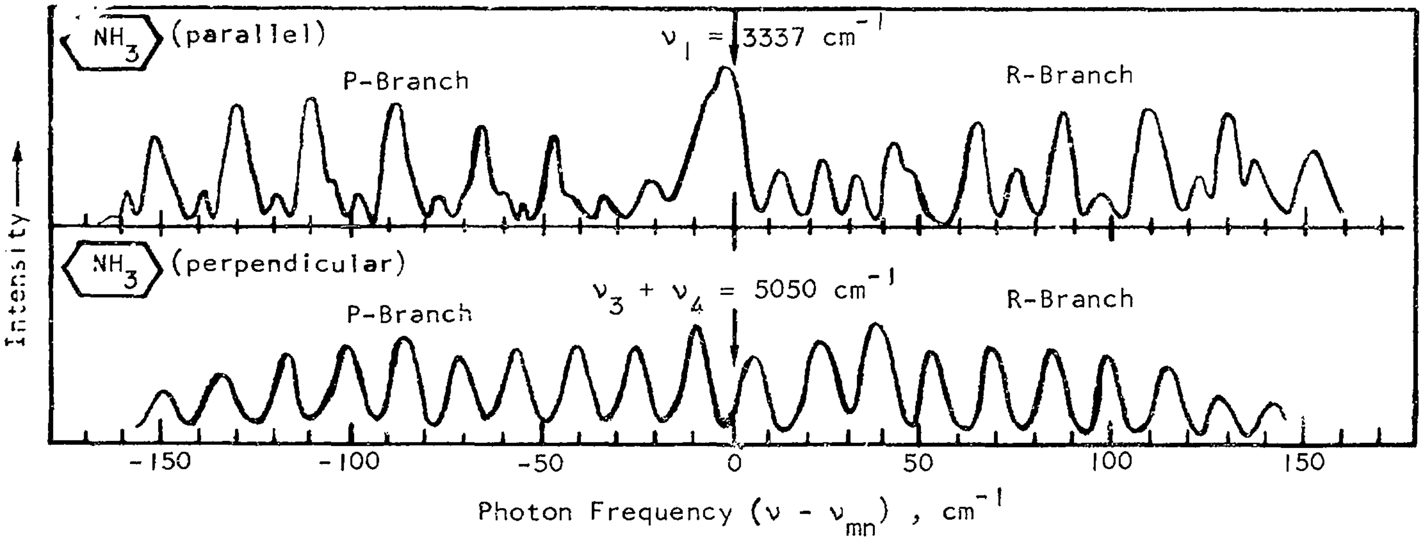

FIGURE 4-6. VIBRATIONAL EMISSION/ABSORPTION BANDS OF THE SYMMETRIC-TOP MOLECULE NH_3 AT T = 300 °K (Refs. 2, 10)

structure is explained in Figure 4-5. The interspersed P- and R-lines are too weak compared to the "bunched" Q-Branches to show up in the medium-resolution spectrum of Figure 4-6.

To determine the band-spread and shape-function, we encounter the same problem as we did with linear molecules if we try to set $b(\nu,\nu_{mn},\Delta\nu_{mn}) = 1$ at $\nu = \nu_{mn}$. Using the same arguments as discussed in connection with Eq. (4.150), we shall choose therefore to set:

$$\boxed{\Delta\nu_{mn} = \sqrt{4\nu_B \; kT/h} \quad , \quad \text{Hz} \quad ,} \tag{4.217}$$

so that for the //-bands the dimensionless shape-function $b(\nu,\nu_{mn},\Delta\nu_{mn})$ equals:

$$\boxed{\begin{aligned} \underset{\begin{pmatrix} 0 \le \nu < \infty \\ //\text{-bands} \end{pmatrix}}{b_\nu^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})} &= \frac{|\nu - \nu_{mn}|}{3\sqrt{\nu_B \; kT/h}} \; \exp-\left\{\frac{(\nu - \nu_{mn})^2}{4\nu_B \; kT/h}\right\} = \\ &= \frac{2|\nu - \nu_{mn}|}{3\;\Delta\nu_{mn}} \; \exp-\left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}}\right)^2 \end{aligned}} \tag{4.218}$$

$$\boxed{\begin{aligned} \underset{\begin{pmatrix} 0 < \nu < \nu_{mn} \\ \nu_{mn} < \nu < \infty \\ //\text{ Bands} \end{pmatrix}}{b_\nu^{Q}(\nu,\nu_{mn},\Delta\nu_{mn})} &= \frac{2\sqrt{\nu_B}}{3\xi_B\sqrt{kT/h}} \; \exp-\left(\frac{\nu_{mn} - \nu}{\xi_B \; kT/h}\right) = \\ &= \frac{4\nu_B}{3\xi_B\Delta\nu_{mn}} \; \exp-\left\{\frac{4\nu_B|\nu_{mn} - \nu|}{\xi_B\Delta\nu_{mn}}\right\} \end{aligned}} \tag{4.219}$$

For the $\perp$ bands, the shape-function $b(\nu,\nu_{mn},\Delta\nu_{mn})$ becomes:

$$\boxed{\begin{aligned}
&\underset{\left(\begin{smallmatrix}0\le\nu<\infty\\ \perp\ \text{bands}\end{smallmatrix}\right)}{b^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})} = \frac{2}{3}\left(\frac{\nu_B}{\pi\nu_A}\right)^{1/2}\left[\exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2 + \right.\\
&\left. - \exp-\left\{\frac{\nu_B}{\nu_A}\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2\left(\left(\frac{\nu_A}{|2\nu_B-\nu_A|}-1\right)^2+1\right)\right\}\right] + \frac{2|\nu-\nu_{mn}|}{3\Delta\nu_{mn}}\left(\frac{\nu_B}{\nu_A}\right)\left(\frac{\nu_B}{\nu_A-\nu_B}\right)^{1/2}\cdot\\
&\cdot\ \exp-\left\{\frac{\nu_B}{\nu_A}\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2\right\}\cdot\left[\operatorname{erf}\left\{\left(\frac{\nu_A}{|2\nu_B-\nu_A|}-1\right)\left(\frac{\nu_B^2}{\nu_A(\nu_A-\nu_B)}\right)^{1/2}\left(\frac{|\nu-\nu_{mn}|}{\Delta\nu_{mn}}\right)\right\}+\right.\\
&\qquad\qquad\left. - \operatorname{erf}\left\{\left(\frac{\nu_A-\Delta_B}{\nu_A}\right)^{1/2}\left(\frac{|\nu-\nu_{mn}|}{\Delta\nu_{mn}}\right)\right\}\right]
\end{aligned}}$$

(4.220)

$$\boxed{\begin{aligned}
&\underset{\substack{(0<\nu<\nu_{mn}+(\nu_A-\nu_B)/\xi_B,\ \text{for}\ \Delta\nu_B>0;\\ \nu_{mn}+(\nu_A-\nu_B)/\xi_B<\nu<\infty,\ \text{for}\ \Delta\nu_B<0)\\ \perp\ \text{Bands}}}{b_\nu^{Q}(\nu,\nu_{mn},\Delta\nu_{mn})} = \left[-\frac{2\nu_B}{3\xi_B\Delta\nu_{mn}}\left(\frac{\nu_A}{\nu_A-\nu_B}\right)^{1/2}\cdot\right.\\
&\qquad\qquad\left.\cdot\ \exp-\left\{\frac{4\nu_B(\xi_B|\nu-\nu_{mn}|-(\nu_A-\nu_B))}{\xi_B^2\ \Delta\nu_{mn}^2}\right\}\right]\\
&\cdot\left[\operatorname{erf}\left\{\left(\frac{4\nu_B(\nu_A-\nu_B)}{\xi_B^2\ \Delta\nu_{mn}^2}\right)^{1/2}\left(\frac{\nu_A-\nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B|\nu_{mn}-\nu|}{(\nu_A-\nu_B)^2}+1\right)^{1/2}-1\right)-1\right)\right\}+\right.\\
&\left.+\operatorname{erf}\left\{\left(\frac{4\nu_B(\nu_A-\nu_B)}{\xi_B^2\ \Delta\nu_{mn}^2}\right)^{1/2}\left(\frac{\nu_A-\nu_B}{\nu_B}\left(\left(\frac{\xi_B\nu_B|\nu_{mn}-\nu|}{(\nu_A-\nu_B)^2}+1\right)^{1/2}+1\right)+1\right)\right\}\right]
\end{aligned}}$$

(4.221)

For the detailed rovibrational structure we find similar to the linear-molecule case that:

$$\boxed{g^{PQR}_{rov}(\nu,\nu_{mn},\Delta\nu_{mn}) = h^{PQR}_{\nu}(J,K,\nu_{mn},\Delta\nu_{mn}) \cdot g_{J,K}(\nu,\nu_{JK},\Delta\nu_{JK})\ ,\ \mathrm{Hz}^{-1}\ ,} \qquad (4.222)$$

where $g_{J,K}(\nu,\nu_{JK},\Delta\nu_{JK})$ is the pressure- or temperature-line-broadening function given in sections 4.3 and 4.4 for a particular line with a given value of J and K, and where:

$$\boxed{\begin{aligned} h^{PQR}_{\nu}(J,K,\nu_{mn},\Delta\nu_{mn}) = {} & \left[\left(\frac{\nu_A^{1/2}\nu_B^{1/2}}{3\pi^{1/2}kT/h}\right)\left\{\frac{\delta\nu_K}{\Delta\nu_{mn}}(2J+3)H(\nu_{mn}-\nu_{JK})H(J)H(-\nu^{Q}_{JK}) + {}\right.\right. \\ & \left.\left. + \frac{\delta\nu_K}{\Delta\nu_{mn}}(2J+1)H(\nu^{Q}_{JK}-\nu_{mn})H(J-1)H(-\nu^{Q}_{JK}) + \frac{(2J+1)}{\xi_B(J+1)}\frac{\delta\nu_K}{\Delta\nu_{mn}}H(J-1)H(-\nu_{JK})\right\}\right] \cdot \\ & H(J-|K|)\cdot\left\{2-\delta(K)\right\}\cdot\left[\exp-\left\{\frac{J(J+1)\ \nu_B + K^2(\nu_A-\nu_B)}{kT/h}\right\}\right]\ ,\end{aligned}} \qquad (4.223)$$

where as before of course $J = 0, 1, 2, 3, \ldots,$ and $K = -J, (-J+1), \ldots, 0, \ldots J-1, J$, and there is one line for each combination (J,K). The parameters ν_{JK}, ν^{Q}_{JK}, and $\delta\nu_K$ were given by Eqs. (4.184) and (4.185).

4.7.3 Spherical-Top Rotors

For spherical-top molecules, the rotational frequencies are given by (see Eq. (3.184)):

P-Branch (- sign) and R-Branch (+ sign)

$$\nu_{(J = \sup(J_m, J_n))} = \nu_{mn} \pm 2\, \nu_{B\zeta}\, J + \Delta\nu_B\, J^2 \text{ , Hz} \qquad (4.224)$$

Q-Branch

$$\nu_{(J = J_m = J_n)} = \nu_{mn} - \Delta\nu_B (J^2 - J) \text{ , Hz ,} \qquad (4.225)$$

where:

$$\nu_{B\zeta} = \frac{c}{2} (B_m + B_n - 2\, B_m \zeta_m) \approx c\, \bar{B}(1 - \zeta_m) = \nu_B(1 - \zeta_m) \text{ , Hz} \qquad (4.226)$$

$$\nu_B = c\, \bar{B} = c(B_m + B_n)/2 \text{ , Hz} \qquad (4.227)$$

$$\Delta\nu_B = c(B_m - B_n) = c \sum_\beta \alpha_\beta^B \left(v_{\beta_n} + \frac{d\beta_n}{2} - v_{\beta_m} - \frac{d\beta_m}{2} \right) \text{ , Hz} \qquad (4.228)$$

Here the Coriolis parameter ζ and the vibrational-rotational interaction parameters α_β^B were discussed in section 3.4.4. Values for ζ were listed for some selected molecules in Table 3-14; Herzberg (Ref. 11) gives values of α_β^B in his tables for a few molecules. In the above we neglected some comparatively small terms, and we approximate $\nu_{B_m} = c\, B_m \approx \nu_B$.

The frequency ν_{mn} is as before the pure vibrational frequency change in the transition $m \to n$ given by Eq. (4.88).

The band-contour functions for the spherical-top rotor are similar to those of the symmetric-top (see Eqs. (4.194) through (4.196)), except that the statistical weights are different (see Eq. (3.185)), that is:

$$g_v^P(J_m) = f_I \frac{(2J_m + 3)^2}{6\ \nu_{B\zeta}\ Z'_r} \exp-\left\{\frac{(J_m + 1)\ \nu_{B_m}(J_m + 2\ \zeta_m)}{kT/h}\right\}, \quad \mathrm{Hz}^{-1} \qquad (0 \leq J_m < \infty) \tag{4.229}$$

$$g_v^Q(J_m) = f_I \frac{(2J_m + 1)^2}{6(J_m + 1)\ \Delta\nu_B\ Z'_r} \exp-\left\{\frac{J_m(J_m + 1)\ \nu_{B_m}}{kT/h}\right\}, \quad \mathrm{Hz}^{-1} \qquad (1 \leq J_m < \infty) \tag{4.230}$$

$$g_v^R(J_m) = f_I \frac{(2J_m - 1)^2}{6\ \nu_{B\zeta}\ Z'_r} \exp-\left\{\frac{J_m\ \nu_{B_m}(J_m + 1 - 2\ \zeta_m)}{kT/h}\right\}, \quad \mathrm{Hz}^{-1} \qquad (1 \leq J_m < \infty) \tag{4.231}$$

Here we took account of Eqs. (3.168) and (3.183), and assumed approximate statistical weights with averaged nuclear-spin factors f_I, that is:

$$w_{J,I} \approx f_I(2J + 1)^2 \tag{4.232}$$

The actual statistical weights if nuclear spin is properly accounted for (Ref. 34) can deviate considerably from (4.232), particularly for the lower J values and small values of I as may be seen from Table 4-5. For higher J-values and higher I-values, the approximation (4.232) becomes better and better as may be seen by comparing the various values in Table 4-5 with those listed in the last column. The values of f_I for an XY_4 molecules with four identical atoms Y, each with nuclear spin I, are according to Table 4-5 approximately:

TABLE 4-5. ACTUAL AND APPROXIMATE STATISTICAL WEIGHTS OF THE ROTATIONAL LEVELS OF TETRAHEDRAL XY_4 MOLECULES TAKING NUCLEAR SPIN INTO ACCOUNT (After Refs. 10,34)*

J	Actual: $w_{JI} = f_I \, w'_{IJ}(2J+1) = w''_{IJ}(2J+1)$				Approximate: ** $w_{JI} = f_I(2J+1)^2$
	I = 0	I = 1/2	I = 1	I = 3/2	All I **
0	1 × 1	5 × 1	15 × 1	36 × 1	f_I × 1 × 1
1	0 × 3	3 × 3	18 × 3	60 × 3	f_I × 3 × 3
2	0 × 5	5 × 5	30 × 5	100 × 5	f_I × 5 × 5
3	1 × 7	11 × 7	51 × 7	156 × 7	f_I × 7 × 7
4	1 × 9	13 × 9	63 × 9	196 × 9	f_I × 9 × 9
5	0 × 11	11 × 11	66 × 11	220 × 11	f_I × 11 × 11
6	2 × 13	21 × 13	96 × 13	292 × 13	f_I × 13 × 13
7	1 × 15	19 × 15	99 × 15	316 × 15	f_I × 15 × 15
8	1 × 17	21 × 17	111 × 17	256 × 17	f_I × 17 × 17
9	2 × 19	27 × 19	132 × 19	412 × 19	f_I × 19 × 19
10	2 × 21	29 × 21	144 × 21	452 × 21	f_I × 21 × 21
11	1 × 23	27 × 23	147 × 23	476 × 23	f_I × 23 × 23
12	3 × 25	37 × 25	177 × 25	548 × 25	f_I × 25 × 25
13	2 × 27	21 × 27	180 × 27	572 × 27	f_I × 27 × 27
14	2 × 29	21 × 29	192 × 29	612 × 29	f_I × 29 × 29
15	3 × 31	24 × 31	213 × 31	668 × 31	f_I × 31 × 31

*The four identical atoms Y are assumed each to have nuclear-spin I.

**$f_I(I = 0) \approx 0.08$; $f_I(I = \frac{1}{2}) \approx 1.05$; $f_I(I = 1) \approx 6.71$; $f_I(I = \frac{3}{2}) \approx$ ≈ 21.33. These values of f_I are averages of J = 10 to J = 15.

$$f_I(I = 0) \approx 0.08 \tag{4.233a}$$

$$f_I(I = 1/2) \approx 1.05 \tag{4.233b}$$

$$f_I(I = 1) \approx 6.71 \tag{4.233c}$$

$$f_I(I = 3/2) \approx 21.33 \tag{4.233d}$$

From Eq. (4.224), we obtain for the P- and R-Branch that:

$$d\nu \approx \pm 2\, \nu_{B\zeta}\, dJ \text{ , Hz ,} \qquad \left\{ \begin{matrix} - = \text{P-Branch} \\ + = \text{R-Branch} \end{matrix} \right\} \tag{4.234}$$

while from (4.225) we get for the Q-Branch:

$$d\nu = \Delta\nu_B (2J - 1)\, dJ \text{ , Hz} \tag{4.235}$$

From (4.234), (4.235), and (4.229), (4.230), and (4.231), we get then for Z_r':

$$Z_r' = \int_{\gamma = 0}^{\infty} Z_r' \left\{ g_v^P(J) + g_v^Q(J) + g_v^R(J) \right\} d\nu = \frac{f_I}{3} \int_{J=0}^{\infty} \Bigg[(2J+3)^2 \cdot$$

$$\cdot \exp - \left\{ \frac{(J^2 + (1+2\zeta_m)\, J + 2\zeta_m)\, \nu_{B_m}}{kT/h} \right\} + (2J+1)^2 \cdot$$

$$\cdot \exp - \left\{ \frac{(J^2 + (4-2\zeta_m)\, J + (3-2\zeta_m))\nu_{B_m}}{kT/h} \right\} + \frac{(2J+3)^2}{2} \frac{2J+1}{J+2} \exp - \left\{ \frac{(J+1)(J+2)\nu_{B_m}}{kT/h} \right\} \Bigg] dJ =$$

$$\approx \frac{f_I}{3} \int_{J=0}^{\infty} \left[12\, J^2 \exp - \left\{ \frac{J^2\, \nu_{B_m}}{kT/h} \right\} \right] dJ = \pi^{1/2}\, f_I \left(\frac{kT}{h\nu_B} \right)^{3/2} \tag{4.236}$$

With (4.236), Eqs. (4.229) through (4.231) become:

$$\underset{(0 \le J_m < \infty)}{g_v^P(J_m)} = \frac{(2J_m+3)^2 \, \nu_B^{1/2}}{6\pi^{1/2} \, (1-\zeta_m)(kT/h)^{3/2}} \exp-\left\{\frac{\nu_B(J_m+1)(J_m+2\zeta_m)}{kT/h}\right\} , \ \mathrm{Hz}^{-1} \tag{4.237}$$

$$\underset{(1 \le J_m < \infty)}{g_v^Q(J_m)} = \frac{(2J_m+1)^2 \, \nu_B^{1/2}}{6\pi^{1/2} \, (J_m+1) \, \xi_B(kT/h)^{3/2}} \exp-\left\{\frac{J_m(J_m+1) \, \nu_B}{kT/h}\right\} , \ \mathrm{Hz}^{-1} \tag{4.238}$$

$$\underset{(1 \le J_m < \infty)}{g_v^R(J_m)} = \frac{(2J_m-1)^2 \, \nu_B^{1/2}}{6\pi^{1/2} \, (1-\zeta_m)(kT/h)^{3/2}} \exp-\left\{\frac{\nu_B \, J_m(J_m+1-2\zeta_m)}{kT/h}\right\} , \ \mathrm{Hz}^{-1} \tag{4.239}$$

Here $\xi_B = \Delta\nu_B/\nu_B$ is again given by (4.207).

Note that the factor f_I cancels when we substituted Z_r' in (4.229) through (4.231). Of course, as mentioned earlier the use of Eq. (4.232) is only approximately correct and at the lower J values, the actual values for g(J) may differ appreciably from the "smoothed" functions (4.237) through (4.239).

Rewriting the g(J) functions as g(ν) with the aid of (4.224) and (4.225) gives next:

$$\boxed{\underset{(0 \le \nu < \infty)}{g_v^{PR}(\nu)} = \left[\frac{(\nu-\nu_{mn})^2}{6\pi^{1/2}(1-\zeta_m)^3 \, \nu_B^{3/2}(kT/h)^{3/2}}\right] \exp-\left\{\frac{(\nu-\nu_{mn})^2}{4(1-\zeta_m)^2 \, \nu_B \, kT/h}\right\} , \ \mathrm{Hz}^{-1}} \tag{4.240}$$

$$\begin{array}{l} g_{\nu}^{Q}(\nu) \\ (0 \leq \nu < \nu_{mn} \text{ , if } \Delta\nu_B > 0; \\ \nu_{mn} < \nu < \infty \text{ , if } \Delta\nu_B < 0) \end{array} = \left[\frac{4|\nu_{mn}-\nu|^{1/2}}{6\pi^{1/2}\xi_B^{3/2}(kT/h)^{3/2}}\right] \exp-\left\{\frac{|\nu_{mn}-\nu|}{\xi_B kT/h}\right\}, \text{ Hz}^{-1} \tag{4.241}$$

Here we have again omitted the constants 3 and 1 in comparison with 2J in the first factor and some other small terms in the exponential as we did before for the other cases. This amounts effectively to a small shift in the value of ν_{mn} which we shall neglect.

For the band-spread function we take again (see the discussion in connection with Eq. (4.150)):

$$\Delta\nu_{mn} = \sqrt{4(1-\zeta_m)^2\ \nu_B\ kT/h}\ , \quad \text{Hz} \tag{4.242}$$

Then the dimensionless shape-function $b(\nu,\nu_{mn},\Delta\nu_{mn}) = (\Delta\nu_{mn}) \times g(\nu,\nu_{mn},\Delta\nu_{mn})$ becomes:

$$\begin{array}{l} b_{\nu}^{PR}(\nu,\nu_{mn},\Delta\nu_{mn}) \\ (0 \leq \nu < \infty) \end{array} = \frac{4(\nu - \nu_{mn})^2}{3\pi^{1/2}\ \Delta\nu_{mn}^2} \exp-\left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}}\right)^2 , \tag{4.243}$$

$$\begin{array}{l} b^{Q}(\nu,\nu_{mn},\Delta\nu_{mn}) \\ (0 \leq \nu < \nu_{mn} \text{ , if } \Delta\nu_B > 0; \\ \nu_{mn} < \nu < \infty \text{ , if } \Delta\nu_B < 0) \end{array} = \frac{16(1-\zeta_m)^3\nu_B^{3/2}|\nu_{mn}-\nu|^{1/2}}{3\pi^{1/2}\xi_B^{3/2}\Delta\nu_{mn}^2} \exp-\left\{\frac{4(1-\zeta_m)^2\nu_B|\nu_{mn}-\nu|}{\xi_B\Delta\nu_{mn}^2}\right\} \tag{4.244}$$

For the detailed rovibrational structure we find similar to the linear-molecule case that:

$$\boxed{g_{rov}^{PQR}(\nu,\nu_{mn},\Delta\nu_{mn}) = h_{v}^{PQR}(J,\nu_{mn},\Delta\nu_{mn}) \cdot g_J(\nu,\nu_J,\Delta\nu_J) \ , \ \mathrm{Hz}^{-1}} \tag{4.245}$$

Here, as before, $g_J(\nu,\nu_J,\Delta\nu_J)$ is the temperature- and/or pressure-broadening line-contour function, and $h_{v}^{PQR}(J,\ \nu_{mn},\Delta\nu_{mn})$ is given by:

$$\boxed{\begin{aligned} h_{v}^{PQR}(J,\nu_{mn},\Delta\nu_{mn}) \ &= \ \left(\frac{h\nu_B}{3\pi^{1/2}\ kT}\right)\Bigg[(2J+3)^2\ \frac{\delta\nu_J}{\Delta\nu_{mn}} \ \cdot \\ &\cdot \left\{\exp-\left(\frac{\nu_B(J+1)(J+2\zeta_m)}{kT/h}\right)\right\} H(J)H(\nu_{mn}-\nu_J)H(-\nu_J^Q) \ + \\ &+ \ (2J-1)^2\,\frac{\delta\nu_J}{\Delta\nu_{mn}}\left\{\exp-\left(\frac{\nu_B\ J(J+1-2\zeta_m)}{kT/h}\right)\right\} H(J-1)H(\nu_J-\nu_{mn})H(-\nu_J^Q) \ + \\ &+ \ \left(\frac{1-\zeta_m}{\xi_B}\right)(2J+1)^2\,\frac{\delta\nu_J^Q}{\Delta\nu_{mn}}\left\{\exp-\left(\frac{J(J+1)\nu_B}{kT/h}\right)\right\} H(J-1)H(-\nu_J) \end{aligned}} \tag{4.246}$$

Here ν_J and $\delta\nu_J$ are given by Eq. (4.155a)-(4.155d), while ν_J^Q and $\delta\nu_J^Q$ are given by (4.180a) and (4.180b) except that ν_B must be replaced by $\nu_{B\zeta}$.

As remarked at the beginning of this subsection, the nuclear spin statistics effect on each J-line was smoothed, which is particularly bad for low values of J and I. Thus (4.246) is only a smoothed approximation. To correct for the nuclear-spin-effect, the parameters $(2J+m)^2$ in Eq. (4.246) should be replaced by:

$$(2J+m)^2 = (2J'+1)^2 \rightarrow \frac{w_{J'I}}{f_I} \qquad (4.247)$$

Here $w_{J'I}$ is the actual statistical weight, values of which in the case of XY_4 molecules may be taken from Table 4-5; $J' = J + (m-1)/2$.

The rotational lines in the P- and R-Branches of spherical-top molecules apparently behave rather regularly with a rotational line spacing of $2\nu_B(1-\zeta)$ according to the above relations. Figures 4-7 and 4-8 show indeed such a rather clean band structure for the infrared-active fundamentals ν_3 and ν_4 of the tetrahedral molecule CH_4 (see section 3.4.4). The ν_4 band (and also slightly the ν_3 band) shows a triple splitting of each rotational line which is due to Coriolis perturbations by normal vibrations other than the one experiencing a transition (Ref. 10). These perturbations can be calculated by a more detailed theory that takes the Coriolis interaction from all the vibrations into account (Refs. 24 and 36), instead of the approximate "first-order" ζ-factor treatment which only accounts for the Coriolis effect by the one transitioning vibration (see also the comments in the paragraph following Eq. (3.176)).

Resolution of the rotational lines in the P- and R-Branches has only been observed experimentally for the lightest spherical-top molecules such as CH_4 . For heavier spherical-top molecules such as octahedral SF_6 and UF_6 , the lines are so closely spaced that the best grating spectrometer still cannot resolve them as may be seen in Figures 4-9a and 4-10. Only with "tunable laser spectrometers" which have become available in the last few years, is it possible to resolve the hithertofore unresolvable bands of the octahedral XY_6 molecules, as shown in Figure 4-9b.

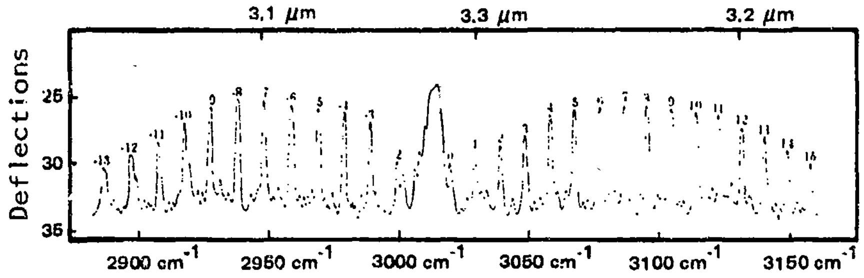

FIGURE 4-7. FINE STRUCTURE OF THE FUNDAMENTAL BAND ν_3 OF CH_4 AT 3.31 μ. The length of the absorbing path was 2 cm at atmospheric pressure. The numbers written on the maxima are (J-1) values, where J = sup(J_m, J_n). (After Ref. 10, 35)

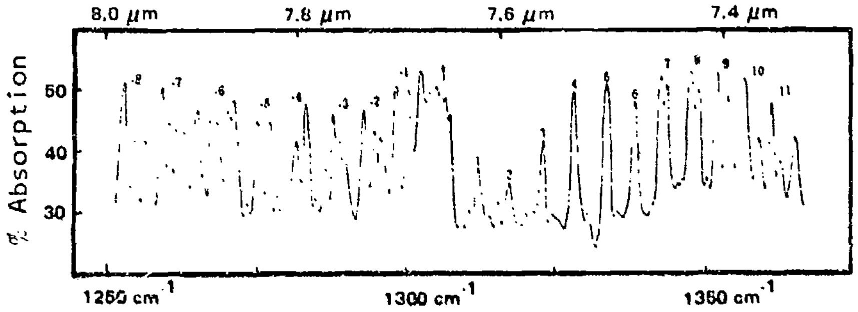

FIGURE 4-8. FINE STRUCTURE OF THE FUNDAMENTAL BAND ν_4 OF CH_4 AT 7.65 μ. The length of the absorbing path was 2 cm at atmospheric pressure. The numbers written on the maxima are (J-1) values, where J = sup(J_m, J_n). (After Refs. 10, 35)

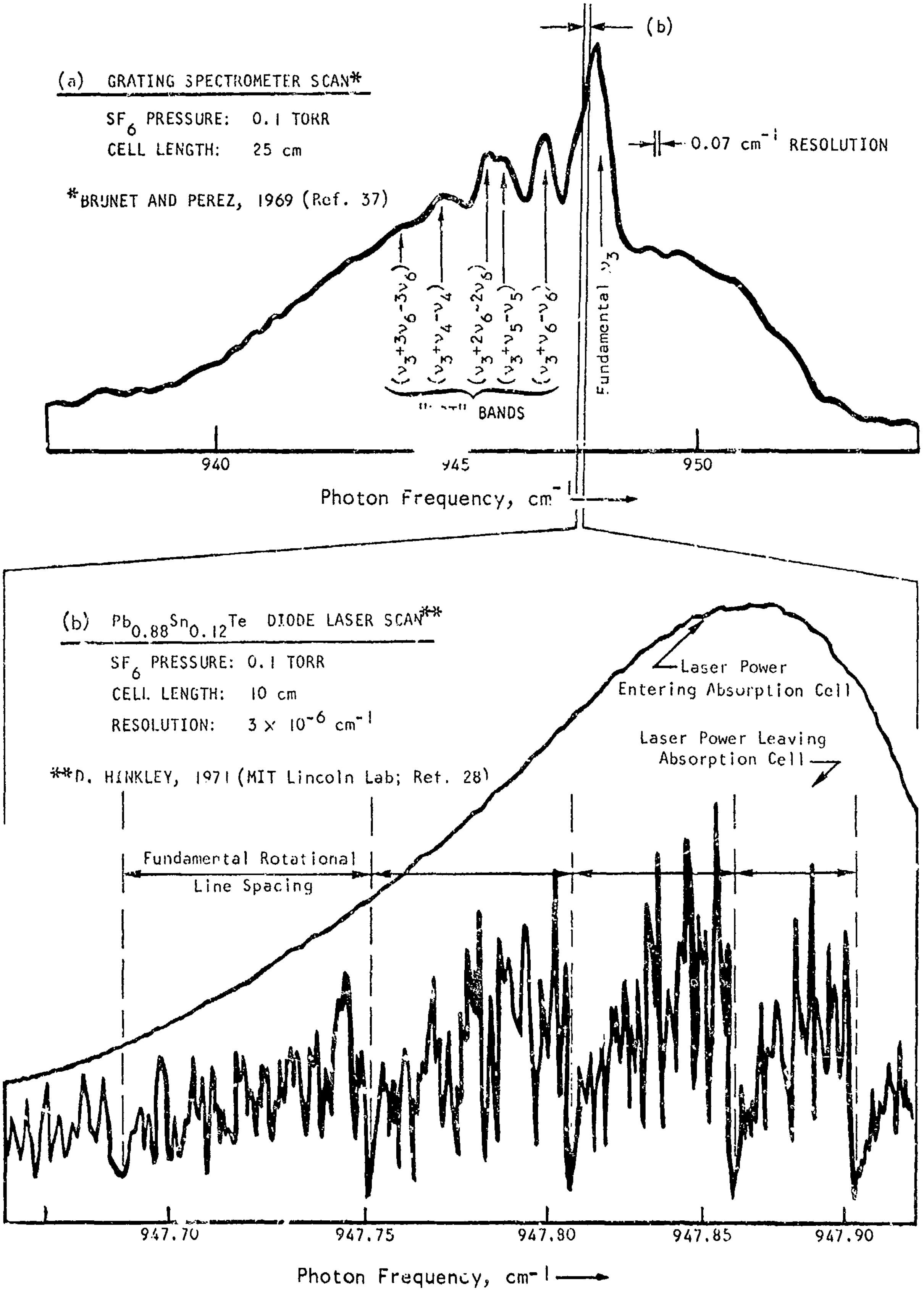

FIGURE 4-9. ABSORPTION SPECTRUM OF ν_3 BAND OF SF$_6$ FROM (a) HIGH-RESOLUTION GRATING SPECTROMETER; (b) TUNABLE DIODE LASER

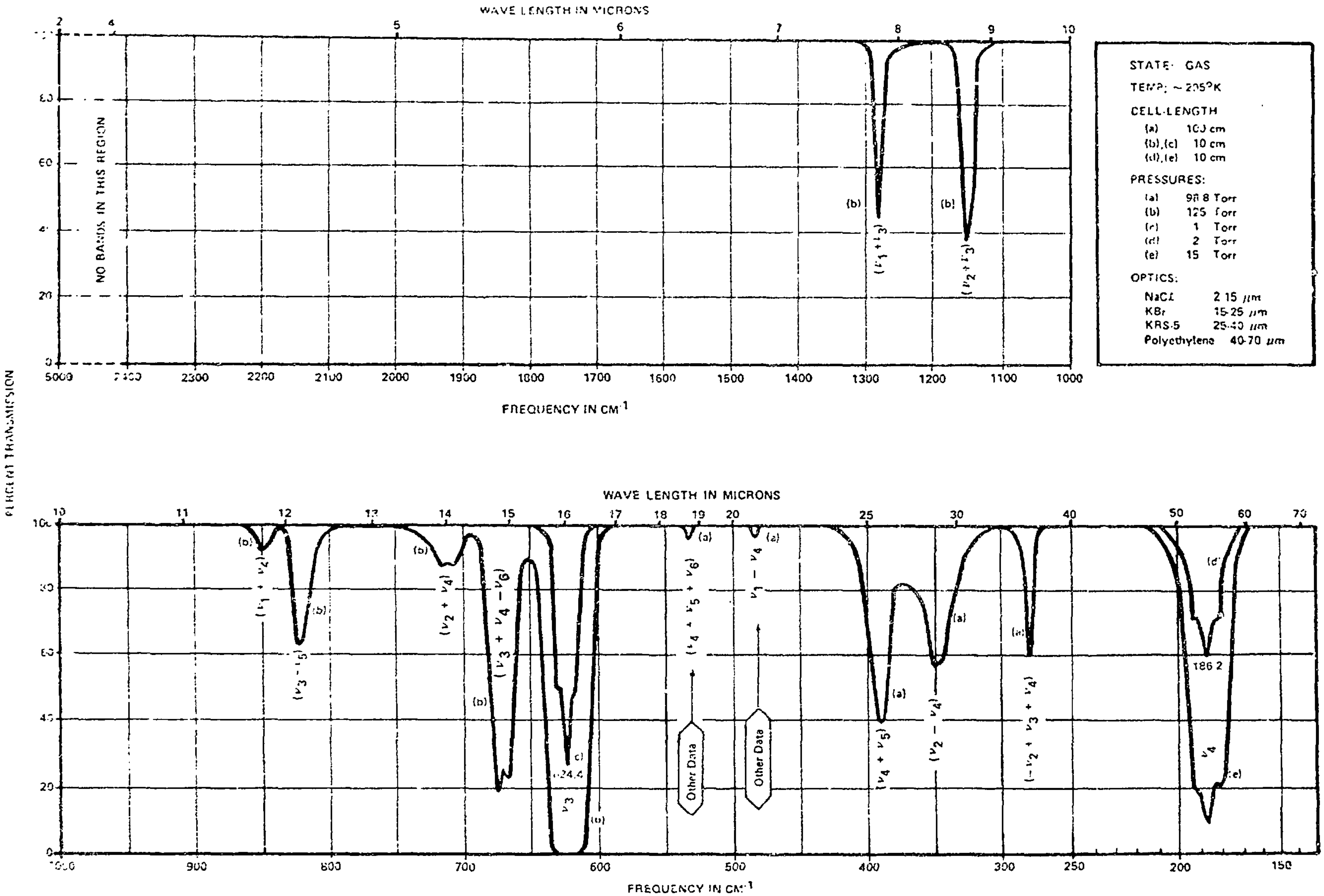

FIGURE 4-10. THE INFRARED SPECTRUM OF UF_6 AS MEASURED BY BURKE, e.a. (2 TO 40 μm) AND CLAASSEN, e.a. (40 TO 70 μm). — (Refs. 27 and 38)

Figure 4-9b reveals that each P-Branch rotational line of an XY_6 molecule is split into an apparent "jungle" of lines. This jungle is due not only to Coriolis splittings of each line by the interactions of the six normal vibrations in XY_6, but is also caused by the fact that the spectrum is that of a superimposition of many "hot" bands and not simply one "cold" band (Ref. 37). For example in the case of Figure 4-9a, not only the vibrational absorption $0 \rightarrow \nu_3$ is observed, but also $\nu_h \rightarrow \nu_3 + \nu_h$, where $\nu_h = \nu_6$, ν_5, $2\nu_6$, ..., etc. This is because at room temperature (which is usually the observation temperature), many of the other normal vibrations with low energy values are excited by thermal collisions, not only singly but also doubly, triply, and in various band combinations. For the heavy molecule UF_6 for example only 0.4% of the gas at 300 °K is in the non-excited ground ("cold") state and 99.6% is in various excited ("hot") vibrational levels. For the lighter molecule SF_6, the "cold" molecular population amounts to about 30% (Ref. 37).*

The various "hot" bands are shifted with respect to each other due to the anharmonic constants $x_{\alpha\beta}$, that is:

$$\left(\nu_{mn}\right)_{hot} = \left(\nu_{mn}\right)_{cold} - \Delta_h \qquad (4.248)$$

where:

$$\Delta_h = \sum_{\alpha}\sum_{\beta} \nu_\alpha \, x_{\alpha\beta} \left[\left(v_{\alpha_m} - v_{\alpha_n}\right) v_{\beta_h} + \left(v_{\beta_m} - v_{\beta_n}\right) v_{\alpha_h} \right] \quad , \qquad (4.249)$$

which is obtained from the relations given in Appendix C. Clearly each corresponding rotational line from the P- or R-Branch of one

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*The heavier the molecule is, the lower the frequencies of the normal vibrations (see Table 3-10) and thus the larger the number of hot bands.

hot band does not fall on the same line of another hot band. In fact the shifts are large enough that the hot Q-Branches of the ν_3 band of SF_6 can be distinguished in Figure 4-9a as separate peaks from six SF_6 hot bands as indicated.

Figure 4-10 shows the infrared-active fundamentals ν_3 and ν_4 of UF_6 with a band shape similar to that of SF_6's ν_3-band. The central peaks are a composite of many hot Q-Branches. Figure 4-10 shows further the many combination bands that are possible in a molecule with many normal vibrations*. Each absorption shown in Figure 4-10 when investigated with much higher resolution will show a superposition of hot bands with a P-, Q-, and R-Branch. However in Figure 4-10, this structure is not resolved enough except for the ν_3 and ν_4 fundamentals, where it is barely noticeable. Clearly for observations such as shown in Figure 4-10, our "smoothed" band-contour functions are more than adequate to calculate absorption profiles.

4.7.4 Asymmetric-Top Rotors

For asymmetric-top rotors the allowed photon frequencies in vibrational absorption or emission bands may be classified in three groups, called "Type-A," "Type-B," and "Type-C" bands (Ref. 10), depending on whether the vibrational dipole moment $\vec{e}_\alpha$ of the α-vibration transition (see section 3.3.2) is along the least moment of inertia (I_A) axis a, the intermediate moment of inertia (I_B) axis b, or the highest moment of inertia (I_C) axis c. This is thus a "three-dimensionalization" of the symmetric-top case where we had only two types of bands, labeled //, and

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*The unusually high intensity of the $(\nu_3+\nu_4-\nu_6)$ band in the vicinity of 670 cm^{-1} is due to Fermi resonance with the strong nearby ν_3 fundamental (see pp. 265, 266, Ref. 10), and with the $(\nu_2+\nu_4)$ band. Some authors have labeled the band at 670 cm^{-1} as $(\nu_2+\nu_6)$, but $z_1 = 0$ for this combination band.

$\perp$, for the case that $\vec{e}_\alpha$ was parallel or perpendicular to the moment of inertia axis of I_B (see section 4.7.2).

The transition selection rules for the three types of bands are (Ref. 10):

Type-A Bands

$$+\,+ \longleftrightarrow -\,+ \text{ , and } +\,- \longleftrightarrow -\,- \tag{4.250}$$

Type-B Bands

$$+\,+ \longleftrightarrow -\,- \text{ , and } +\,- \longleftrightarrow -\,+ \tag{4.251}$$

Type-C Bands

$$+\,+ \longleftrightarrow +\,- \text{ , and } -\,+ \longleftrightarrow -\,- \tag{4.252}$$

where the first sign in the designations (++) , (+-), etc., for a rotational state indicates whether the rotational eigenfunction is symmetric (+) or antisymmetric (-) for a 180° rotation about the axis c and the second sign gives the rotational eigenfunction's symmetry property for a 180° rotation about the axis a (Ref. 10).

In addition to the symmetry selection rules (4.250) through (4.252), we have the general selection rules:

$$\Delta J = 0 \text{ , } \pm 1 \text{ ; } \quad J = 0 \not\longleftrightarrow J = 0 \tag{4.253}$$

and:

$$(\text{Overall Species X}) \longleftrightarrow (\text{Overall Species X}) \text{ ,} \tag{4.254a}$$

$$(\text{Overall Species X}) \not\longleftrightarrow (\text{Overall Species Y}) \text{ ,} \tag{4.254b}$$

where X is the overall group species of the molecule (see Ref. 10), that is $X = A_i$, B_i , E_i , or F_i (i has various possible designations: i = 1, 2, 3, or i = 1g, 1u, 2g, 2u, ... , depending on the type of molecule). By "overall" species we mean the overall symmetry of the total wavefunction $\psi = \psi^e \psi^v \psi^r$, where ψ^e , ψ^v , and ψ^r refer to the purely electronic, vibrational, and rotational eigenfunctions, respectively.

With the above selection rules and Eq. (3.192), the allowed photon frequencies in the P- and R-Branch of an absorption/emission band may be written:

<u>P-Branch (-) and R-Branch (+):</u>

$$\underset{\substack{(J = \sup(J_m, J_n)) \\ (J \geq 1)}}{\nu_{JW} = \nu^{PR}(J,W)} = \nu_{mn} \pm 2\nu_{BC}\, J + \Delta\nu_{BC}\, J^2 + \nu_{ABC}\Big[W(J) - W(J-1)\Big] \;, \text{ Hz} \;, \tag{4.255}$$

where ν_{mn} is the vibrational level change as before and:

$$\nu_{BC} = \frac{1}{2}\,(\nu_B + \nu_C) = \frac{c}{2}\,(B + C) \quad , \quad \text{Hz} \tag{4.256}$$

$$\nu_B = \frac{1}{2}\,(\nu_{B_m} + \nu_{B_n}) = \frac{c}{2}\,(B_m + B_n) \;, \text{ Hz} \tag{4.257}$$

$$\nu_C = \frac{1}{2}\,(\nu_{C_m} + \nu_{C_n}) = \frac{c}{2}\,(C_m + C_n) \quad , \quad \text{Hz} \tag{4.258}$$

$$\Delta\nu_{BC} = \frac{1}{2}\,(\nu_{B_m} - \nu_{B_n} + \nu_{C_m} - \nu_{C_n}) \quad , \quad \text{Hz} \tag{4.259}$$

$$\nu_{ABC} = \nu_A - \frac{\nu_B + \nu_C}{2} = c\left(A - \frac{B + C}{2}\right) \text{, Hz} \qquad (4.260)$$

$$\nu_A = \frac{1}{2}(\nu_{A_m} + \nu_{A_n}) = \frac{c}{2}(A_m + A_n) \text{, Hz ,} \qquad (4.261)$$

and W(J) and W(J-1) have a series of 2J + 1 discrete values given by Eq. (3.193). Thus $\nu^{PR}(J)$ as given by (4.255) is multivalued, having (2J+1) sublevels for each J. For the Q-Branch we have:

Q-Branch:

$$\underset{(J \geq 1)}{\nu^Q_{JW}} = \nu_{mn} + J(J+1)\,\Delta\nu_{BC} + \nu_{ABC}(W^Q_m(J) - W^Q_n(J)) \text{ , Hz ,} \qquad (4.262)$$

where $W^Q_m(J)$ and $W^Q_n(J)$ are again W values determined by Eq. (3.193) but where the second value $W^Q_n(W_m)$ or $W^Q_m(W_n)$ in the transition is restricted by selection rules for Q-Branch ($\Delta J=0$) transitions.

Clearly there is a considerable splitting of each rotational line of given J and because of this, it is very difficult to write down general relations for every asymmetric-top molecule. Each molecule is best studied separately. We shall primarily consider the asymmetric-top molecule H_2O because of its occurrence in many applications. For other molecules, Refs. 10 and 16 (and the references given there) should be consulted.

For the H_2O molecule, only Type-A and Type-B bands occur for respectively the ν_3 vibration (Type A) and the ν_1 and ν_2 vibrations (Type B) as shown schematically in Figures 4-11 and 4-12. Type-C bands

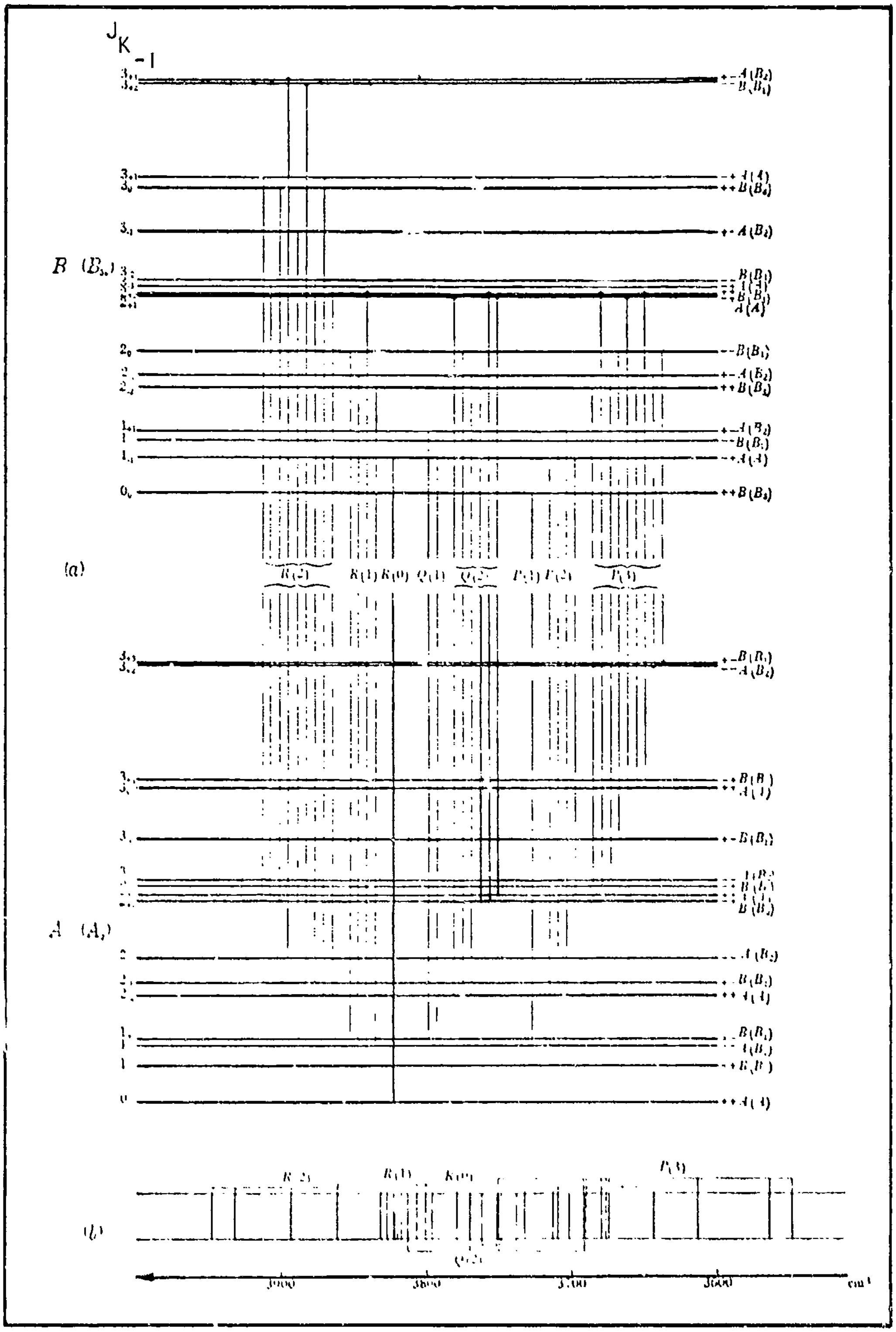

FIGURE 4-11. (a) ENERGY LEVEL DIAGRAM FOR A TYPE-A BAND OF AN ASYMMETRIC-TOP MOLECULE AND (b) SPECTRUM FOR THE LOWEST J VALUES. — Both the energy level diagram and the spectrum are drawn for the fundamental ν_3 vibration of H_2O (after Ref. 10).

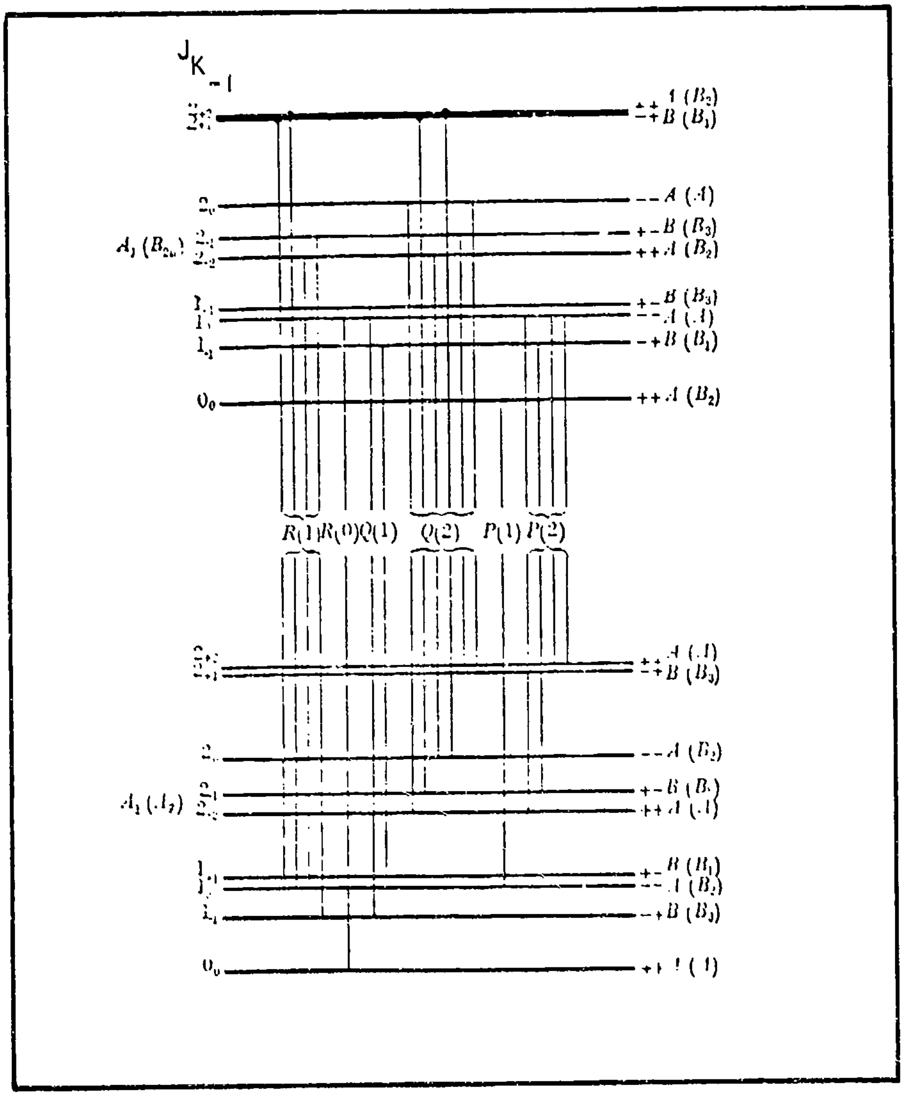

FIGURE 4-12. ENERGY LEVEL DIAGRAM FOR A TYPE-B BAND OF AN ASYMMETRIC-TOP MOLECULE. — The energy levels are drawn to scale for the fundamental ν_1 of H_2O (after Ref. 10).

can only occur for molecules with more than three atoms (e.g., the ν_6 band of H_2CO), and thus H_2O has no Type-C bands (Ref. 10). Both the Type-A and Type-B band spectra of H_2O look rather complicated, the main distinction being that for "Type-A" bands, a considerable fraction of the Q-Branch lines fall near the band center similar to the // bands of the symmetric-top, while for "Type-B" bands no Q-Branch lines fall in the center but they are dispersed through the P- and R-Branch lines analogous to the ⊥ bands of the symmetric-top.

That it is possible to calculate all lines of an asymmetric-top molecule provided sufficient data are available is evident from Figure 4-13, where Nielsen's calculations (Ref. 39) are compared with the actual experimental fine structure of the $2\nu_2$ band of H_2O. In many applications however, the major portion of the complicated fine structure is lost as shown in Figure 4-14, where the infrared absorption spectrum of H_2O is shown as observed by a medium-resolution sensor.

Many slightly-asymmetric-top rotors show a Type-A spectrum very close to that of a //-band spectrum of a symmetric-top rotor as illustrated in Figure 4-15. Therefore in many applications it appears to be sufficiently accurate to model the Type-A band-contour functions of an asymmetric-top after the //-band-contour functions of the symmetric-top, making the following substitutions:

$$K^2 \longrightarrow W \qquad (4.263)$$

$$\nu_B \longrightarrow \frac{\nu_B + \nu_C}{2} \qquad (4.264)$$

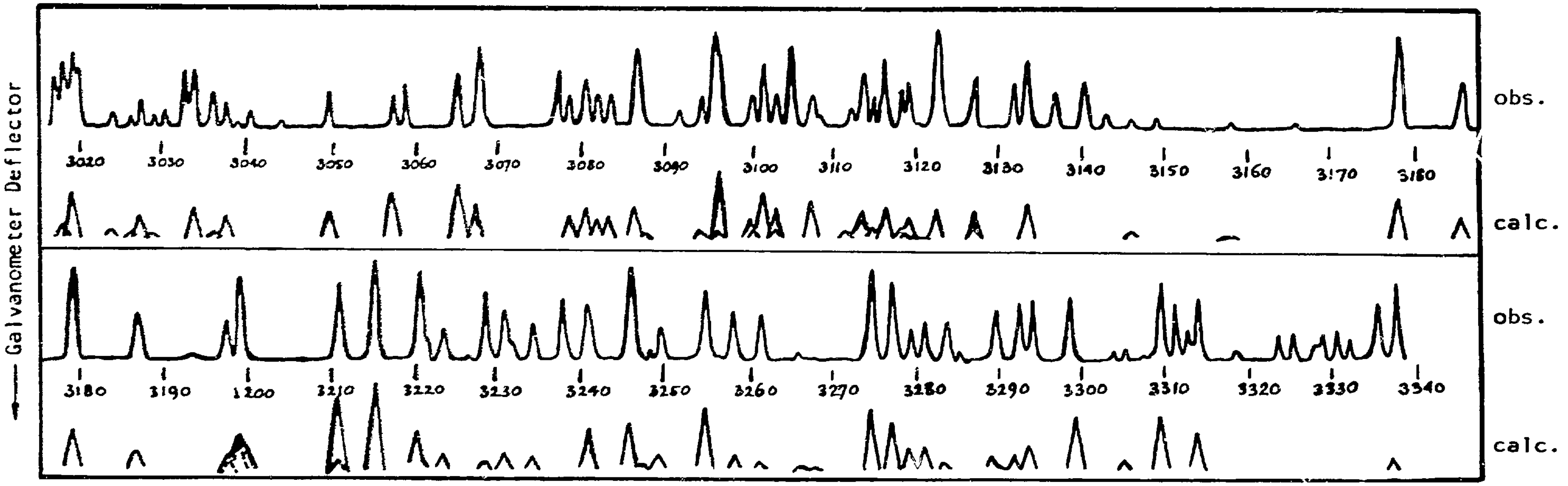

FIGURE 4-13. FINE STRUCTURE OF THE OVERTONE $2\nu_2$ OF H_2O AT 3.17 μ. — Both the observed spectrum (continuous curve) and the calculated spectrum (small triangles below the curve) are given. The numbers shown are the frequencies in units of cm^{-1} (after Ref. 39).

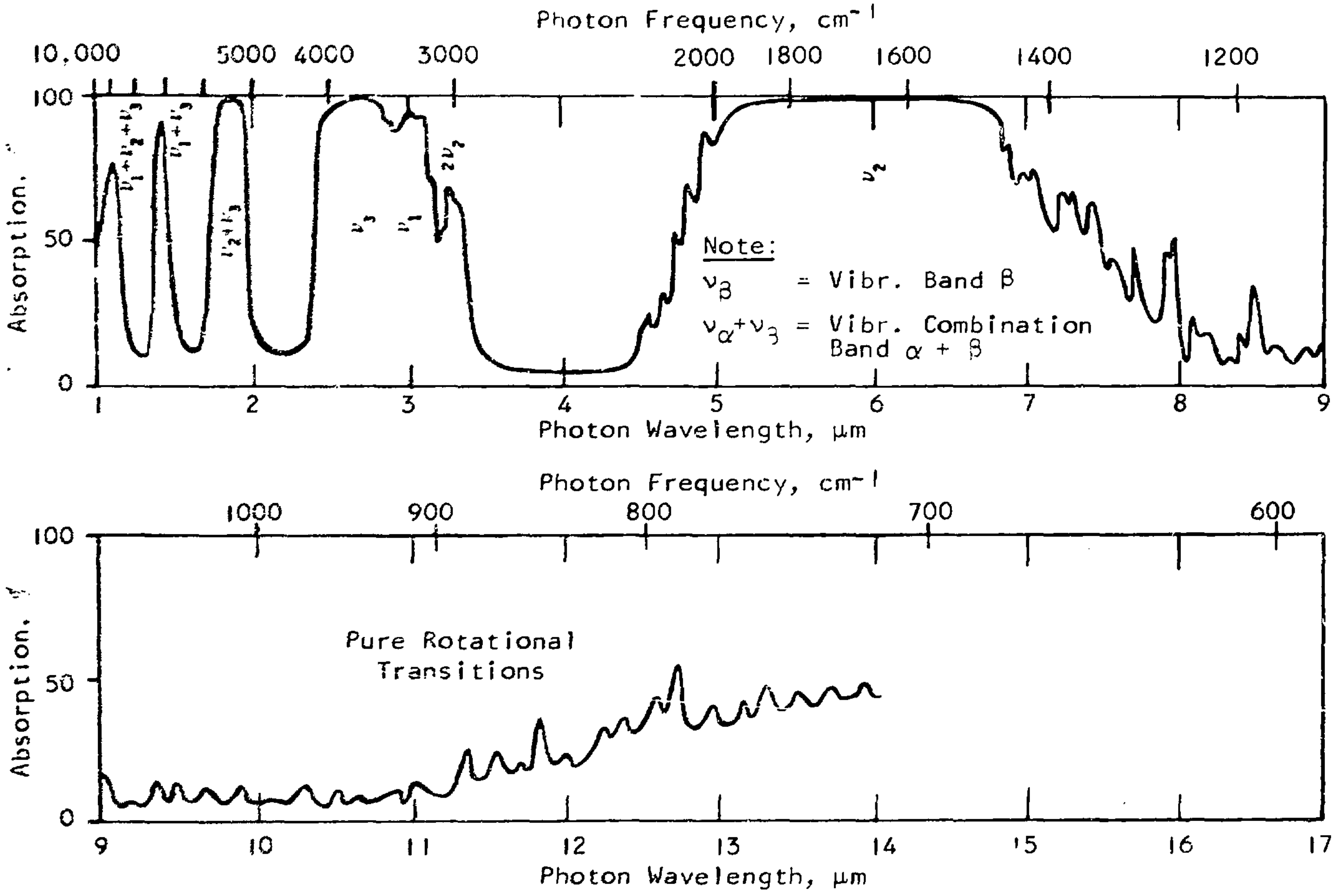

FIGURE 4-14. INFRARED ABSORPTION SPECTRUM OF H_2O FOR (pressure) × (pathlength) ≈ 50 Torr·m
(Adapted from Ref. 40)

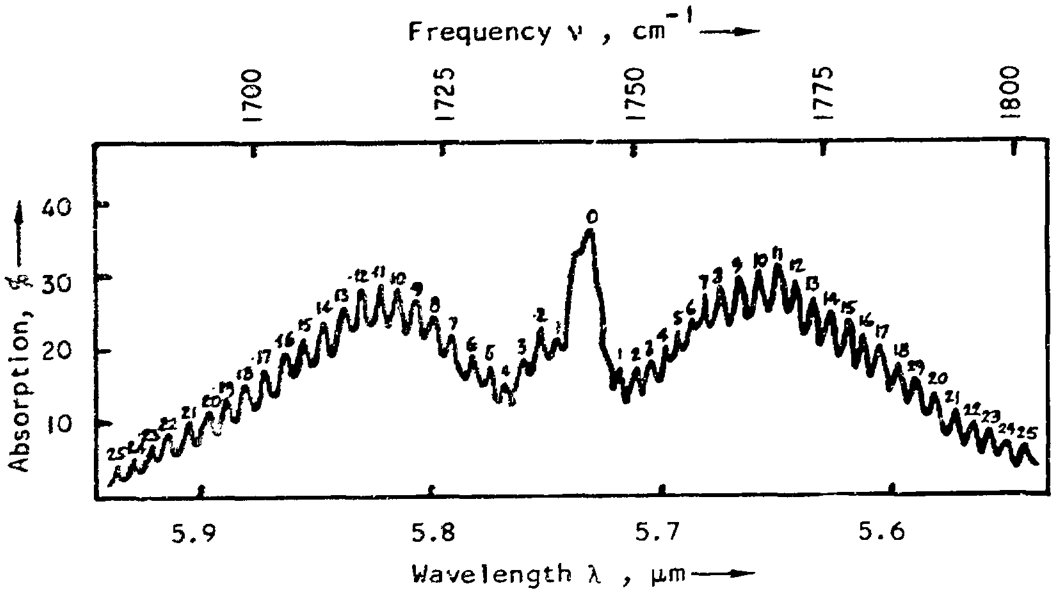

FIGURE 4-15. FINE STRUCTURE OF THE FUNDAMENTAL ν_2 OF H_2CO at 5.73 µ. — The length of the absorbing path was about 10 cm at an unknown pressure. The numbers on the maxima are (J-1) values, where $J = \sup(J_m, J_n)$. (After Refs. 10, 39.)

With the substitutions (4.263) and (4.264) we then obtain, using (4.204) through (4.206):

$$g_v^P(J) = \frac{(2J+3)\ \nu_A^{1/2}\ H(J^2-W)\ u^{PR}(J,W)}{3\pi^{1/2}\ (kT/h)^{3/2}} \cdot$$
$$(0 \leq J < \infty)$$

$$\cdot \quad \exp-\left[\frac{J(J+1)\left(\frac{\nu_B+\nu_C}{2}\right) + W\left(\nu_A - \frac{\nu_B+\nu_C}{2}\right)}{kT/h}\right] \quad , \ \text{Hz}^{-1} \qquad (4.265)$$

$$g_v^Q(J) = \frac{(2J+1)\ \nu_A^{1/2}\ H(J^2-W)\ u^Q(J,W)}{3\pi^{1/2}(J+1)\ \xi_{BC}(kT/h)^{3/2}} \cdot$$
$$(1 \leq J < \infty)$$

$$\cdot \quad \exp-\left[\frac{J(J+1)\left(\frac{\nu_B+\nu_C}{2}\right) + W\left(\nu_A - \frac{\nu_B+\nu_C}{2}\right)}{kT/h}\right] \quad , \ \text{Hz}^{-1} \qquad (4.266)$$

$$g_v^R(J) = \frac{(2J-1)\ \nu_A^{1/2}\ H(J^2-W)\ u^{PR}(J,W)}{3\pi^{1/2}\ (kT/h)^{3/2}} \cdot$$
$$(1 \leq J < \infty)$$

$$\cdot \quad \exp-\left[\frac{J(J+1)\left(\frac{\nu_B+\nu_C}{2}\right) + W\left(\nu_A - \frac{\nu_B+\nu_C}{2}\right)}{kT/h}\right] \quad , \ \text{Hz}^{-1} \qquad (4.267)$$

Here, for Type-A bands, the factor $u(J,W)$ is given by:

$$\underset{\text{(Type-A bands)}}{u^{PR}(J,W)} = \Big(2 - \delta(W)\Big) \tag{4.268a}$$

$$\underset{\text{(Type-A bands)}}{u^{Q}(J,W)} = \Big(2 - \delta(W)\Big) , \tag{4.268b}$$

where $\delta(x)$ is the Dirac delta function defined before (see Eq. (4.149)). The factor ξ_{BC} is given by:

$$\xi_{BC} = \frac{\Delta\nu_{BC}}{\nu_{BC}} = \frac{B_m - B_n + C_m - C_n}{\frac{1}{2}\left(B_m + B_n + C_m + C_n\right)} = \frac{c}{\nu_{BC}}\left[\sum_{\beta}\alpha_{\beta}^{B}\left(\nu_{\beta_m} - \nu_{\beta_n}\right) + \alpha_{\beta}^{C}\left(\nu_{\beta_m} - \nu_{\beta_n}\right)\right] \tag{4.269}$$

Values of α_{β}^{A} , α_{β}^{B} , and α_{β}^{C} for H_2O are listed in Table 4-6. The ν_3 vibrational band of H_2O which is of Type A, can be fairly well approximated by Eqs. (4.265) through (4.269).

The ν-dependent g_ν-functions for Type-A bands become, similarly to Eqs. (4.213) and (4.214):

$$\boxed{\underset{\left(\substack{0 \le \nu < \infty \\ \text{Type-A Bands}}\right)}{g_{\nu}^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})} = \frac{|\nu - \nu_{mn}|}{3(\nu_B + \nu_C)\ kT/h} \exp-\left\{\frac{(\nu - \nu_{mn})^2}{2(\nu_B + \nu_C)\ kT/h}\right\} ,\ \text{Hz}^{-1}} \tag{4.270}$$

$$\boxed{\underset{\left(\substack{0 < \nu < \nu_{mn}\ ,\ \text{if } \Delta\nu_{BC} > 0 \\ \nu_{mn} < \nu < \infty\ ,\ \text{if } \Delta\nu_{BC} < 0 \\ \text{Type-A Bands}}\right)}{g_{\nu}^{Q}(\nu,\nu_{mn},\Delta\nu_{mn})} = \frac{h}{3\zeta_{BC}kT} \exp-\left\{\frac{|\nu_{mn} - \nu|}{\xi_{BC}kT/h}\right\} ,\ \text{Hz}^{-1}} \tag{4.271}$$

TABLE 4-6. ROTATIONAL CONSTANTS OF H_2O IN THE ELECTRONIC GROUND STATE (After Ref. 10)

Fundamental Rotational Constants A, B, C				Vibration-Rotation Interaction Constants α_β^A, α_β^B, α_β^C			Rovibrational Band Types*	
Lowest Vibrational Level (0)		Equilibrium Position (e)		ν_1-Vibration ($\beta = 1$)	ν_2-Vibration ($\beta = 2$)	ν_3-Vibration ($\beta = 3$)	Normal Vibration (cm^{-1})	Band-Type
cm^{-1}	THz	cm^{-1}	THz	cm^{-1}	cm^{-1}	cm^{-1}		
$A_o = 27.88$	$\nu_A^o = 0.8358$	$A_e = 27.42$	$\nu_A^e = 0.8193$	$\alpha_1^A = +0.737$	$\alpha_2^A = -3.323$	$\alpha_3^A = +1.241$	$\nu_1(3657)$	Type-B
$B_o = 14.51$	$\nu_B^o = 0.4347$	$B_e = 14.57$	$\nu_B^e = 0.4368$	$\alpha_1^B = +0.222$	$\alpha_2^B = -0.157$	$\alpha_3^B = +0.112$	$\nu_2(1595)$	Type-B
$C_o = 9.29$	$\nu_C^o = 0.2782$	$C_e = 9.49$	$\nu_C^e = 0.2845$	$\alpha_1^C = +0.180$	$\alpha_2^C = +0.135$	$\alpha_3^C = +0.129$	$\nu_3(3756)$	Type-A

*The Q-Branch for Type-B bands is diffuse and spread over the P- and R-Branches; for Type-A bands, the Q-Branch is mostly at the band-center.

The band-spread $\Delta\nu_{mn}$ for an asymmetric-top rotor we shall take to be:

$$\boxed{\Delta\nu_{mn} = \sqrt{2(\nu_B + \nu_C)\ kT/h}\ ,\ \text{Hz}} \tag{4.272}$$

and then the dimensionless shape-functions $b(\nu,\nu_{mn},\Delta\nu_{mn})$ for Type-A bands can be written:

$$\boxed{\underset{\begin{pmatrix} 0 \le \nu \le \infty \\ \text{Type-A Bands} \end{pmatrix}}{b_\nu^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})} = \frac{2|\nu - \nu_{mn}|}{3\ \Delta\nu_{mn}} \exp-\left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}}\right)^2} \tag{4.273}$$

$$\boxed{\underset{\begin{pmatrix} 0 < \nu \le \nu_{mn}\ ,\ \text{if } \Delta\nu_{BC} > 0 \\ \nu_{mn} \le \nu < \infty\ ,\ \text{if } \Delta\nu_{BC} < 0 \\ \text{Type-A Bands} \end{pmatrix}}{b_\nu^{Q}(\nu,\nu_{mn},\Delta\nu_{mn})} = \frac{2(\nu_B+\nu_C)}{3\xi_{BC}\Delta\nu_{mn}} \exp-\left\{\frac{2(\nu_B+\nu_C)\,|\nu_{mn}-\nu|}{\xi_{BC}\Delta\nu_{mn}^2}\right\}} \tag{4.274}$$

For Type-B bands, the selection rule (4.251) applies, which in effect forbids transitions with $\Delta K_{\pm 1} = \pm 1$ for all branches and also $\Delta K_{\pm 1} = 0$ for the Q-Branch. Thus $\Delta K_{\pm} = 0, \pm 2, \ldots.$ apply to P- and R-Branch transitions and $\Delta K_{\pm} = \pm 2, \ldots.$ to Q-Branch transitions as indicated in Figure 4-12. The meaning of the parameters K_{+1} and K_{-1} was discussed in section 3.4.5 (following Eq. (3.208)). Note here that in contrast to symmetric-top rotors for which $\Delta K = 0, \pm 1$, the asymmetric-top rotor can have $\Delta K_{\pm 1} = \pm 2, \pm 3$, etc.

As shown in Figure 4-16, the Type-B band of the asymmetric-top goes over into a ⊥ band of a symmetric-top or linear rotor when $\rho = \nu_B/\nu_A \to 0$, that is when $\nu_A \to \infty$. Although the similarity of Type-B bands and ⊥ bands is less good than that of Type-A and // bands, for many applications it appears satisfactory to model the Type-B bands of the asymmetric-top rotor after the ⊥ bands of the symmetric-top rotor using again the substitutions (4.263) and (4.264).

Because of the selection rule (4.251), instead of Eq. (4.268), we now have to use the following expression in the relations (4.265) through (4.267) for Type-B bands:

$$\underset{\text{(Type-B Bands)}}{u^{PR}(J,W)} = 1 - \delta(W-1) \tag{4.275}$$

$$\underset{\text{(Type-B Bands)}}{u^{Q}(J,W)} = H(|W_m^{1/2}| - |W_n|^{1/2} - 2) \tag{4.276}$$

Here $H(x)$ and $\delta(x)$ are the Heaviside unit step function and the Dirac delta function defined by Eq. (4.149).

The band-shape function for Type-B bands, modeled after Eqs. (4.220) and (4.221), then takes the form:

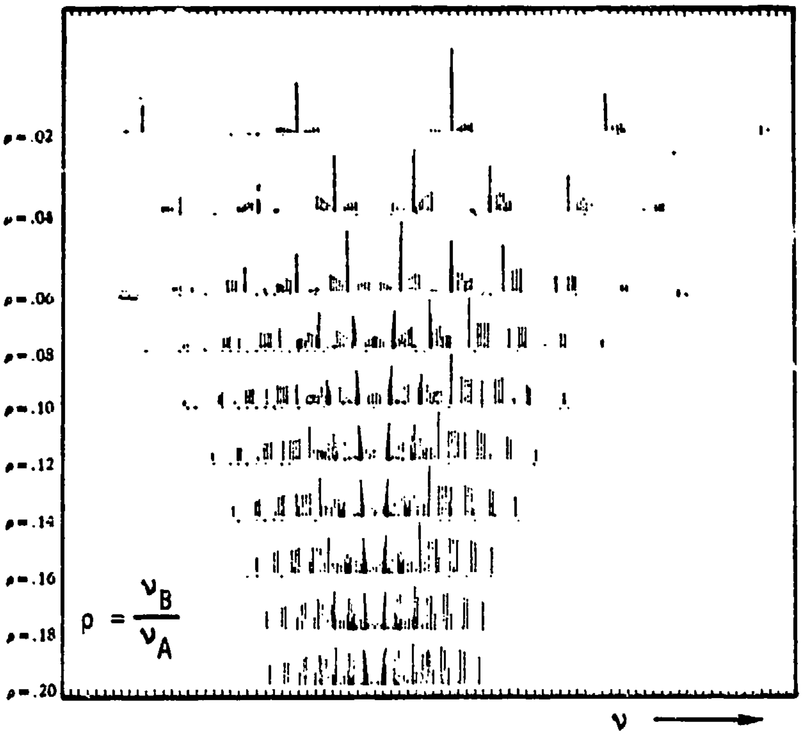

FIGURE 4-16. TYPE-B BANDS FOR $\rho = \nu_B/\nu_A = 0.02, \ldots, 0.20$. The intervals between divisions at the bottom as well as at the top are 5 ν_C. Room temperature and $I_C = 20 \times 10^{-40}$ gm cm^2 are assumed. (After Refs. 10, 39.)

$$\begin{gathered}
\underset{\begin{pmatrix} 0 < \nu < \infty \\ \text{Type-B Bands} \end{pmatrix}}{b_\nu^{PR}(\nu, \nu_{mn}, \Delta\nu_{mn})} = \frac{2}{3\Delta\nu_{mn}} \left(\frac{\nu_B + \nu_C}{2\pi\nu_A} \right)^{1/2} \left[\exp - \left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}} \right)^2 \right. + \\
\left. - \exp - \left\{ \frac{\nu_B + \nu_C}{2\nu_A} \left(\left(\frac{\nu_B + \nu_C}{\Delta\nu_{mn}} \right)^2 \left(\frac{\nu_A}{|\nu_B + \nu_C - \nu_A|} - 1 \right)^2 + 1 \right) \right\} \right] + \\
+ \frac{2|\nu - \nu_{mn}|}{3\Delta\nu_{mn}} \left(\frac{\nu_B + \nu_C}{2\nu_A} \right) \left(\frac{\nu_B + \nu_C}{2\nu_A - \nu_B - \nu_C} \right)^{1/2} \left(\exp - \left\{ \frac{\nu_B + \nu_C}{2\nu_A} \left(\frac{\nu - \nu_{mn}}{\Delta\nu_{mn}} \right)^2 \right\} \right) \cdot \\
\cdot \left[\operatorname{erf} \left\{ \left(\frac{\nu_A}{|\nu_B + \nu_C - \nu_A|} - 1 \right) \left(\frac{(\nu_B + \nu_C)^2}{2\nu_A (2\nu_A - \nu_B - \nu_C)} \right) \left(\frac{|\nu - \nu_{mn}|}{\Delta\nu_{mn}} \right) \right\} \right. + \\
\left. - \operatorname{erf} \left\{ \left(\frac{\nu_A - \nu_B}{\nu_A} \right)^{1/2} \left(\frac{|\nu - \nu_{mn}|}{\Delta\nu_{mn}} \right) \right\} \right]
\end{gathered}$$

(4.277)

$$\begin{gathered}
\underset{\begin{pmatrix} 0 < \nu < \nu_{mn} \text{ , if } \Delta\nu_{BC} > 0 \\ \nu_{mn} < \nu < \infty \text{ , if } \Delta\nu_{BC} < 0 \\ \text{Type-B Bands} \end{pmatrix}}{b_\nu^{Q}(\nu, \nu_{mn}, \Delta\nu_{mn})} = \frac{\nu_B + \nu_C}{3\xi_{BC}\Delta\nu_{mn}} \left(\frac{2\nu_A}{2\nu_A - \nu_B - \nu_C} \right)^{1/2} \cdot \\
\cdot \left[\exp - \left\{ \frac{(\nu_B + \nu_C)\left(2\xi_{BC}|\nu - \nu_{mn}| - (2\nu_A - \nu_B - \nu_C)\right)}{\xi_{BC}^2 \, \Delta\nu_{mn}^2} \right\} \right] \cdot
\end{gathered}$$

$$
\begin{aligned}
&\cdot \left[\operatorname{erf}\left\{ \left(\frac{(\nu_B + \nu_C)(2\nu_A - \nu_B - \nu_C)}{\xi_{BC}^2 \, \Delta\nu_{mn}^2} \right)^{1/2} \cdot \right. \right. \\
&\left. \cdot \left(\frac{2\nu_A - \nu_B - \nu_C}{\nu_B + \nu_C} \left(\left(\frac{2\xi_{BC}(\nu_B+\nu_C)\,|\nu_{mn}-\nu|}{(2\nu_A-\nu_B-\nu_C)^2} + 1 \right)^{1/2} - 1 \right) - 1 \right) \right\} + \\
&+ \operatorname{erf}\left\{ \left(\frac{(\nu_B + \nu_C)(2\nu_A - \nu_B - \nu_C)}{\xi_{BC}^2 \, \Delta\nu_{mn}^2} \right)^{1/2} \cdot \right. \\
&\left. \left. \cdot \left(\frac{2\nu_A - \nu_B - \nu_C}{\nu_B + \nu_C} \left(\left(\frac{2\xi_{BC}(\nu_B+\nu_C)\,|\nu_{mn}-\nu|}{(2\nu_A-\nu_B-\nu_C)^2} + 1 \right)^{1/2} + 1 \right) + 1 \right) \right\} \right]
\end{aligned}
\qquad (4.278)
$$

Of course the functions $g_v(\nu,\nu_{mn},\Delta\nu_{mn})$ are given by (4.277) and (4.278) divided by $\Delta\nu_{mn}$, since $g_v(\nu,\nu_{mn},\Delta\nu_{mn}) = b_v(\nu,\nu_{mn},\Delta\nu_{mn})/\Delta\nu_{mn}$.

For the detailed rovibrational structure of an asymmetric-top rotor we can write:

$$
\boxed{g_{rov}^{PQR}(\nu,\nu_{mn},\Delta\nu_{mn}) = h_v^{PQR}(J,W,\nu_{mn},\Delta\nu_{mn}) \cdot g_{J,W}(\nu,\nu_{JW},\Delta\nu_{JW}) \;,\ \mathrm{Hz}^{-1}}
\qquad (4.279)
$$

Here $g_{J,W}$ is the pressure or temperature line-broadening function given in sections 4.3 and 4.4 for a particular line with given value of J and W, and:

$$\boxed{\begin{aligned}
h_{\nu}^{PQR}(J,W,\nu_{mn},\Delta\nu_{mn}) &= \left(\frac{\nu_A^{1/2}\left(\frac{\nu_B+\nu_C}{2}\right)^{1/2}}{3\pi^{1/2}\;kT/h}\right)\cdot\Big\{(2J+3)H(\nu_{mn}-\nu_{JW})\cdot \\
&\cdot H(-\nu_{JW}^{Q})H(J)\,u^{PR}(J,W)\,\frac{\delta\nu_W}{\Delta\nu_{mn}} + (2J+1)H(\nu_{JW}-\nu_{mn})H(-\nu_{JW}^{Q})H(J-1)\cdot \\
&\cdot u^{PR}(J,W)\,\frac{\delta\nu_W}{\Delta\nu_{mn}} + \frac{2J+1}{\xi_{BC}(J+1)}\,H(-\nu_{JW})H(J-1)\;u^{Q}(J,W)\,\frac{\delta\nu_W^{Q}}{\Delta\nu_{mn}}\Big\}\cdot \\
&\cdot H(J^2-W)\cdot\left[\exp-\left\{\frac{J(J+1)\left(\frac{\nu_B+\nu_C}{2}\right)+W(\nu_A-\nu_B)}{kT/h}\right\}\right],
\end{aligned}}$$

(4.280a)

where for Type-A bands $u^{PR}(J,W)$ and $u^{Q}(J,W)$ are given by Eq. (4.268), and for Type-B bands they are given by Eqs. (4.275) and (4.276). The parameter ν_{JW} and ν_{JW}^{Q} were defined in Eqs. (4.255) and (4.262), while $\delta\nu_W$ and $\delta\nu_W^{Q}$ are defined by:

$$\delta\nu_W = \nu_{ABC}\big(W(J)-W(J-1)\big)\left[\int_{\nu=\nu_{JW}-\frac{1}{2}\nu_{ABC}\left(W(J)-W(J-1)\right)}^{\nu=\nu_{JW}+\frac{1}{2}\nu_{ABC}\left(W(J)-W(J-1)\right)} g_{JW}(\nu,\nu_{JW},\Delta\nu_{JW})\;d\nu\right]^{-1} \quad (4.280b)$$

$$\delta\nu_W^{Q} = \nu_{ABC}\;\Delta W_Q\left[\int_{\nu=\nu_{JW}^{Q}-\frac{1}{2}\Delta W_Q\,\nu_{ABC}}^{\nu_{JW}^{Q}+\frac{1}{2}\Delta W_Q\,\nu_{ABC}} g_{JW}(\nu,\nu_{JW},\Delta\nu_{JW})\;d\nu\right]^{-1} \quad (4.280c)$$

$$\Delta W_Q = W_m(J) - W_n(J) - W_m(J-1) + W_n(J-1) \quad (4.280d)$$

Here ν_{ABC} was defined by Eq. (4.260).

4.8 VIBRATIONAL BROADENING OF ELECTRONIC TRANSITIONS

4.8.1 Diatomic Vibrators

To obtain the smeared-out band-shape function of a vibrationally broadened electronic transition, we proceed in an analogous manner to that given in section 4.7 for rotationally-broadened vibrational transitions. The fraction of molecules in an electronic state Λ, vibrational state v, and rotational state J is given by:

$$N_{\Lambda,v,J} = N_o f_\Lambda f_v f_J \tag{4.281}$$

where N_o is the total number of molecules, f_v and f_J were given by Eqs. (4.80) and (4.81), and:

$$f_\Lambda = \frac{w_\Lambda \exp-\left(\frac{h\nu_\Lambda}{kT}\right)}{Z_\Lambda} \tag{4.282}$$

$$Z_\Lambda = \sum_\Lambda w_\Lambda \exp-\left(\frac{h\nu_\Lambda}{kT}\right) \approx 1 \text{ , for } T \lesssim 3000^\circ K \tag{4.283}$$

Here $h\nu_\Lambda$ is the energy level of a general electronic state Λ.

Ignoring the rotational substructure, the energy levels or frequencies of the various vibrational levels of a diatomic molecule in the electronic state Λ are to first order given by:

$$\nu_{\Lambda,v} = \nu_{\Lambda_i} + \nu_{v_i} = \nu_{\Lambda_i} + \left(v_i + \frac{1}{2}\right)\nu_{e_i} - \left(v_i + \frac{1}{2}\right)^2 x_{e_i}\nu_{e_i} \quad , \tag{4.284}$$

where:

$$\nu_{v_i} = \left(v_i + \frac{1}{2}\right)\nu_{e_i} - \left(v_i + \frac{1}{2}\right)^2 x_{e_i}\nu_{e_i} \ , \ \mathrm{Hz} \tag{4.285}$$

Here ν_{e_i} is the fundamental vibrational frequency of the diatomic molecule in the electronic state i, and x_{e_i} is the anharmonic coefficient of the diatomic vibration discussed in section 3.3.1 and Appendix C. The values of the vibrational constants ν_{e_i} and x_{e_i} depend on the electronic level i that the molecule is in, that is $\nu_{e_m} \neq \nu_{e_n}$ and $x_{e_m} \neq x_{e_n}$ in general. If no subscript is used on ν_e and x_e , it is assumed that the molecule is in the ground electronic level.

According to Eqs. (1.23) and (1.24), the number of photons emitted from a diatomic molecule at electronic level Λ_m , deexciting to electronic level Λ_n is:

$$\frac{dN_\varphi}{dt} = N_o f_{\Lambda_m} A_{\substack{mn\\ elc}} = N_m A^o_{\substack{mn\\ elc}} F^{vib/rot}_{mn} f_{v,J} \ , \ \frac{\text{photons}}{\text{sec}} \tag{4.286}$$

in which:

$$N_m = N_o f_{\Lambda_m} \tag{4.287}$$

In what follows we shall not specify what particular rotational transition occurred (any allowed one can take place), but only what the vibrational energy perturbation is since the latter is a much stronger perturbation than the former. Then we can simplify Eq. (4.286) to:

$$\frac{dN_\varphi}{dt} = N_m A^{\circ}_{\substack{mn\\ elc}} F^{vib}_{mn} f_{v_m} = N_m A^{\circ}_{\substack{mn\\ elc}} G^{elc}_{mn} \, , \quad \frac{\text{photons}}{\text{sec}} \, , \tag{4.288}$$

where:

$$F^{vib}_{mn} = \frac{{}^{\circ}C^{vib}_{mn}}{w_{v_m}(v_m)} \tag{4.289}$$

$$G^{elc}_{mn} = F^{vib}_{mn} f_{v_m} = {}^{\circ}C^{vib}_{mn} \left[\exp\text{-}\left(v_m \, h\nu_{e_m} \big/ kT\right)\right] \Big/ Z_{v_m} \tag{4.290}$$

Here Z_{v_m} is the normalization factor which in the case of a diatomic molecule equals $Z_v = \left[1 - \exp\text{-}(h\nu_e/kT)\right]^{-1}$.

Now by the same reasoning as was given for ${}^{\circ}C^{rot}_{mn}$ via Eqs. (4.97) through (4.100), we must have that:

$${}^{\circ}C^{vib}_{mn} = w_m(v_m) \tag{4.291}$$

Further since for a diatomic molecule always $w_m = 1$, we get that:

$$G^{elc}_{mn}(v_m) = \left[\exp\text{-}\left(\frac{v_m \, h\nu_{e_m}}{kT}\right)\right] \Big/ Z_{v_m} \tag{4.292}$$

Defining next the function $g_e(\nu)$ for the strength per unit of emitted photon frequency range according to Eq. (1.29), we must divide Eq. (4.292) by the parameter:*

$$\Delta\nu_{sp} = \left|\frac{dv_m}{d\nu}\right|^{-1} = \left|\frac{d}{d\nu}\left(\frac{\nu_{v_m}}{\nu_{e_m}\left(1-(2v_m+1)x_{e_m}\right)}\right)\right|^{-1} \approx \nu_{e_m}\left|\frac{d\nu_{v_m}}{d\nu}\right|^{-1} , \text{ Hz} \tag{4.293}$$

which we shall develop further below. Thus:

$$g_e(\nu) \equiv \left(G^{vib}_{mn}(\nu)\right) \cdot \left(\frac{dv_m}{d\nu}\right) = \frac{\exp-\left(\dfrac{v_m\, h\nu_{e_m}}{kT}\right)}{Z'_{v_m}\ \Delta\nu_{sp}} , \text{ Hz}^{-1} \tag{4.294}$$

Here we primed Z'_{v_m}, since we shall assume $g_e(\nu)$ to be continuous and therefore the normalization factor should be redetermined. The approximation $\nu_{e_m}\left[1 - (2v_m+1)x_{e_m}\right] \approx \nu_{e_m}$ in (4.293) is quite reasonable usually.

The photon emission frequencies ν of vibronic transitions are according to Eq. (4.284):

$$\begin{aligned}\nu = \nu'_{mn} + \nu_{v_m} - \nu_{v_n} &= \nu'_{mn} + \left(v_m + \frac{1}{2}\right)\nu_{e_m} - \left(v_m + \frac{1}{2}\right)^2 x_{e_m}\nu_{e_m} + \\ &- \left(v_n + \frac{1}{2}\right)\nu_{e_n} + \left(v_n + \frac{1}{2}\right)^2 x_{e_n}\nu_{e_n} = \\ &= \nu_{mn} + \left(\nu_{o_m}v_m - \nu_{o_n}v_n\right) - \left(x_{e_m}\nu_{e_m}\, v_m^2 - x_{e_n}\nu_{e_n}\, v_m^2\right) , \text{ Hz} ,\end{aligned} \tag{4.295}$$

---

*The approach followed here is generally similar to one given in Ref. 41.

where:

$$\nu'_{mn} = \nu_{\Lambda_m} - \nu_{\Lambda_n} \tag{4.296}$$

$$\nu_{mn} = \nu'_{mn} + \frac{1}{2}\left(\nu_{e_m} - \nu_{e_n}\right) - \frac{1}{4}\left(x_{e_m}\nu_{e_m} - x_{e_n}\nu_{e_n}\right), \text{ Hz} \tag{4.297*}$$

$$\nu_{o_i} = \nu_{e_i} - x_{e_i}\nu_{e_i}, \text{ Hz} \tag{4.298*}$$

The subscripts m and n on v, ν_e, and x_e refer to the upper electronic state m, and the lower electronic state n, as before.

Note that if $\nu_e = \nu_{e_m} = \nu_{e_n}$ and $x_e = x_{e_m} = x_{e_n}$, Eq. (4.295) reduces to:

$$\nu = \nu_{mn} + \nu_o\left(v_m - v_n\right) - x_e\nu_e\left(v_m^2 - v_n^2\right), \text{ Hz} \tag{4.299}$$

Here $\nu_{mn} \rightarrow \nu_{mn}$, and ν_o is still defined by Eq. (4.298). Usually the difference between ν_{mn} and ν'_{mn} is extremely small even if $\nu_{e_m} \neq \nu_{e_n}$, and no great error is made if we set $\nu_{mn} = \nu'_{mn}$.

In contrast to the sharp selection rules for allowed changes in the rotational quantum number J in intervibrational transitions, no general selection rules can be formulated for allowed changes in the vibrational quantum number v in interelectronic transitions. However the Franck-Condon

---

*Herzberg (Ref. 2) uses the symbols $\omega_e = (\nu_e/c)$, cm^{-1}, and $\omega_e x_e = (x_e\nu_e/c)$, cm^{-1}, in his tables.

principle may be applied to simplify matters, as illustrated in Figures 4-17 and 4-18. According to this principle, if the molecular equilibrium distance r_{e_n} for the molecular potential curve of the lower electronic state equals that of the upper electronic state r_{e_m}, transitions with $v_n = v_m$ will be highly favored. In fact the probability or ratio of the $v_n = v_m$ transitions to all transitions $v_n \neq v_m$ and $v_n = v_m$ is given in this case by (Ref. 42):

$$p(v_n = v_m) = \frac{I(v_n = v_m)}{\sum\limits_{v_n} I(v_m \rightarrow v_n)} = \frac{\sqrt{\nu_{e_n} \nu_{e_m}}}{\frac{1}{2}\left(\nu_{v_n} + \nu_{v_m}\right)} \qquad (4.300)$$

For most molecules ν_{e_m} differs only by some 10 to 50 percent from ν_{e_n}. Even if $\nu_{e_m} = \frac{1}{2} \nu_{e_n}$, the probability or fraction of $v_n = v_m$ transitions equals 0.9426 according to (4.300). Thus for electronic molecular transitions with $r_{e_n} = r_{e_m}$, we have for all practical purposes the selection rule $v_n = v_m$ or $\Delta v = 0$.

For cases that $r_{e_m} - r_{e_n} \neq 0$, we get two preferred Δv's according to the Franck-Condon principle, as illustrated in Figure 4-19. To obtain analytical values, we shall assume the "Morse potential" shown in Figure 4-20 for the molecular potential energy (Ref. 16):

$$U_i = D_{e_i} \left\{1 - \exp{-\beta_i (s - r_{e_i})}\right\}^2 \quad , \ \mathrm{cm}^{-1} , \qquad (4.301)$$

or:

$$\nu_{v_i} = \nu_{d_i} \left\{1 - \exp{-\beta_i (s - r_{e_i})}\right\}^2 \quad , \ \mathrm{Hz} \qquad (4.302)$$

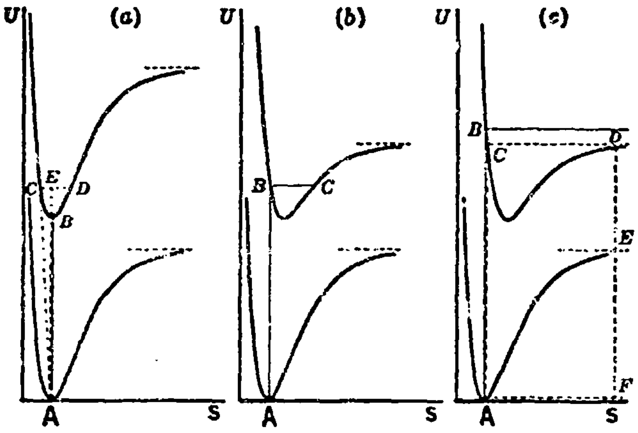

FIGURE 4-17. POTENTIAL CURVES EXPLAINING THE INTENSITY DISTRIBUTION IN ABSORPTION ACCORDING TO THE FRANCK-CONDON PRINCIPLE. In (c), AC gives the energy of the dissociation limit, EF the dissociation energy of the ground state, and DE the excitation energy of the dissociation products (after Ref. 2).

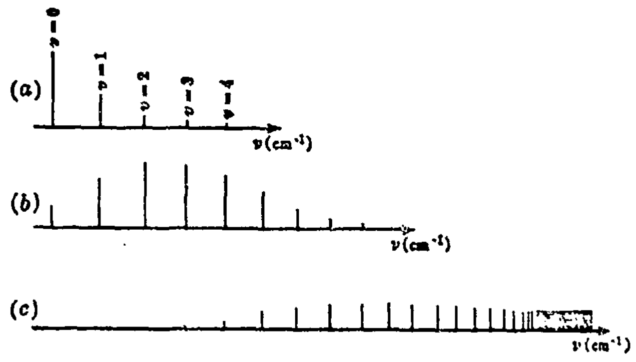

FIGURE 4-18. THREE TYPICAL CASES OF INTENSITY DISTRIBUTION IN ABSORPTION BAND SERIES (SCHEMATIC). For the sake of simplicity, the bands are drawn with the same separations in the three cases. Naturally, these cases would be observed in different band systems, which would in general not have the same band separations (after Ref. 2).

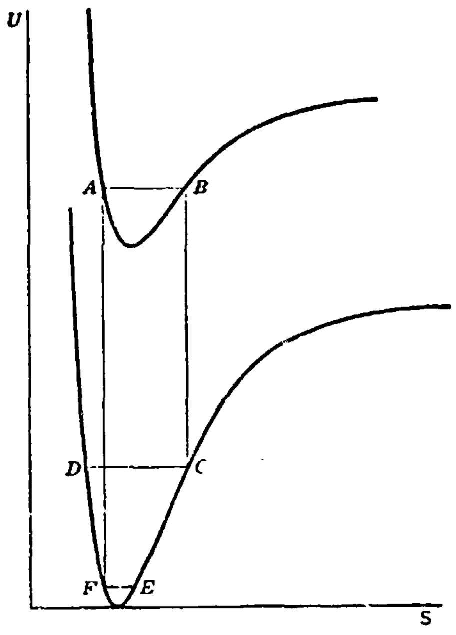

FIGURE 4-19. POTENTIAL CURVES EXPLAINING THE INTENSITY DISTRIBUTION IN EMISSION ACCORDING TO THE FRANCK-CONDON PRINCIPLE (after Ref. 2).

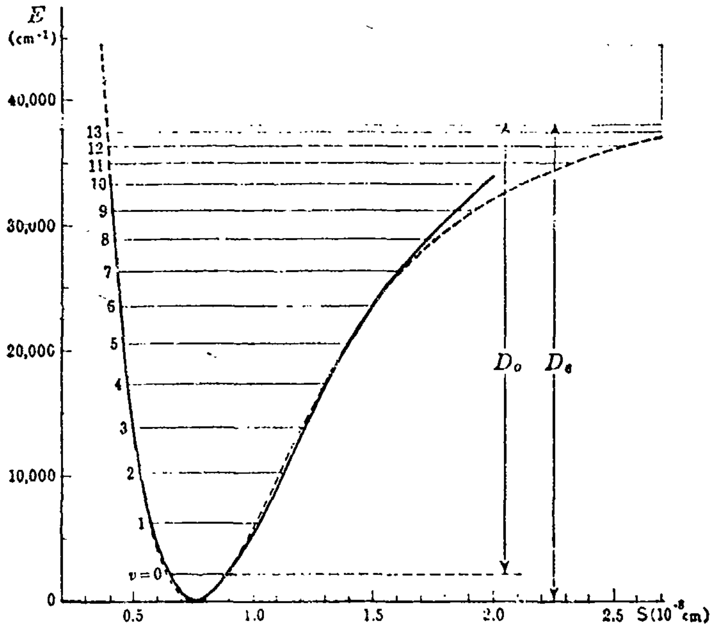

FIGURE 4-20. POTENTIAL CURVE OF THE H_2 GROUND STATE WITH VIBRATIONAL LEVELS AND CONTINUOUS TERM SPECTRUM. The full curve is drawn according to Rydberg's data. The broken curve is a Morse curve. The continuous term spectrum, above v = 14, is indicated by vertical hatching. The vibrational levels are drawn up to the potential curve, that is, their end points correspond to the classical turning points of the vibration. It must be remembered that in quantum theory these sharp turning points are replaced by broad maxima of the probability amplitude ψ (after Ref. 2).

The subscript i in (4.301) and (4.302) refers to the electronic level i, that is for each electronic level i, a different Morse potential with different values of the three constants D_e, β, and r_e exists. These constants are defined by:

D_{e_i} = Molecular dissociation constant for electronic level i, cm^{-1}, tabulated for different molecules in Herzberg's tables (Ref. 2).

$$\nu_{d_i} = c\, D_{e_i} \text{ , Hz} \tag{4.303}$$

r_{e_i} = Equilibrium distance of vibrating partners in electronic state i, cm, tabulated by Herzberg for different molecules (Ref. 2).

$$\beta_i = \left(\frac{2\pi^2\, \bar{M}_{AB}}{h\nu_{d_i}}\right)^{1/2} \nu_{e_i} \text{ , } cm^{-1} \tag{4.304}$$

Here:

$$\bar{M}_{AB} = \frac{M_A\, M_B}{M_A + M_B} \text{ , gms} \tag{4.305}$$

M_A, M_B = Mass of vibrating partners A and B, gms, of the two atoms making up the diatomic molecule.

From (4.304) we see that conversely, the fundamental vibrational frequency ν_{e_i} is related to the Morse constants by (Ref. 16):

$$\nu_{e_i} = \beta_i \left(\frac{D_{e_i}\, hc}{2\pi^2\, \bar{M}_{AB}}\right)^{1/2} \text{ , Hz} \tag{4.306}$$

Similarly, the anharmonic constant x_{e_i} can be shown to be related to the Morse constants by (Ref. 16):

$$x_{e_i} = \frac{\nu_{e_i}}{4c\, D_{e_i}} \tag{4.307}$$

Herzberg (Ref. 2), has tabulated values of $\omega_{e_i} = \nu_{e_i} c^{-1}$, D_{e_i}, and r_{e_i} for various molecules, and thus the Morse constants for these molecules can be directly obtained (β_i is gotten via (4.304)).

From Eqs. (4.302) and (4.285), we can calculate analytically the two v_n values (which we shall label v_n^- and v_n^+) of the lower electronic state (levels FE and CD in Figure 4.20) corresponding to a given value v_m of the upper electronic state:

$$v_n^-(v_m) + \frac{1}{2} = \frac{1}{2\, x_{e_n}} \left\{ 1 - \sqrt{1 - \frac{4\, \nu_{v_n}^-\, x_{e_n}}{\nu_{e_n}}} \right\} \approx \frac{\nu_{v_n}^-}{\nu_{e_n}}\, , \tag{4.308}$$

and:

$$v_n^+(v_m) + \frac{1}{2} = \frac{1}{2\, x_{e_n}} \left\{ 1 - \sqrt{1 - \frac{4\, \nu_{v_n}^+\, x_{e_n}}{\nu_{e_n}}} \right\} \approx \frac{\nu_{v_n}^+}{\nu_{e_n}} \tag{4.309}$$

Here:

$$\nu_{v_n}^- = \nu_{d_n} \left[1 - \left\{ 1 + \sqrt{\frac{\nu_{v_m}}{\nu_{d_m}}} \right\}^{\gamma_n} \exp -\beta_n \left(r_{e_m} - r_{e_n} \right) \right]^2 , \ \text{Hz} \tag{4.310}$$

$$\nu^{+}_{v_n} = \nu_{d_n}\left[1 - \left\{1 - \sqrt{\frac{\nu_{v_m}}{\nu_{d_m}}}\right\}^{\gamma_n} \exp-\beta_n\left(r_{e_m} - r_{e_n}\right)\right]^2 \quad , \text{ Hz} \quad , \qquad (4.311)$$

while ν_{v_m} is given by Eq. (4.286) and the parameter γ_n is given by:

$$\gamma_n = \frac{\beta_n}{\beta_m} = \left(\frac{\nu_{e_n}}{\nu_{e_m}}\right)\left(\frac{\nu_{d_m}}{\nu_{d_n}}\right)^{1/2} \qquad (4.312)$$

The parameter β_i was defined in Eq. (4.304).

The above expressions were developed for emission m → n. For absorption n → m, the same expressions (4.308) through (4.312) apply with subscripts m and n interchanged.

The values v^{-}_{n} and v^{+}_{n} that one calculates from (4.308) and (4.309) would not be exact integers. The precise quantum states v^{-}_{n} and v^{+}_{n} to which the molecule would relax would be those with integers nearest the values of v^{-}_{n} and v^{+}_{n} calculated from (4.308) and (4.309). Since we are interested in obtaining averaged smeared-out band-contours anyway, this small correction is not serious and we shall use analytically continuous values of v^{-}_{n} and v^{+}_{n} as calculated from (4.308) and (4.309) in the following. Note that the $v_n = v_m$ case is automatically included in these expressions.

Returning to our development of an expression for $g_e(\nu, \nu_{mn}, \Delta\nu_{mn})$, we must now substitute an explicit expression for $v_m = v_m(\nu-\nu_o)$ in Eq. (4.294) based on Eq. (4.295) and Eqs. (4.308) through (4.312). Since we have two possible emitted photons for each value of v_m, each of which has 50 percent chance of being emitted, we can write (4.294) in the form:

$$g_e(\nu, \nu_{mn}, \Delta\nu_{mn}) = \frac{0.5 \exp - \left(\frac{h\nu^-_{v_m}}{kT} \right)}{Z'_{v_m} \; \Delta\nu^-_{sp}} + \frac{0.5 \exp - \left(\frac{h\nu^+_{v_m}}{kT} \right)}{Z'_{v_m} \; \Delta\nu^+_{sp}} \; , \; \text{Hz}^{-1} \qquad (4.313)$$

Here $\nu^+_{v_m}$ and $\nu^-_{v_m}$ are the vibrational frequencies in the upper electronic state m giving rise to lower electronic states n with vibrational frequencies $\nu^+_{v_n}$ and $\nu^-_{v_n}$. That is $\nu^-_{v_m} = \nu_{v_m}(\nu^-_{v_n})$ and $\nu^+_{v_m} = \nu_{v_m}(\nu^+_{v_n})$. Also therefore $\nu^-_{v_m} = \nu_{v_m}(\nu^-)$ and $\nu^+_{v_m} = \nu_{v_m}(\nu^+)$, where $\nu = \nu^-$ and $\nu = \nu^+$ are the two frequencies of the photons emitted in the $v_m \rightarrow v_n^-$ and $v_m \rightarrow v_n^+$ transitions, which according to Eq. (4.295) are given by:

$$\nu = \nu^- = \nu_{mn} + \nu_{v_m} - \nu^-_{v_n} \; , \; \text{Hz} \, , \qquad (4.314)$$

$$\nu = \nu^+ = \nu_{mn} + \nu_{v_m} - \nu^+_{v_n} \; , \; \text{Hz} \qquad (4.315)$$

The main frequency difference ν_{mn} in (4.314) and (4.315) is actually ν'_{mn} but no great error results if we set $\nu_{mn} = \nu'_{mn}$ as remarked earlier. The parameter ν_{v_m} was defined by (4.285). The parameters $\Delta\nu^-_{sp} = \Delta\nu_{sp}(\nu^-_{v_m})$ and $\Delta\nu^+_{sp} = \Delta\nu_{sp}(\nu^+_{v_m})$ in Eq. (4.313) are the differential frequency spacings (defined by Eq. (4.293)) for the $v_m \rightarrow v_n^-$ and the $v_m \rightarrow v_n^+$ transitions.

Since $\nu^-_{v_n}$ and $\nu^+_{v_n}$ are functions of ν_{v_m} via Eqs. (4.310) and (4.311), it is possible to solve for ν_{v_m} in terms of ν_{mn} and ν from (4.314) and (4.315). We have from (4.314):

$$\frac{\nu^- - \nu_{mn}}{\nu_{d_m}} = y - \frac{\nu_{d_n}}{\nu_{d_m}}\left[1 - \left\{1 + \sqrt{y}\right\}^{\gamma_n} \exp{-\beta_n\left(r_{e_m} - r_{e_n}\right)}\right]^2 , \qquad (4.316)$$

where:

$$y = \frac{\nu_{v_m}}{\nu_{d_m}} \qquad (4.317)$$

and from (4.315):

$$\frac{\nu^+ - \nu_{mn}}{\nu_{d_m}} = y - \frac{\nu_{d_n}}{\nu_{d_m}}\left[1 - \left\{1 - \sqrt{y}\right\}^{\gamma_n} \exp{-\beta_n\left(r_{e_m} - r_{e_n}\right)}\right]^2 \qquad (4.318)$$

To solve for y from Eqs. (4.316) and (4.318), we shall use the following approximations:

$$\left(1 - \sqrt{y}\right)^{\gamma_n} \approx 1 - \gamma_n \sqrt{y} \qquad (4.319)$$

$$\left(1 + \sqrt{y}\right)^{\gamma_n} \approx 1 + \gamma_n \sqrt{y} \qquad (4.320)$$

These approximations are quite good since γ_n has a value close to 1 almost always, and $y = \nu_{v_m}/\nu_{d_m} << 1$.

With Eqs. (4.319) and (4.320), the two solutions for y become:

$$y_{\pm} = \frac{\nu^{\pm}_{v_m}}{\nu_{d_m}} = \frac{\nu - \nu_{mn} + \nu_{d_m}\left\{1 - \exp{-\beta_n}\left(r_{e_m} - r_{e_n}\right)\right\}^2}{\nu_{d_m} - \nu_{d_n}\,\gamma_n^2\,\exp{-2\beta_n}\left(r_{e_m} - r_{e_n}\right)} +$$

$$+ \frac{2\,\nu_{d_n}^2\,\gamma_n^2\left\{\exp{-2\beta_n}\left(r_{e_m} - r_{e_n}\right)\right\}\left\{1 - \exp{-\beta_n}\left(r_{e_m} - r_{e_n}\right)\right\}^2}{\left[\nu_{d_m} - \nu_{d_n}\,\gamma_n^2\,\exp{-2\beta_n}\left(r_{e_m} - r_{e_n}\right)\right]^2} \cdot$$

$$\cdot \left[1 \pm \sqrt{1 + \frac{\left\{\nu-\nu_{mn}+\nu_{d_m}\gamma_n^2\left(1-\exp{-\beta_n}\left(r_{e_m}-r_{e_n}\right)\right)^2\right\}\left\{\nu_{d_m}-\nu_{d_n}\gamma_n^2\,\exp{-2\beta_n}\left(r_{e_m}-r_{e_n}\right)\right\}}{\nu_{d_n}^2\gamma_n^2\left\{\exp{-2\beta_n}\left(r_{e_m}-r_{e_n}\right)\right\}\left\{1-\exp{-\beta_n}\left(r_{e_m}-r_{e_n}\right)\right\}^2}}\right] \tag{4.321}$$

Equation (4.321) can be written in the more compact form:

$$\nu^{-}_{v_m} = \rho_n\left[\nu - \nu_q + 2\,\nu_p\left\{1 - \sqrt{1 + (\nu-\nu_q)/\nu_p}\right\}\right], \text{ Hz} \tag{4.322}$$

$$\nu^{+}_{v_m} = \rho_n\left[\nu - \nu_q + 2\,\nu_p\left\{1 + \sqrt{1 + (\nu-\nu_q)/\nu_p}\right\}\right], \text{ Hz} \tag{4.323}$$

where:

$$\rho_n = \left[1 - \left(\nu_{e_n}/\nu_{e_m}\right)^2\left\{\exp{-2}\,\beta_n\left(r_{e_m} - r_{e_n}\right)\right\}\right]^{-1} = \left[1 - \xi_n^2\,B_n^2\right]^{-1} \tag{4.324}$$

$$\nu_q = \nu_{mn}-\nu_{d_n}\left\{1 - \exp{-\beta_n}\left(r_{e_m}-r_{e_n}\right)\right\}^2\left(\frac{\nu_{e_n}}{\nu_{e_m}}\right)^2 = \nu_{mn}-\nu_{d_n}\left(1-B_n\right)^2\,\xi_n^2\ , \text{ Hz} \tag{4.325}$$

$$\nu_p = \nu_{d_n} \frac{\left\{1 - \exp\text{-}\beta_n\left(r_{e_m} - r_{e_n}\right)\right\}^2}{\left(\nu_{e_m}/\nu_{e_n}\right)^2 \exp\text{-}2\beta_n\left(\dot{}_{e_m} - r_{e_n}\right) - 1} =$$

$$= \nu_{d_n} \frac{\xi_n^2 B_n^2 (1-B_n)^2}{1 - \xi_n^2 B_n^2} = \rho_n \nu_{d_n} \xi_n^2 B_n^2 (1-B_n)^2 \qquad (4.326)$$

Here we abbreviate for convenience:

$$\xi_n = \nu_{e_n}/\nu_{e_m} \qquad (4.327)$$

$$B_n = \exp\text{-}\beta_n\left(r_{e_m} - r_{e_n}\right) \qquad (4.328)$$

Using Eqs. (4.332) and (4.323) we can now evaluate $\Delta\nu_{sp}^+$ and $\Delta\nu_{sp}^-$ defined by Eq. (4.293):

$$\Delta\nu_{sp}^+ = \left(\nu_{e_m}/\rho_n\right)\left[1 + 2\left\{1 + (\nu-\nu_q)/\nu_p\right\}^{-1/2}\right]^{-1}, \text{ Hz} \qquad (4.329)$$

$$\Delta\nu_{sp}^- = \left(\nu_{e_m}/\rho_n\right)\left[1 - 2\left\{1 + (\nu-\nu_q)/\nu_p\right\}^{-1/2}\right]^{-1}, \text{ Hz} \qquad (4.330)$$

Now as the value of ν varies, the values taken on by $\nu_{v_m}^+$ and $\nu_{v_m}^-$ can never become negative or imaginary, nor can either of the two exponential terms in expression (4.313) become negative, meaning that $\Delta\nu_{sp}^-$ and $\Delta\nu_{sp}^+$ must both be positive always. By inspection fo Eqs. (4.322) and (4.323), and Eqs. (4.329) and (4.330), we then find that ν can only range over the limits:

$$\text{For } \nu^{+}_{v_m} : (\nu_q - \nu_p) \leq \nu \leq \infty \tag{4.331}$$

$$\text{For } \nu^{-}_{v_m} : (\nu_q + 3\nu_p) \leq \nu \leq \infty \tag{4.332}$$

Thus according to (4.332) and (4.332), for $(\nu_q - \nu_p) \leq \nu \leq (\nu_q + 3\nu_p)$ only $v_m \rightarrow v^{+}_n$ transitions are possible.

Substituting Eqs. (4.332), (4.323), (4.329), and (4.330) into Eq. (4.313) with the restrictions (4.332) and (4.332) yields next:

$$g_e(\nu, \nu_{mn}, \Delta\nu_{mn}) = \frac{H(\nu - \nu_q + \nu_p)}{2Z'_{v_m} \, \nu_{e_m}/\rho_n} \left[\left\{ H(\nu - \nu_q - 3\nu_p) \right\} \left\{ 1 - \frac{2}{\sqrt{1 + \frac{\nu - \nu_q}{\nu_p}}} \right\} \cdot \right.$$

$$\cdot \exp - \left\{ \frac{\nu - \nu_q + 2\nu_p\left(1 - \sqrt{1 + (\nu - \nu_q)/\nu_p}\right)}{kT/(h\rho_n)} \right\} + \left\{ 1 + \frac{2}{\sqrt{1 + \frac{\nu - \nu_q}{\nu_p}}} \right\} \cdot$$

$$\left. \cdot \exp - \left\{ \frac{\nu - \nu_q + 2\nu_p\left(1 + \sqrt{1 + (\nu - \nu_q)/\nu_p}\right)}{kT/(h\rho_n)} \right\} \right], \ \mathrm{Hz}^{-1} \tag{4.333}$$

Here $H(x)$ is the Heaviside unit step function defined before (see Eq. (4.149a).

To find the normalization constant Z'_{v_m}, we must integrate Eq. (4.333) over ν:

$$Z'_{\nu_m} = \frac{\rho_n}{2\nu_{e_m}} \left[\int_{\nu=\nu_q+3\nu_p}^{\infty} d\nu \left\{ \exp-\left(\frac{\nu-\nu_q+2\nu_p\left(1-\sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/h\rho_n} \right) \right\} \cdot \right.$$

$$\cdot \left\{ 1 - \frac{2}{\sqrt{1+\frac{\nu-\nu_q}{\nu_p}}} \right\} + \int_{\nu=\nu_q-\nu_p}^{\infty} d\nu \left\{ \exp-\left(\frac{\nu-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/h\rho_n} \right) \right\} \cdot$$

$$\left. \cdot \left\{ 1 + \frac{2}{\sqrt{1+\frac{\nu-\nu_q}{\nu_p}}} \right\} \right] = \frac{kT}{h\nu_{e_m}} \left[\exp-\left(\frac{h\rho_n\nu_p}{kT} \right) \right] + \Delta = \frac{kT}{h\nu_{e_m}} \left[\exp-\left(\frac{h\rho_n\nu_p}{kT} \right) \right] \tag{4.334}$$

Here Δ is the contribution to the integration from the factors $\pm 2\left\{1 + (\nu-\nu_q)/\nu_p\right\}^{-1/2}$. It is given by:

$$\Delta = \left(\frac{kT}{h\nu_{e_m}} \right) \left(\frac{\pi kT}{h\rho_n\nu_p} \right)^{1/2} \left[1 - \operatorname{erf}\left(\frac{h\rho_n\nu_p}{kT} \right)^{1/2} - 1 + \operatorname{erf}\left(\frac{h\rho_n\nu_p}{kT} \right)^{1/2} \right] = 0 \tag{4.335}$$

The function erf(x) in the above is the error function. Using (4.324) and (4.326), Z'_{ν_n} can be expressed in terms of the ξ_n and B_n defined in (4.327) and (4.328):

$$\boxed{Z'_{\nu_m} = \left(\frac{kT}{h\nu_{e_m}} \right) \exp-\left\{ \left(\frac{\xi_n B_n (1-B_n)}{1 - \xi_n^2 B_n^2} \right)^2 \left(\frac{h\nu_{d_n}}{kT} \right) \right\}} \tag{4.336}$$

The band-spread $\Delta\nu_{mn}$ is again obtained by setting $\Delta\nu_{mn} = \left[g_e(\nu=\nu_{mn},\nu_{mn},\Delta\nu_{mn})\right]^{-1}$. The result with the aid of (4.333) and (4.334) is:

$$\boxed{\Delta\nu_{mn} = \left[\frac{2kT/(h\rho_n)}{1 + 2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right] \cdot \exp\left\{\frac{\nu_{mn}-\nu_q+\nu_p\left(1+2\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}, \text{ Hz}} \tag{4.337}$$

or in terms of the ξ_n and B_n parameters:

$$\boxed{\Delta\nu_{mn} = \frac{(1-\xi_n^2B_n^2)\left(\frac{2kT}{h}\right)}{1+2B_n/A_n} \exp\left\{\chi_n^2A_n(A_n+2B_n)\left(\frac{h\nu_{d_n}}{kT}\right)\right\}, \text{ Hz}} \tag{4.338}$$

Here we abbreviate for convenience:

$$\chi_n = \frac{\xi_n(1-B_n)}{1-\xi_n^2B_n^2} = \rho_n\xi_n(1-B_n) \tag{4.339}$$

$$A_n = \left\{1 + (1-\xi_n^2)B_n^2\right\}^{1/2} \tag{4.440}$$

Rewriting next (4.333), using expressions (4.337) and (4.338) yields finally:

$$\boxed{\begin{aligned}
g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = {} & \left[\frac{\exp-\left\{\dfrac{h(\nu-\nu_{mn})\rho_n}{kT}\right\}}{\Delta\nu_{mn}}\right]\cdot\Bigg[\left\{\frac{1-2\left(1+(\nu-\nu\ )/\nu_p\right)^{-1/2}}{1+2\left(1+(\nu_{mn}-\nu_q)/\nu_p\right)^{-1/2}}\right\}\cdot \\
& \cdot\left\{\exp-\left(\frac{2h\rho_n\nu_p}{kT}\sqrt{1+\frac{\nu-\nu_q}{\nu_p}}\right)\right\}\cdot\left\{H(\nu-\nu_q-3\nu_p)\right\}+\left\{\frac{1+2\left(1+(\nu-\nu_q)/\nu_p\right)^{-1/2}}{1+2\left(1+(\nu_{mn}-\nu_q)/\nu_p\right)^{-1/2}}\right\}\cdot \\
& \cdot\left\{\exp+\left(\frac{2h\rho_n\nu_p}{kT}\sqrt{1+\frac{\nu-\nu_q}{\nu_p}}\right)\right\}\left\{H(\nu-\nu_q+\nu_p)\right\}\Bigg]\ ,\ \mathrm{Hz}^{-1}
\end{aligned}} \tag{4.341a}$$

or in terms of the parameters ξ_n , B_n , χ_n , and A_n:

$$\boxed{\begin{aligned}
g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = {} & \frac{\exp-\left\{\dfrac{h(\nu-\nu_{mn})}{(1-\xi_n^2B_n^2)kT}\right\}}{\Delta\nu_{mn}}\cdot\Bigg[\left\{\frac{1-2B_n\left(A_n^2+\dfrac{\rho_n}{\chi_n^2}\left(\dfrac{\nu-\nu_{mn}}{\nu_{d_n}}\right)\right)^{-1/2}}{1+2B_n/A_n}\right\}\cdot \\
& \cdot\left\{\exp-2B_n\chi_n^2\left(\frac{h\nu_{d_n}}{kT}\right)\sqrt{A_n^2+\frac{\rho_n}{\chi_n^2}\left(\frac{\nu-\nu_{mn}}{\nu_{d_n}}\right)}\right\}\cdot\left\{H\left(\nu-\nu_{mn}-\frac{\chi_n^2}{\rho_n}\left(1+(3-\xi_n^2)B_n^2\right)\nu_{d_n}\right)\right\}+ \\
& +\left\{\frac{1+2B_n\left(A_n^2+\dfrac{\rho_n}{\chi_n^2}\left(\dfrac{\nu-\nu_{mn}}{\nu_{d_n}}\right)\right)^{-1/2}}{1+2B_n/A_n}\right\}\left\{\exp+2B_n\chi_n^2\left(\frac{h\nu_{d_n}}{kT}\right)\sqrt{A_n^2+\frac{\rho_n}{\chi_n^2}\left(\frac{\nu-\nu_{mn}}{\nu_{d_n}}\right)}\right\}\cdot \\
& \cdot\left\{H\left(\nu-\nu_{mn}+\frac{\chi_n^2}{\rho_n}\left(B_n^2(1+\xi_n^2)-1\right)\nu_{d_n}\right)\right\}\Bigg]\ ,\ \mathrm{Hz}^{-1}
\end{aligned}} \tag{4.341b}$$

The dimensional shape function $b_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \Delta\nu_{mn}\, g_e(\nu,\nu_{mn},\Delta\nu_{mn})$ is of course also given by (4.341) with $\Delta\nu_{mn}$ removed from the denominator.

Equation (4.341) gives the envelope of the vibronic transition band-system of a diatomic molecule. To obtain the vibrational band details of a vibronic band-system, we can write analogously to the rovibrational case (see the discussion surrounding Eq. (4.156)):

$$g_{vnc}(\nu,\nu_{mn},\Delta\nu_{mn}) = b_e(\nu_s,\nu_{mn},\Delta\nu_{mn})\,\frac{\delta\nu_s}{\Delta\nu_{mn}}\, g_v(\nu,\nu_s,\Delta\nu^v_{mn}) \;, \ \mathrm{Hz}^{-1} \tag{4.342}$$

Here $b_e(\nu_s,\nu_{mn},\Delta\nu_{mn})$ is the same function as $b_e(\nu,\nu_{mn},\Delta\nu_{mn})$ except that ν is no longer continuous and has only the discrete values ν_s , that is:

$$\boxed{\begin{aligned} b_e(\nu_s,\nu_{mn},\Delta\nu_{mn}) = \ & \exp-\left\{\frac{h(\nu_s-\nu_{mn})}{(1-\xi_n^2B_n^2)kT}\right\} \cdot \left[\left\{\frac{1-2B_n\left(A_n^2+\dfrac{\rho_n}{\chi_n^2}\left(\dfrac{\nu_s-\nu_{mn}}{\nu_{d_n}}\right)\right)^{-1/2}}{1+2B_n/A_n}\right\}\cdot\right. \\ & \cdot\left\{\exp-\left(2B_n\chi_n^2\left(\frac{h\nu_{d_n}}{kT}\right)\sqrt{A_n^2+\frac{\rho_n}{\chi_n^2}\;\frac{\nu_s-\nu_{mn}}{\nu_{d_n}}}\right)\right\}\cdot\left\{H\left(\nu_s-\nu_{mn}-\frac{\chi_n^2}{\rho_n}\left(1+(3-\xi_n^2)B_n^2\right)\nu_{d_n}\right)\right\}+ \\ & +\left\{\frac{1+2B_n\left(A_n^2+\dfrac{\rho_n}{\chi_n^2}\left(\dfrac{\nu_s-\nu_{mn}}{\nu_{d_n}}\right)\right)^{-1/2}}{1+2B_n/A_n}\right\}\cdot\left\{\exp+\left(2B_n\chi_n^2\left(\frac{h\nu_{d_n}}{kT}\right)\sqrt{A_n^2+\frac{\rho_n}{\chi_n^2}\;\frac{\nu_s-\nu_{mn}}{\nu_{d_n}}}\right)\right\}\cdot \\ & \left.\cdot\left\{H\left(\nu_s-\nu_{mn}+\frac{\chi_n^2}{\rho_n}\left(B_n^2(1+\xi_n^2)-1\right)\nu_{d_n}\right)\right\}\right] \end{aligned}} \tag{4.343}$$

The discrete-valued variable ν_s is given by:

$$\nu_s = \nu_{mn} + (\nu_{o_m} v_m - \nu_{o_n} v_n) - (x_{e_m} \nu_{e_m} v_m^2 - x_{e_n} \nu_{e_n} v_n^2) \text{ , Hz ,} \qquad (4.344a)$$

where:

$$\nu_{o_i} = \nu_{e_i} (1 - x_{e_i}) \text{ , Hz ,} \qquad (4.334b)$$

and:

$$v_m = 0, 1, 2, 3, \ldots\ldots\ldots , \qquad (4.344c)$$

$$v_n = 0, 1, 2, 3, \ldots\ldots\ldots , \qquad (4.344d)$$

while $\delta\nu_s$ is the spacing between successive vibrational bands in the vibronic band-system, given by:

$$\delta\nu_s = \Delta\nu_s \left[\int_{\nu=\nu_s - \frac{1}{2}\Delta\nu_s}^{\nu_s + \frac{1}{2}\Delta\nu_s} g_v(\nu, \nu_s, \Delta\nu^v_{mn}) \, d\nu \right]^{-1} \text{ , Hz ,} \qquad (4.345a)$$

where:

$$\Delta\nu_s = \Delta\nu^{\pm}_{sp}(\nu=\nu_s) = \frac{\nu_{e_m}}{\rho_n} \left[1 \pm 2 \left\{ 1 + (\nu_s - \nu_q)/\nu_p \right\}^{-1/2} \right]^{-1} \text{ , Hz} \qquad (4.345b)$$

Note from (4.345a) that if $\Delta\nu_s \gg \Delta\nu^v_{mn}$, that is if the bands are separated as is often the case, then:

$$\underset{(\Delta\nu_s \gg \Delta\nu^v_{mn})}{\delta\nu_s} = \Delta\nu_s \text{ , Hz ,} \qquad (4.345c)$$

since the integral in (4.345a) is unity, while in the case of overlapping bands ($\Delta\nu_s \ll \Delta\nu_{mn}^{v}$) we have:

$$\underset{(\Delta\nu_s \ll \Delta\nu_{mn}^{v})}{\delta\nu_s} = \Delta\nu_{mn}^{v} \text{ , Hz ,} \qquad (4.345d)$$

since the integral in (4.345a) equals $(\Delta\nu_s/\Delta\nu_{mn}^{v})$ in this case.

The function $g_v(\nu,\nu_s,\Delta\nu_{mn}^{v})$ in (4.344) and (4.345a) is the vibrational band contour function given in section 4.7 for various types of molecules, the only difference being that ν_s is substituted for ν_{mn} in the expressions given there, and $\Delta\nu_{mn}^{v}$ is the spread of the individual vibrational band which is labeled $\Delta\nu_{mn}$ in section 4.7. The parameter $\Delta\nu_{mn}$ in this section refers of course to the spread of the vibronic band-system.

To get finally the rovibronic spectral detail, showing individual rotational lines in each vibrational band of the vibronic band-system, we simply substitute $g_{rov}(\nu,\nu_s,\Delta\nu_{mn}^{v})$ for $g_v(\nu,\nu_s,\Delta\nu_{mn}^{v})$, that is:

$$g_{rvc}(\nu,\nu_{mn},\Delta\nu_{mn}) = g_e(\nu_s,\nu_{mn},\Delta\nu_{mn})\; g_v(J,\nu_s,\Delta\nu_{mn}^{v}) \cdot g_J(\nu,\nu_{s_J},\Delta\nu_J)\; \delta\nu_s\; \delta\nu_J \text{ , Hz}^{-1} \qquad (4.346)$$

Here $\cdot g_{rov}(\nu,\nu_s,\Delta\nu_{mn}^{v} = g_v(J,\nu_s,\Delta\nu_{mn}^{v})\; g_J(\nu,\nu_{s_J},\Delta\nu_J)\; \delta\nu_J$ as discussed in section 4.7. The ν_{s_J} are given by the same formulas as the expressions for ν_J in section 4.7 except that ν_{mn} in those equations must be replaced by ν_s. Of course $J = 0, 1, 2, \ldots\ldots.$, and $\Delta\nu_J$ is the pressure- or temperature-broadened spread of an individual rotational line, whicle $\delta\nu_J$ is the spacing between rotational lines if they are separated or equal to Eqs. (4.155d), (4.180b), (4.185b), (4.280b), or (4.280c) whichever is applicable, if adjacent rotational lines overlap. Note from these relations that in case of substantial line overlap, $\delta\nu_J = \Delta\nu_J$. Explicit expressions for $g_v(J,\nu_s,\Delta\nu^v_{mn})$ and $g_J(\nu,\nu_{sJ},\Delta\nu_J)$ were given in section 4.7 and sections 4.3, 4.4, and 4.5, respectively.

4.8.2 Polyatomic Vibrators

For a polyatomic molecule which possesses not one, but several normal vibrations $\alpha = 1, 2, 3$, etc., we must modify Eqs. (4.292) and (4.294) for the diatomic molecule to:

$$G^{elc}_{mn}(v_{\alpha_m}) = {}^{o}C^{vib}_{mn}\left[\exp-\left(\frac{v_{\alpha_m}\,h\nu_{\alpha_m}}{kT}\right)\right] \Big/ Z'_{\alpha_m} =$$

$$= w_{\alpha_m}(v_{\alpha_m})\left[\exp-\left(\frac{v_{\alpha_m}\,h\nu_{\alpha_m}}{kT}\right)\right] \Big/ Z'_{\alpha_m} \quad , \tag{4.347}$$

and:

$$g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \sum_{\alpha} \frac{w_{\alpha_m}(v_{\alpha_m})\,\exp-\left(\frac{v_{\alpha_m}\,h\nu_{\alpha_m}}{kT}\right)}{Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}} \quad , \ \mathrm{Hz}^{-1} \tag{4.348}$$

Here the weight $w_{\alpha_m}(v_{\alpha_m})$ was given by Eq. (3.91d), and:

$$\Delta\nu_{sp\alpha_m} = \left(\frac{d\nu_{\alpha_m}}{d\nu}\right)^{-1} \quad , \ \mathrm{Hz} \tag{4.349}$$

The photon emission frequencies are similarly to (4.295) given by:

$$\nu = \nu_{mn} + \nu_{\alpha_m} v_{\alpha_m} - \nu_{\alpha_n} v_{\alpha_n} - x_{\alpha_m} \nu_{\alpha_m} v^2_{\alpha_m} - x_{\alpha_n} \nu_{\alpha_n} v^2_{\alpha_n} \text{ , Hz ,} \qquad (4.350)$$

where we make the approximation $\nu_\alpha(1-x_\alpha) \approx \nu_\alpha$. Equations (4.301) through (4.312) which apply for the diatomic molecule also hold for polyatomic molecules, except that all subscripts e must be replaced by subscripts α. Thus for each normal vibration α of a polyatomic molecule, there is a set of relations (4.301) through (4.312). In addition to changing e to α, the reduced mass $\bar{M}_{AB}$ used in Eqs. (4.304) and (4.306) must be replaced by M_α, and Eq. (4.305) no longer holds. Instead of Eq. (4.305), M_α must be calculated via the expressions given in Appendices A and B for the various types of polyatomic molecules. Tables 3-7 through 3-10 gave values of M_α for a number of polyatomic molecules. Estimated values of D_α and thus ν_{d_α} may be obtained from Appendix C.

Values for the parameter r_α, that is the mean separation of the vibrating components of a normal vibration α in a polyatomic molecule are difficult to obtain, particularly values of r_{α_m} and r_{α_n} of two different electronic states m and n. Actually we only need to know the difference:

$$\Delta r_{\alpha_{mn}} = r_{\alpha_m} - r_{\alpha_n} \text{ , cm ,} \qquad (4.351)$$

in the expressions for the band-series contour functions. For most molecules:

$$0.01 \lesssim \left| \frac{\Delta r_{\alpha_{mn}}}{r_{\alpha_m}} \right| \lesssim 0.1 \quad , \qquad (4.352)$$

and in many cases $r_{\alpha_m} > r_{\alpha_n}$ if m is a higher electronic level than n. However $r_{\alpha_n} < r_{\alpha_m}$ also occurs frequently. Herzberg (Ref. 11) lists a few values of r_{α_i} for some selected molecules in his reference tables.

The equations leading to an expression for $g_e(\nu,\nu_{mn},\Delta\nu_{mn})$ developed in subsection (4.8.1) for diatomic molecules, can be directly taken over for polyatomic molecules except that the weighting function $w_{\alpha_m}(v_{\alpha_m})$ must now also be taken into account and summations over α must be carried out. Thus instead of (4.313) we get for a polyatomic molecule:

$$g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{1}{2}\sum_{{}^1\alpha}\left[\frac{\exp-\left(\frac{h\nu^-_{\alpha v_m}}{kT}\right)}{{}^1Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}} + \frac{\exp-\left(\frac{h\nu^+_{\alpha v_m}}{kT}\right)}{{}^1Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}}\right] +$$

$$+\frac{1}{2}\sum_{{}^2\alpha}\left[\frac{\left(\frac{\nu^-_{\alpha v_m}}{\nu_{\alpha_m}}+\frac{1}{2}\right)\exp-\left(\frac{h\nu^-_{\alpha v_m}}{kT}\right)}{{}^2Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}} + \frac{\left(\frac{\nu^+_{\alpha v_m}}{\nu_{\alpha_m}}+\frac{1}{2}\right)\exp-\left(\frac{h\nu^+_{\alpha v_m}}{kT}\right)}{{}^2Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}}\right] +$$

$$+\frac{1}{2}\sum_{{}^3\alpha}\left[\frac{\left(\frac{\nu^-_{\alpha v_n}}{\nu_{\alpha_m}}+\frac{1}{2}\right)}{2\;{}^3Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}}\cdot\left(\frac{\nu^-_{\alpha v_m}}{\nu_{\alpha_m}}+\frac{3}{2}\right)\exp-\left(\frac{h\nu^-_{\alpha v_m}}{kT}\right) +\right.$$

$$\left.+\frac{\left(\frac{\nu^+_{\alpha v_m}}{\nu_{\alpha_m}}+\frac{1}{2}\right)\left(\frac{\nu^+_{\alpha v_m}}{\nu_{\alpha_m}}+\frac{3}{2}\right)\exp-\left(\frac{h\nu^+_{\alpha v_m}}{kT}\right)}{{}^3Z'_{\alpha_m}\,\Delta\nu_{sp\alpha_m}}\right],\ \mathrm{Hz}^{-1} \qquad (4.353)$$

Here we added the subscript α on $\nu^-_{v_m}$ and $\nu^+_{v_m}$ to indicate that each normal vibration α has its own set of values for these parameters.

The summation ${}^1\alpha$ in Eq. (4.353) is over non-degenerate normal vibrations ($d_\alpha = 1$), ${}^2\alpha$ is over doubly-degenerate normal vibrations ($d_\alpha = 2$), and ${}^3\alpha$ is over triply-degenerate normal vibrations ($d_\alpha = 3$), while we set:

$$v^-_{\alpha_m} = \left(\nu^-_{\alpha v_m}/\nu_{\alpha_m}\right) - \frac{1}{2} \ , \qquad (4.354)$$

$$v^+_{\alpha_m} \approx \left(\nu^+_{\alpha v_m}/\nu_{\alpha_m}\right) - \frac{1}{2} \ , \qquad (4.355)$$

similarly to Eqs. (4.308) and (4.309) for the diatomic vibrator. Equation (3.91) was also used in (4.353) to get explicit values of the weight w_{α_m} in terms of $\nu^-_{\alpha v_m}$ and $\nu^+_{\alpha v_m}$ for the three types of degenerate vibrations. The normalizing factors Z'_{v_m} are further labeled with a pre-superscript 1, 2, or 3 for non-, doubly-, or triply-degenerate normal vibrations and subscript α is added in place of subscript v (which is simply dropped since it is already clear that we are dealing with vibrational factors) to indicate that there is a different Z'_{α_m} factor for each normal vibration α.

Equations (4.314) through (4.332) for the diatomic molecule also apply to each normal vibration of the polyatomic molecule except for the addition or substitution of subscript α for subscript e. Equation (4.333) for the diatomic molecule, transforms next to the following expression for a polyatomic molecule:

$$g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \sum_{\alpha} \frac{H(\nu-\nu_q+\nu_p)}{2\,Z'_{\alpha_m}\,\nu_{\alpha_m}/\rho_n} \left[\left\{ H(\nu-\nu_q-3\nu_p) \right\} \left\{ 1 - \frac{2}{\sqrt{1+(\nu-\nu_q)/\nu_p}} \right\} \cdot \right.$$

$$\cdot\, w^-_{\alpha_m} \exp - \left\{ \frac{\nu - \nu_q + 2\nu_p\left(1 - \sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)} \right\} + \left\{ 1 + \frac{2}{\sqrt{1+(\nu-\nu_q)/\nu_p}} \right\} \cdot$$

$$\left. \cdot\, w^+_{\alpha_m} \exp - \left\{ \frac{\nu - \nu_q + 2\nu_p\left(1 + \sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)} \right\} \right], \ \mathrm{Hz}^{-1} \tag{4.356}$$

Here the summation is over all three types ($i = 1, 2, 3$) of the normal vibrations $\alpha = {}^i\alpha$ (non-degenerate, doubly-degenerate, and triply-degenerate). In the summations ν_p, ν_q, and ρ_n all depend on α also of course. For clarity we shall not add any superscripts or subscripts α to these parameters however. For non-degenerate vibrations (${}^1\alpha$) we have:

$$w^-_{\alpha_m} = w^+_{\alpha_m} = 1 \ , \ (d_\alpha = 1) \ , \tag{4.357a}$$

for doubly-degenerate vibrations (${}^2\alpha$):

$$w^{\pm}_{\alpha_m} = \nu^{\pm}_{\alpha\nu_m}/\nu_{\alpha_m} + \frac{1}{2}, \ (d_\alpha = 2) \ , \tag{4.357b}$$

while for triply-degenerate vibrations (${}^3\alpha$):

$$w^{\pm}_{\alpha_m} = \frac{1}{2}\left(\nu^{\pm}_{\alpha\nu_m}/\nu_{\alpha_m} + \frac{3}{2}\right)\left(\nu^{\pm}_{\alpha\nu_m}/\nu_{\alpha_m} + \frac{1}{2}\right), \ (d_\alpha = 3) \tag{4.357c}$$

The normalization constants Z'_{α_m} are next evaluated in the same manner as in Eq. (4.334) for the diatomic molecule. For the non-degenerate normal vibrations, the normalization constant $Z'_{\alpha_m} = {}^1Z'_{\alpha_m}$ is identical to Z'_{v_m} given by Eq. (4.334) (except for the labeling of subscripts α in place of subscripts e), that is:

$$\boxed{{}^1Z'_{\alpha_m} = \frac{kT}{h\nu_{\alpha_m}} \exp-\left(\frac{h\rho_n \nu_p}{kT}\right) ,} \tag{4.358a}$$

or in terms of the ξ_n , B_n , and χ_n parameters defined in (4.327), (4.328), and (4.339):

$$\boxed{{}^1Z'_{\alpha_m} = \frac{kT}{h\nu_{\alpha_m}} \exp-\left\{\left(\chi_n B_n\right)^2 \left(\frac{h\nu_{d_n}}{kT}\right)\right\}} \tag{4.358b}$$

Of course the ν_p , ν_q , ρ_n , B_n , ξ_n , and χ_n all depend on α in the above and in what follows.

For the doubly-degenerate vibrations the normalization constant $Z'_{\alpha_m} = {}^2Z'_{\alpha_m}$ is:

$${}^2Z'_{\alpha_m} = \frac{\rho_n}{2\nu_{\alpha_m}} \left[\int_{\nu=\nu_2+3\nu_p}^{\infty} d\nu \left\{ \frac{1}{2} + \frac{\rho_n}{\nu_{\alpha_m}} \left(\nu-\nu_q + 2\nu_p \left(1 - \sqrt{1+(\nu-\nu_q)/\nu_p} \right)\right)\right\} \cdot \right.$$

$$\cdot \left\{1 - \frac{2}{\sqrt{1-(\nu-\nu_q)/\nu_p}}\right\} \cdot \exp-\left\{\frac{\nu - \nu_q + 2\nu_p\left(1 - \sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\} +$$

$$+ \int_{\nu=\nu_q-\nu_p}^{\infty} d\nu \left\{\frac{1}{2} + \frac{\rho_n}{\nu_{\alpha_m}}\left(\nu - \nu_q + 2\nu_p\left(1 + \sqrt{1+(\nu-\nu_q)/\nu_p}\right)\right)\right\} \cdot$$

$$\cdot \left\{1 + \frac{2}{\sqrt{1-(\nu-\nu_q)/\nu_p}}\right\} \cdot \exp-\left\{\frac{\nu - \nu_q + 2\nu_p\left(1 + \sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}\Bigg] =$$

$$\boxed{{}^2Z'_{\alpha_m} = \left(\frac{kT}{h\nu_{\alpha_m}}\right)^2 \left(1 + 3\,\frac{h\rho_n\nu_p}{kT} + \frac{1}{2}\,\frac{h\nu_{\alpha_m}}{kT}\right) \cdot \exp-\left(\frac{h\rho_n\nu_p}{kT}\right)} \qquad (4.359a)$$

or in terms of the ξ_n, B_n, and χ_n parameters:

$$\boxed{{}^2Z'_{\alpha_m} = \left(\frac{kT}{h\nu_{\alpha_m}}\right)^2 \left(1 + \frac{1}{2}\,\frac{h\nu_{\alpha_m}}{kT} + 3\,\chi_n^2 B_n^2\,\frac{h\nu_{d_n}}{kT}\right) \cdot \exp-\left(\chi_n^2 B_n^2\,\frac{h\nu_{d_n}}{kT}\right)} \qquad (4.359b)$$

The normalization constant $Z_{\alpha_m} = {}^3Z_{\alpha_m}$ for triply-degenerate vibrations is finally:

$${}^3Z'_{\alpha_m} = \frac{\rho_n}{4\nu_{\alpha_m}}\left[\int_{\nu=\nu_q+3\nu_p}^{\infty} d\nu \left\{1 - \frac{2}{\sqrt{1-(\nu-\nu_q)/\nu_p}}\right\} \cdot\right.$$

$$\cdot\left\{\frac{1}{2}+\frac{\rho_n}{\nu_{\alpha_m}}\left(\nu-\nu_q+2\nu_p\left(1-\sqrt{1+(\nu-\nu_q)/\nu_p}\right)\right)\right\}\left\{\frac{3}{2}+\frac{\rho_n}{\nu_{\alpha_m}}\left(\nu-\nu_q+2\nu_p\left(1-\sqrt{1+(\nu-\nu_q)/\nu_p}\right)\right)\right\}\cdot$$

$$\cdot\exp-\left\{\frac{\nu-\nu_q+2\nu_p\left(1-\sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}+\int_{\nu=\nu_q-\nu_p}^{\infty}d\nu\left\{1+\frac{2}{\sqrt{1-(\nu-\nu_q)/\nu_p}}\right\}\cdot$$

$$\cdot\left\{\frac{1}{2}+\frac{\rho_n}{\nu_{\alpha_m}}\left(\nu-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu-\nu_q)/\nu_p}\right)\right)\right\}\cdot$$

$$\cdot\left\{\frac{3}{2}+\frac{\rho_n}{\nu_{\alpha_m}}\left(\nu-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu-\nu_q)/\nu_p}\right)\right)\right\}\exp-\left\{\frac{\nu-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}\Bigg]=$$

$$\boxed{\begin{aligned}{}^3Z'_{\alpha_m}=&\left(\frac{kT}{h\nu_{\alpha_m}}\right)^2\left\{\exp-\left(\frac{h\rho_n\nu_p}{kT}\right)\right\}\cdot\left\{5\left(\frac{h\rho_n\nu_p}{kT}\right)+\frac{3}{16}\left(\frac{h\nu_{\alpha_m}}{kT}\right)+\right.\\&\left.+\frac{29}{2}\left(\frac{kT}{h\nu_{\alpha_m}}\right)\left(\frac{h\rho_n\nu_p}{kT}\right)^2+1+\frac{kT}{h\nu_{\alpha_m}}\right\}\end{aligned}} \tag{4.360a}$$

or in terms of the ξ_n, B_n, and χ_n parameters:

$$\boxed{\begin{aligned}{}^3Z'_{\alpha_m}=&\left(\frac{kT}{h\nu_{\alpha_m}}\right)^2\left\{\exp-\left(\chi_n^2B_n^2\frac{h\nu_{d_n}}{kT}\right)\right\}\cdot\left\{5\chi_n^2B_n^2\left(\frac{h\nu_{d_n}}{kT}\right)+\right.\\&\left.+\frac{3}{16}\left(\frac{h\nu_{\alpha_m}}{kT}\right)+\frac{29}{2}\chi_n^4B_n^4\left(\frac{h\nu_{d_n}^2}{\nu_{\alpha_m}kT}\right)+1+\frac{kT}{h\nu_{\alpha_m}}\right\}\end{aligned}} \tag{4.360b}$$

The spread of the band-system is next obtained by setting again $\Delta\nu_{mn} = \left[g_e(\nu=\nu_{mn},\nu_{mn},\Delta\nu_{mn})\right]^{-1}$, using Eq. (4.356). We get:

$$\boxed{\left(\Delta\nu_{mn}\right)^{-1} = \left(\Delta\nu_{mn}\right)^{-1}_{{}^1\alpha} + \left(\Delta\nu_{mn}\right)^{-1}_{{}^2\alpha} + \left(\Delta\nu_{mn}\right)^{-1}_{{}^3\alpha}\ ,\ \text{Hz}^{-1}} \tag{4.361}$$

where:

$$\left(\Delta\nu_{mn}\right)_{{}^1\alpha} = \sum_{{}^1\alpha}\left(\frac{2\ {}^1Z'_{\alpha_m}\ \nu_{\alpha_m}/\rho_n}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right)\exp\left\{\frac{\nu_{mn}-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\} =$$

$$\boxed{\left(\Delta\nu_{mn}\right)_{{}^1\alpha} = \sum_{{}^1\alpha}\left(\frac{2kT}{h\rho_n}\right)\left[\frac{\exp\left\{\dfrac{\nu_{mn}-\nu_q+\nu_p\left(1+2\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right]\ ,\ \text{Hz}} \tag{4.362}$$

$$\left(\Delta\nu_{mn}\right)_{{}^2\alpha} = \sum_{{}^2\alpha}\left(\frac{2\ {}^2Z'_{\alpha_m}\ \nu_{\alpha_m}/\rho_n}{1+2\left\{1+(\nu_{mn}-\nu_a)/\nu_p\right\}^{-1/2}}\right)\exp\left\{\frac{\nu_{mn}-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu_{mn}-\nu_q)\nu_p}\right)}{kT/(h\rho_n)}\right\} =$$

$$\boxed{\begin{aligned}\left(\Delta\nu_{mn}\right)_{{}^2\alpha} &= \sum_{{}^2\alpha}\left(\frac{2kT}{h\rho_n}\right)\left(\frac{kT}{h\nu_{\alpha_m}}\right)\cdot\left(3\ \frac{h\rho_n\nu_p}{kT} + \frac{1}{2}\ \frac{h\nu_{\alpha_m}}{kT} + 1\right)\cdot\\ &\cdot\left[\frac{\exp\left\{\dfrac{\nu_{mn}-\nu_q+\nu_p\left(1+2\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right]\ ,\ \text{Hz}\end{aligned}} \tag{4.363}$$

$$\left(\Delta\nu_{mn}\right)_{{}^3\alpha} = \sum_{{}^3\alpha}\left(\frac{2\;{}^3Z'_{\alpha_m}\;\nu_{\alpha_m}/\rho_n}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right)\exp\left\{\frac{\nu_{mn}-\nu_q+2\nu_p\left(1+\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\} =$$

$$\boxed{\begin{aligned}\left(\Delta\nu_{mn}\right)_{{}^3\alpha} = \sum_{{}^3\alpha}\left(\frac{2kT}{h\rho_n}\right)\left(\frac{kT}{h\nu_{\alpha_m}}\right)\Bigg\{5\left(\frac{h\rho_n\nu_p}{kT}\right) + \frac{3}{16}\left(\frac{h\nu_{\alpha_m}}{kT}\right) + \frac{29}{3}\left(\frac{kT}{h\nu_{\alpha_m}}\right)\left(\frac{h\rho_n\nu_p}{kT}\right)^2 + 1 + \\ + \frac{kT}{h\nu_{\alpha_m}}\Bigg\}\cdot\left[\frac{\exp\left\{\dfrac{\nu_{mn}-\nu_q+\nu_p\left(1+2\sqrt{1+(\nu_{mn}-\nu_q)/\nu_p}\right)}{kT/(h\rho_n)}\right\}}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right], \text{ Hz}\end{aligned}}$$

(4.364)

Here three separate summations must be carried out over the three possible types of vibrations, namely the non-, doubly-, and triply-degenerate normal vibrations ${}^1\alpha$, ${}^2\alpha$, and ${}^3\alpha$ of the molecule, which have different normalizing constants ${}^1Z'_{\alpha_m}$, ${}^2Z'_{\alpha_m}$, and ${}^3Z'_{\alpha_m}$.

With the three $\left(\Delta\nu_{mn}\right)_{i_\alpha}$ defined by (4.362) through (4.364), Eq. (4.356) can now be written:

$$\boxed{\begin{aligned}g_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \sum_{i=1}^{3}\sum_{i_\alpha}\left\{\frac{\exp-\left(\dfrac{\nu-\nu_{mn}}{kT/(h\rho_n)}\right)}{\left(\Delta\nu_{mn}\right)_{i_\alpha}}\right\}\cdot\Bigg[\left\{\frac{1-2\left\{1+(\nu-\nu_q)/\nu_p\right\}^{-1/2}}{1+2\left\{1+(\nu_{mn}-\nu_q)/\nu_p\right\}^{-1/2}}\right\}\cdot \\ \cdot\left\{\exp\frac{-2\nu_p\sqrt{1+(\nu-\nu_q)/\nu_p}}{kT/(h\rho_n)}\right\}\left\{H(\nu-\nu_q-3\nu_p)\right\} + \left\{\frac{1+2\left\{1+(\nu-\nu_q)/\nu_p\right\}^{-1/2}}{1+2\left\{1+(\nu_{mn}-\nu_q/\nu_p\right\}^{-1/2}}\right\}\cdot \\ \cdot\left\{\exp\frac{2\nu_p\sqrt{1+(\nu-\nu_q)/\nu_p}}{kT/(h\rho_n)}\right\}\left\{H(\nu-\nu_q+\nu_p)\right\}\Bigg], \text{ Hz}^{-1}\end{aligned}}$$

(4.365)

Of course the parameters ν_p , ν_q , and ρ_n all depend on α in this expression.

The shape function $b_e(\nu,\nu_{mn},\Delta\nu_{mn})$ is given by:

$$b_e(\nu,\nu_{mn},\Delta\nu_{mn}) = \left\{g_e(\nu,\nu_{mn},\Delta\nu_{mn})\right\} \left\{ \sum_{i_\alpha} \left(\Delta\nu_{mn}\right)^{-1}_{i_\alpha} \right\}^{-1} , \qquad (4.366)$$

where we used Eq. (4.361). Here $g_e(\nu,\nu_{mn},\Delta\nu_{mn})$ is of course given by Eq. (4.365).

To obtain the structure of the vibrational bands in the vibronic band-system, we can use Eq. (4.342) again which in that form applies to both diatomic and polyatomic molecules. However (4.366) with $\nu = \nu_s = \nu_{\alpha s}$ must be used. The discrete variable ν_s and the spacing $\delta\nu_s$ are instead of (4.344) and (4.345) now given by:

$$\nu_s \rightarrow \nu_{\alpha s} = \nu_{mn} + \left(\nu_{\alpha_m} v_{\alpha_m} - \nu_{\alpha_n} v_{\alpha_n}\right) - \left(x_{\alpha_m} \nu_{\alpha_m} v^2_{\alpha_m} - x_{\alpha_n} \nu_{\alpha_n} v^2_{\alpha_n}\right) , \text{ Hz} \qquad (4.367)$$

and:

$$\delta\nu_s \rightarrow \delta\nu_{\alpha s} = \Delta\nu_{\alpha s} \left[\int_{\nu=\nu_s - \frac{1}{2}\Delta\nu_{\alpha s}}^{\nu_s + \frac{1}{2}\Delta\nu_{\alpha s}} g_v(\nu,\nu_{\alpha s},\Delta\nu^{v\alpha}_{mn})\, d\nu \right]^{-1} , \quad \text{Hz} \qquad (4.368a)$$

$$\Delta\nu_{\alpha s} = \Delta\nu^{\pm}_{\alpha s} = \Delta\nu^{\pm}_{sp\alpha_m}(\nu=\nu_s) = \left(\frac{\nu_{\alpha_m}}{\rho_n}\right) \left[1 \pm \left\{(\nu_s - \nu_q)/\nu_t\right\}^{-1/2} \right]^{-1} , \text{ Hz}$$

(4.368b)

$$\delta\nu_{\alpha s} = \Delta\nu_{\alpha s} \qquad (4.368c)$$
$$(\Delta\nu_{\alpha s} \gg \Delta\nu_{mn}^{v\alpha})$$

$$\delta\nu_{\alpha s} = \Delta\nu_{mn}^{v\alpha} \qquad (4.368d)$$
$$(\Delta\nu_{\alpha s} \ll \Delta\nu_{mn}^{v\alpha})$$

Here v_{α_m} and v_{α_n} in (4.367) have the values 0, 1, 2, 3,...., as before. The parameter $\Delta\nu_{mn}^{v\alpha}$ is the spread of the vibrational band of the α vibration in the m → n electronic transition.

Similarly, for the detailed rovibrational structure giving individual rotational lines, we can use Eq. (4.346) whose form again applies to both diatomic and polyatomic molecules, provided we use (4.366), (4.367), and (4.368) instead of (4.343), (4.344), and (4.345).

5. APPLICATIONS AND EXAMPLES

5.1 SUMMARY OF KEY RELATIONS

In this section we list for ready reference all the key relations that were derived in the previous chapters. In Table 5-1, the formal expressions for photon absorption and emission are summarized as discussed in Chapter 2, namely the molecular emission rate ($\sec^{-1}$) or inverse decay time of an excited molecule, and the absorption and stimulated absorption cross-sections σ_{abs} and $\sigma_{s.e.}$ (cm^2) of a molecule.

Table 5-2 summarizes next expressions for the photonic matrix elements* $(R^2_{mn})_o$, connection coefficients C^o_{mn} , and weights w^o_m , w^o_n , of electronic, vibrational, and rotational main transitions, as derived and discussed in Chapter 3.

Finally, Table 5-3 lists expressions for broadening functions of lines (natural, doppler, collisional, and stark broadening), bands (rotational broadening), and band-systems (vibrational broadening), as evaluated in Chapter 4.

From Tables 5-1, 5-2, and 5-3, it is possible to obtain complete analytical expressions for any photon-molecule excitation or deexcitation interaction, except ionization.

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*We use the adjective "photonic" here to distinguish the transitions under consideration here from transitions in which energy is exchanged between two molecules or between the molecule and an electron. These particle energy exchange transitions follow different selection rules.

TABLE 5-1. EXPRESSIONS FOR ABSORPTION OR EMISSION RATES AND CROSS-SECTIONS

PHOTON PROCESS	PHYSICAL EXPRESSION	DISCUSSION
SPONTANEOUS EMISSION OR DEEXCITATION (For Main Transition m → n)	(a) Total Deexcitation (Emission) Rate per Molecule*: $A^o_{mn} = \frac{1}{\tau^o_{mn}} = \frac{64\pi^4 e^2 \nu^3_{mn}}{3hc^3} \left(\frac{C_{mn} R^2_{mn}}{w_m} \right)_o =$ $= 2.6833 \times 10^{-21} \underset{(Hz^3)}{\nu^3_{mn}} \left(C_{mn}/w_m \right)_o \underset{(cm^2)}{\left(R^2_{mn} \right)_o}$, sec^{-1} (b) Spectral Emission Rate per Unit Frequency Range:* $\frac{dA_{mn}}{d\nu} = \underset{(sec^{-1})}{A^o_{mn}} \cdot \underset{(Hz^{-1})}{g_o(\nu, \nu_{mn}, \Delta\nu_{mn})}$, $sec^{-1} \cdot Hz^{-1}$	pp. 28 through 35
PHOTON ABSORPTION (For Main Transition n → m)	(a) Total Absorption Rate per Molecule:* $K^o_{nm} = \frac{1}{\tau^o_{nm}} = \int_{\nu=0}^{\infty} (dF_\varphi(\nu)/d\nu)\, \sigma_{nm\,abs}(\nu)\, d\nu$, sec^{-1} (Differential photon fluences $dF_\varphi / d\nu$ (photons $\cdot$ $cm^{-2} \cdot sec^{-1}$) for natural sources are discussed on pp. 37 through 40).	pp. 36 through 41

*Subscript o refers to the main transition process which is either electronic (o = elc), vibrational (o = vib), rotational (o = rot).

TABLE 5-1. EXPRESSIONS FOR ABSORPTION OR EMISSION RATES AND CROSS-SECTIONS (Cont.)

PHOTON PROCESS	PHYSICAL EXPRESSION	DISCUSSION
PHOTON ABSORPTION (Cont.) (For Main Transition n → m)	For laser beams of Γ_φ photons$\cdot$cm$^{-2}\cdot$sec^{-1} and frequency $\nu = \nu_L$: $K^o_{nm} = \Gamma_\varphi \underset{abs}{\sigma_{nm}}(\nu{=}\nu_L)$, sec^{-1} (b) Spectral Absorption Cross-Section:* $\underset{abs}{\sigma_{nm}}(\nu) = \frac{8\pi^3 e^2 \nu_{nm}}{3hc}\left(\frac{C_{nm}R^2_{nm}}{w_n}\right)_o g_o(\nu,\nu_{nm},\Delta\nu_{nm}) =$ $= 0.0960\ \underset{(Hz)}{\nu_{nm}}\left(\frac{C_{nm}}{w_n}\right)_o \underset{(cm^2)}{\left(R^2_{nm}\right)_o}\ \underset{(Hz^{-1})}{g_o(\nu,\nu_{nm},\Delta\nu_{nm})}$, cm^2	pp. 36 through 41
STIMULATED EMISSION (For Main Transition m → n)	(a) Total Stimulated Emission Rate per Molecule:* $D^o_{mn} = \int_{\nu=o}^{\infty} (dF_\varphi(\nu)/d\nu)\ \underset{s.e.}{\sigma_{mn}}(\nu)\ d\nu$, sec^{-1} (Differential photon flueces $dF_\varphi/d\nu$ (photons $\cdot$ cm$^{-2}\cdot$sec^{-1}) for natural sources are discussed on pp. 43 through 45).	pp. 42 through 45

*Subscript o refers to the main transition process which is either electronic (o = elc), vibrational (o = vib), rotational (o = rot).

TABLE 5-1. EXPRESSIONS FOR ABSORPTION OR EMISSION RATES AND CROSS-SECTIONS (Cont.)

PHOTON PROCESS	PHYSICAL EXPRESSION	DISCUSSION
STIMULATED EMISSION (Cont.) (For Main Transition m → n)	For laser beams of Γ_φ photons · cm^{-2} · sec^{-1} and frequency $\nu = \nu_L$: $D^{o}_{mn} = \Gamma_\varphi \underset{s.e.}{\sigma_{mn}}(\nu{=}\nu_L) \quad , \quad sec^{-1}$ (b) <u>Stimulated Emission Cross-Section:*</u> $\underset{s.e.}{\sigma_{mn}}(\nu) = \frac{8\pi^3 e^2 \nu_{mn}}{3hc} \left(\frac{C_{mn}}{w_m}\right)_o \left(R^2_{mn}\right)_o g_o(\nu,\nu_{mn},\Delta\nu_{mn}) =$ $= 0.0960 \underset{(Hz)}{\nu_{mn}} \left(\frac{C_{mn}}{w_m}\right)_o \underset{(cm^2)}{\left(R^2_{mn}\right)_o} \underset{(Hz^{-1})}{g_o(\nu,\nu_{mn},\Delta\nu_{mn})}, \ cm^2$	pp. 42 through 45

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*Subscript o refers to the main transiton process which is either electronic (o = elc), vibrational (o = vib), rotational (o = rot).

TABLE 5-2. PHOTONIC MATRIX ELEMENTS, CONNECTION FACTORS, AND WEIGHTS OF ELECTRONIC, VIBRATIONAL, AND ROTATIONAL TRANSITIONS IN MOLECULES*

TYPE OF TRANSITION	MATRIX ELEMENT R^2_{mn}, cm² **	CONNECTION FACTOR C_{mn}	WEIGHT w_k ($k = m$ or $k = n$)
ELECTRONIC (Sec. 3.2; pp. 54-85) (a) Hydrogen Atom	$R^2_{mn\,elc}$ = Eqs. (3.19) and (3.20) on pp. 54, 55; see also Tables 3-1 and 3-2 on pp. 58, 60.	C_{mn} = Eq. (3.36) on pp. 66, 67, 68 or C_{mn} = Eq. (3.38) on p. 69	$w_k = 2J_k+1$ or $w_k = (2S_k+1)(2L_k+1)$
(b) Hydrogen-like Atoms (K, Na, Cs, Rb, etc.)	$R^2_{mn\,elc}$ = Eq. (3.22) on pp. 56, 57; see also Tables 3-1 and 3-2 on pp. 58, 60.	Same as for Hydrogen Atom	Same as for Hydrogen Atom
(c) Other Atoms	Approximate Expressions: $R^2_{mn\,elc}$ = Eq. (3.45) on p. 74, if $n_m \neq n_n$. $R^2_{mn\,elc}$ = Eq. (3.43) on p. 74, if $n_m = n_n$.	Same as for Hydrogen Atom	Same as for Hydrogen Atom
	Coarse Approximation (p. 81): $R^2_{mn\,elc} = \frac{h}{16\pi^2 m_e \nu_{mn}} = \frac{4.606 \times 10^{-12}}{\nu_{mn(Hz)}}$	Same as for Hydrogen Atom	Same as for Hydrogen Atom
(d) Molecules	Approximate Expressions: $R^2_{mn\,elc}$ = Eq. (3.47) on p. 75, if $n_m \neq n_n$. $R^2_{mn\,elc}$ = Eq. (3.46) on p. 75, if $n_m = n_n$. Coarse Approximation (p. 81): $R^2_{mn\,elc} \approx \frac{h}{16\pi^2 m_e \nu_{nm}} = \frac{4.606 \times 10^{-12}}{\nu_{mn(Hz)}}$	$C_{mn} = w_m w_n = d_{X_m} d_{X_n} (2S_m+1)\cdot(2S_n+1)$	(i) Linear Molecules: $w_k = 2S_k+1$, if $\Lambda_K = 0$ $w_k = 2(2S_k+1)$, if $\Lambda_k \neq 0$ (ii) Nonlinear Molecules: $w_k = d_{X_k}(2S_k+1)$

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*Units and definitions of parameters are given in Chapter 7.

**If an equation occupies too much space, it is not written out here; referral to the text is made instead.

TABLE 5-2. PHOTONIC MATRIX ELEMENTS, CONNECTION FACTORS, AND WEIGHTS OF ELECTRONIC, VIBRATIONAL, AND ROTATIONAL TRANSITIONS IN MOLECULES* (Cont.)

TYPE OF TRANSITION	MATRIX ELEMENT R^2_{mn}, cm²	CONNECTION FACTOR C_{mn}	WEIGHT w_k ($k = m$ or $k = n$)
VIBRATIONAL (a) Diatomic Molecules (Sec. 3.3.1; pp. 86-94)	(i) For $v_m - v_n = 1$ (p.92): $R^2_{mn} = \frac{v_m h z_1^2}{8\pi^2 \bar{M}_{AB} \nu_{mn}} = 5.0548 \times 10^{-5} \left(\frac{v_m z_1^2}{\underset{(amu)}{\bar{M}_{AB}} \; \underset{(Hz)}{\nu_{mn}}} \right)$ (ii) For $v_m - v_n \neq 1$ (p. 94): $R^2_{mn} = \left(\frac{h z_1^2}{8\pi^2 \bar{M}_{AB} \nu_{mn}} \right) \left(\frac{v_m!}{v_n!} \right) \left(\frac{x_e^{(v_m - v_n - 1)}}{v_m - v_n} \right) =$ $= 5.0548 \times 10^{-5} \left(\frac{z_1^2}{\underset{(amu)}{\bar{M}_{AB}} \; \underset{(Hz)}{\nu_{mn}}} \right) \left(\frac{v_m!}{v_n!} \right) \left(\frac{x_e^{(v_m - v_n - 1)}}{v_m - v_n} \right)$ Values of z_1, $\bar{M}_{AB}$, and x_e are tabulated in Table 3-6 on p. 90.	$C_{mn} = w_m w_n = 1$	$w_k = 1$
(b) Polyatomic Molecules	(i) For $v_{\alpha_m} - v_{\alpha_n} = \Delta v_\alpha = 1$, (p.97): $R^2_{mn} = \frac{v_{\alpha_m} h z_\alpha^2}{8\pi^2 M_\alpha \nu_\alpha} = 5.0548 \times 10^{-5} \left(\frac{v_{\alpha_m} z_\alpha^2}{\underset{(amu)}{M_\alpha} \; \underset{(Hz)}{\nu_\alpha}} \right)$	(i) For $\Delta v_\alpha = 1$: $C_{mn} = w_{\alpha_m} w_{\alpha_n}$	$w_{\alpha_k} = 1$, if $d_{X_\alpha} = 1$ $w_{\alpha_k} = (v_{\alpha_k} + 1)$, if $d_{X_\alpha} = 2$ $w_{\alpha_k} = \frac{1}{2}(v_{\alpha_k} + 1)(v_{\alpha_k} + 2)$, if $d_{X_\alpha} = 3$

*Units and definitions of parameters are given in Chapter 7.

TABLE 5-2. PHOTONIC MATRIX ELEMENTS, CONNECTION FACTORS, AND WEIGHTS OF ELECTRONIC, VIBRATIONAL, AND ROTATIONAL TRANSITIONS IN MOLECULES* (Cont.)

TYPE OF TRANSITION	MATRIX ELEMENT R^2_{mn} , cm^2	CONNECTION FACTOR C_{mn}	WEIGHT w_k ($k = m$ or $k = n$)
VIBRATIONAL (Cont.) (b) Polyatomic Molecules (cont.) (Sec. 3.3.2; pp. 95-111)	(ii) For $(v_{\alpha_m}, v_{\beta_m}, \ldots) \rightarrow (v_{\alpha_n}, v_{\beta_n}, \ldots)$ and $\Delta v_\alpha \neq 1$, (p. 98): $R^2_{mn} = \frac{hz^2_{mn}}{8\pi^2 M_{mn} v_{mn} x_{mn}} \prod_\alpha \left(\frac{v_{\alpha_m}!}{v_{\alpha_n}!}\right)^{\delta_\alpha} \left(\frac{x_\alpha^{\lvert v_{\alpha_m}-v_{\alpha_n}\rvert f}}{(\lvert v_{\alpha_m}-v_{\alpha_n}\rvert + 1)^2}\right)$ $M_{mn} = \left[\sum_\alpha M_\alpha^{-1/2} \lvert v_{\alpha_m} - v_{\alpha_n}\rvert\right]^{-2}$; $x_{mn} = \left[\sum_\alpha x_\alpha^{-1/2} \lvert v_{\alpha_m} - v_{\alpha_n}\rvert\right]^{-2}$ $z_{mn} = (v_{mn} M_{mn} x_{mn})^{1/2} \left\lvert \sum_\alpha \left(\frac{\lvert v_{\alpha_m}-v_{\alpha_n}\rvert + 1}{\lvert v_{\alpha_m}-v_{\alpha_n}\rvert}\right)\left(\frac{z_\alpha \vec{e}_\alpha}{M_\alpha^{1/2} v_\alpha^{1/2} x_\alpha^{f/2}}\right)\right\rvert$ $v_{mn} = \sum_\alpha (v_{\alpha_m} - v_{\alpha_n}) v_\alpha$; $f = 1 - \frac{1}{2} \frac{\left(\sum_\alpha \lvert v_{\alpha_m} - v_{\alpha_n}\rvert\right)! - 1}{\left(\sum_\alpha \lvert v_{\alpha_m} - v_{\alpha_n}\rvert\right)! + 1}$ $\delta_\alpha = 1$, if $v_{\alpha_m} > v_{\alpha_n}$, $\delta_\alpha = -1$, if $v_{\alpha_m} < v_{\alpha_n}$. Values of z_α , M_α , and x_α for triatomic molecules are given in Table 3-7 (p. 106); for four-atomic molecules in Table 3-8 (p. 108); for five-atomic tetrahedral molecules in Table 3-9 (p. 110); and for seven-atomic octahedral molecules in Table 3-10 (p. 111).	(ii) For $(v_{\alpha_m}, \ldots) \rightarrow (v_{\alpha_n}, \ldots)$: $C_{mn} = \prod_\alpha w_{\alpha_m} w_{\alpha_n}$	$w_{\alpha_k} = 1$, if $d_{X_\alpha} = 1$ $w_{\alpha_k} = (v_{\alpha_k} + 1)$, if $d_{X_\alpha} = 2$ $w_{\alpha_k} = \frac{1}{2}(v_{\alpha_k}+1)(v_{\alpha_k}+2)$, if $d_{X_\alpha} = 3$

*Units and definitions of parameters are given in Chapter 7.

TABLE 5-2. PHOTONIC MATRIX ELEMENTS, CONNECTION FACTORS, AND WEIGHTS OF ELECTRONIC, VIBRATIONAL AND ROTATIONAL TRANSITIONS IN MOLECULES* (Cont.)

TYPE OF TRANSITION	MATRIX ELEMENT R^2_{mn} , cm²	CONNECTION FACTOR C_{mn}	WEIGHT w_k ($k = m$ or $k = n$)
<u>ROTATIONAL</u> (a) Diatomic Molecules (Sec. 3.4.1; pp. 112-118)	$R^2_{mn} = \dfrac{Jd_o^2}{(2J+1)(2J-1)}$ $(J = \sup(J_m, J_n);\ \Delta J = 1)$ Values of d_o for diatomic molecules are given in Table 3-11, p. 116.	$C_{mn} = w_m w_n = (2J_m+1)(2J_n+1) =$ $= (2J+1)(2J-1)$	$w_k = 2J_k+1$
(b1) Symmetric Linear Molecules (Sec. 3.4.2; pp. 119-128)	$R^2_{mn} = 0$, since $d_o = 0$	$C_{mn} = w_m w_n$	$w_k = 2J_k+1$
(b2) Asymmetric Linear Molecules (Sec. 3.4.2, pp. 119-128)	<u>(i) For ΔJ = 1:</u> $R^2_{mn} = \dfrac{J^2 - \ell^2}{J}\left(\dfrac{d_o^2}{(2J+1)(2J-1)}\right)$ $(J = \sup(J_m, J_n);\ \ell = v_b,\ v_b-2,\ v_b-4,\ \ldots\ldots -v_b)$ <u>(ii) For ΔJ = 0:</u> $R^2_{mn} = \left(\dfrac{\ell^2}{J}\right)\left(\dfrac{2J-1}{J-1}\right) d_o^2$ $(J = J_m = J_n;\ \ell = v_b,\ v_b-2,\ v_b-4,\ \ldots\ldots -v_b)$ Values of d_o for linear molecules are given in Table 3-12, p. 124.	<u>(i) For ΔJ = 1:</u> $C_{mn} = w_m w_n = (2J_m+1)(2J_n+1) =$ $= (2J+1)(2J-1)$ <u>(ii) For ΔJ = 0:</u> $C_{mn} = (2J+1)^2$	$w_k = 2J_k+1$

*Units and definitions of parameters are giv·n in Chapter 7.

TABLE 5-2. PHOTONIC MATRIX ELEMENTS, CONNECTION FACTORS, AND WEIGHTS OF ELECTRONIC, VIBRATIONAL, AND ROTATIONAL TRANSITIONS IN MOLECULES* (Cont.)

TYPE OF TRANSITION	MATRIX ELEMENT R^2_{mn}, cm² **	CONNECTION FACTOR C_{mn}	WEIGHT w_k ($k = m$ or $k = n$)
ROTATIONAL (Cont.) (c) Symmetric-Top Molecules (Sec. 3.4.3; pp. 129-140)	(i) For $\Delta J = 1$; $K = \lvert K_m \rvert = \lvert K_n \rvert$: $R^2_{mn} = d_o^2 \left(\frac{J^2 - K^2}{J(2J+1)(2J-1)} \right)$ $(J = \sup(J_m, J_n))$ (ii) For $\Delta J = 0$; $K = \lvert K_m \rvert = \lvert K_n \rvert$: $R^2_{mn} = d_o^2 \left(\frac{K^2}{J(J+1)(2J+1)} \right)$ $(J = J_m = J_n)$ Values for d_o for symmetric-top molecules are given in Table 3-13, p. 140.	(i) For $\Delta J = 1$: $C_{mn} = w_m w_n = (2J_m+1)(2J_n+1) =$ $= (2J+1)(2J-1)$ (ii) For $\Delta J = 0$: $C_{mn} = (2J+1)^2$	$w_k = 2J_k+1$
(d) Spherical-Top Molecules (Sec. 3.4.4; pp. 141-148)	$R^2_{mn} = 0$, since $d_o = 0$ for spherical-tops	$C_{mn} = w_m w_n = (2J_m+1)^2(2J_n+1)^2$	$w_k = (2J_k+1)^2$
(e) Asymmetric-Top Molecules (Sec. 3.4.5; pp. 148-158)	R^2_{mn} = Eq. (3.202), p. 154. Table 3-15, p. 158, gives values of parameters of asymmetric-top molecules to be used in Eq. (3.202).	C_{mn} = Eqs. (3.203), (3.204), or (3.205), p. 154	$w_k = 2J_k+1$

*Units and definitions of parameters are given in Chapter 7.

**Expressions for R^2_{mn} which require considerable explanation are not written out here but referred to the text.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION*

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
NATURAL (Sec. 4.2; pp. 169-171)	$b_N = \frac{\left\{(\Delta\nu_{mn})_N/\pi\right\}^2}{(\nu-\nu_{mn})^2 + \left\{(\Delta\nu_{mn})_N/\pi\right\}^2}$	$(\Delta\nu_{mn})_N = \frac{\gamma_{mn}}{4} = \frac{A_{mn}}{4}$ (A_{mn} is given by Eq. (2.8), p. 30)
COLLISIONAL (Pressure) (Sec. 4.4; pp. 174-177)	$b_C = \frac{\left\{(\Delta\pi_{mn})_C/\pi\right\}^2}{(\nu-\nu_{mn})^2 + \left\{(\Delta\nu_{mn})_C/\pi\right\}^2}$	$(\Delta\nu_{mn})_C = 3.3841 \times 10^{26} \frac{\sigma_{1-2}P}{\sqrt{\mu_{1-2}T}}$ (σ_{1-2} given in Table 4-1, p. 176) (μ_{1-2} given by Eq. (4.48), p. 175)
NATURAL + COLLISIONAL (Sec. 4.5; p. 178)	$b_{N,C} = \frac{\left\{(\Delta\nu_{mn})_{N,C}/\pi\right\}^2}{(\nu-\nu_{mn})^2 + \left\{(\Delta\nu_{mn})_{N,C}/\pi\right\}^2}$	$(\Delta\nu_{mn})_{N,C} = (\Delta\nu_{mn})_N + (\Delta\nu_{mn})_C$
DOPPLER (Temperature) (Sec. 4.3; pp. 172-173)	$b_D = \exp-\left\{\frac{\nu-\nu_{mn}}{(\Delta\nu_{mn})_D/\sqrt{\pi}}\right\}^2$	$(\Delta\nu_{mn})_D = \frac{\nu_{mn}}{c}\left(\frac{2\pi kT}{M}\right)^{1/2}$
STARK (Ion Plasma) (Sec. 4.6; pp. 185-189)	$b_S = \left\{\frac{1.5(\Delta\nu_{mn})_S}{1.5(\Delta\nu_{mn})_S + (\nu-\nu_{mn})}\right\}^{5/2}$	$(\Delta\nu_{mn})_S = 2.78 \times 10^{-19} Z_i n_i^{2/3} C_m$ (C_m is tabulated in Table 4-3, p. 188)

*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
<u>DOPPLER + COLLISIONAL + NATURAL</u> (Sec. 4.5; pp. 179-184)	$b_{D,C,N} = \frac{I(a,\xi)}{I(a,o)} = \frac{\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp - z^2}{a^2 + (\xi-z)^2}\,dz}{\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp - z^2}{a^2 + z^2}\,dz}$, where: $a = \frac{1}{\sqrt{\pi}}\left\{\frac{(\Delta\nu_{mn})_C + (\Delta\nu_{mn})_N}{(\Delta\nu_{mn})_D}\right\}$ $\xi = \frac{\pi^{1/2}(\nu-\nu_{mn})}{(\Delta\nu_{mn})_D}$ $I(a,\xi)$ is tabulated in Table 4-2, p. 183.	$(\Delta\nu_{mn})_{D,C,N} = \frac{(\Delta\nu_{mn})_D}{I(a,o)}$

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*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Broadening of Vibrational Transitions) (a) Diatomic Molecules (Sec. 4.7.1; pp. 210-220)	Band: $b_\nu^{PR} = \frac{\lvert\nu-\nu_{mn}\rvert}{\Delta\nu_{mn}} \exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2$ Detailed Lines: $b_{rov}^{PR} = \tilde{h}_\nu^{PR}\, b_J$ $\tilde{h}_\nu^{PR} = w_I\left(\frac{h\nu_B}{kT}\right)^{1/2}\left\{\exp-\left(\frac{J(J+1)h\nu_B}{kT}\right)\right\}\left\{(J+\frac{3}{2})H(\nu_{mn}-\nu_J)H(J) + (J-\frac{1}{2})H(\nu_J-\nu_{mn})H(J-1)\right\}\cdot\left(\frac{\delta\nu_J}{\Delta\nu_J}\right)$ $b_J = b_D$, b_C, b_N, or $b_{D,C,N}$ with $\nu_{mn} = \nu_J$ ν_J is given by Eqs. (4.155a), (4.155b), p. 217. w_I is given by Eq. (4.158a), p. 219. Values of $\nu_B = c\,B_e$ are given in Table 3-11, p. 116.	$\Delta\nu_{mn} = \left(\frac{4\nu_B kT}{h}\right)^{1/2} = 2.89 \times 10^5\, \nu_B^{1/2}\, T^{1/2}$ (Hz) (°K) $\delta\nu_J = \delta\nu_J' \left[\int_{\nu=\nu_J-\frac{1}{2}\delta\nu_J'}^{\nu=\nu_J+\frac{1}{2}\delta\nu_J'} b_J(\nu,\nu_J,\Delta\nu_J)\frac{d\nu}{\Delta\nu_J}\right]^{-1}$ $\delta\nu_J' = 2\nu_B$ $\delta\nu_J = \delta\nu_J'$, if $\delta\nu_J' > \Delta\nu_J$; $\delta\nu_J = \Delta\nu_J$, if $\delta\nu_J' \ll \Delta\nu_J$ $\Delta\nu_J = (\Delta\nu_{mn})_D$, $(\Delta\nu_{mn})_C$, $(\Delta\nu_{mn})_N$, or $(\Delta\nu_{mn})_{D,C,N}$
(b) Linear Molecules (Sec. 4.7.1; pp. 220-226)	Band: $b_\nu^{PR} = S^{PR}\left(\frac{\lvert\nu-\nu_{mn}\rvert}{\Delta\nu_{mn}}\right)\exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2$ $(0 < \nu < \infty)$ $b_\nu^{Q} = S^{Q}\left(\frac{4\nu_B}{\xi_B\Delta\nu_{mn}}\right)\exp-\left(\frac{4\nu_B\lvert\nu_{mn}-\nu_B^Q-\nu\rvert}{\xi_B\Delta\nu_{mn}^2}\right)$ $\begin{pmatrix} 0 < \nu \le \nu_{mn}-\nu_B^Q, \text{ if } \Delta\nu_B > 0 \\ \nu_{mn}-\nu_B^Q < \nu < \infty, \text{ if } \Delta\nu_B < 0 \end{pmatrix}$ $\xi_B = \lvert\Delta\nu_B\rvert/\nu_B = \left\lvert\sum_\beta \alpha_\beta(\nu_{\beta_m}-\nu_{\beta_n})\right\rvert \left[\frac{1}{2}(\nu_{B_m}+\nu_{B_n})\right]^{-1}$	$\Delta\nu_{mn} = \left(\frac{4\nu_B kT}{h}\right)^{1/2} = 2.89 \times 10^5\, \nu_B^{1/2}\, T^{1/2}$ (Hz) (°K) (NOTE: For symmetric linear molecules such as CO_2, substitute $2\nu_B$ for ν_B)

*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Cont.) (b) Linear Molecules (Cont.) (Sec. 4.7.1; pp. 220-226)	$\nu_B^Q = (\ell_m^2-\ell_n^2)\nu_B$; $S^{PR} = \frac{2}{3}$, $S^Q = \frac{1}{3}$ for most cases except that $S^{PR} = 1$, $S^Q = 0$ for stretching vibrations of symmetric molecules such as CO_2 CS_2, UO_2 . Values of $\nu_B = c\ B_e$ and α_B are given in Table 3-12, p. 124. Detailed Lines: $b_{rov}^{PQR} = \tilde{h}_\nu^{PQR} \cdot b_J$ $\tilde{h}_\nu^{PQR} = S^{PR}\left(\frac{h\nu_B}{kT}\right)^{1/2} \left[\exp-\left\{\frac{J(J+1)h\nu_B}{kT}\right\}\right] \cdot \Big[H(-\nu_J^Q)w_I^{PR}(J+\frac{3}{2}) \cdot$ $\cdot\ H(\nu_{mn}-\nu_J)H(J)\frac{\delta\nu_J}{\Delta\nu_J} + H(-\nu_J^Q)w_I^{PR}(J-\frac{1}{2})H(\nu_J-\nu_{mn})H(J-1)\frac{\delta\nu_J}{\Delta\nu_J} +$ $+\ 3S^Q H(-\nu_J)w^Q_I\left(\frac{J+\frac{1}{2}}{\xi_B(J+1)}\right)H(J-1)\frac{\delta\nu_J^Q}{\Delta\nu_J}\Big]$ $b_J = b_D$, b_C , b_N , or $b_{D,C,N}$ with $\nu_{mn} = \nu_J$ or ν_J^Q ν_J is given by Eqs. (4.155a) and (4.155b); p. 217. ν_J^Q is given by Eq. (4.180a), p. 225. w_I^{PR} is given by Eq. (4.158), p. 219; w_I^Q given by Eq. (4.183), pp. 225-226. Values of $\nu_B = c\ B_e$ and α_B^B are given in Table 3-12, p. 124.	$\Delta\nu_{mn} = \left(\frac{4\nu_B kT}{h}\right)^{1/2} = 2.89 \times 10^5\ \nu_B^{1/2}\ T^{1/2}$ (Hz) (°K) (NOTE: For symmetric linear molecules such as CO_2 , substitute $2\nu_B$ for ν_B) $\delta\nu_J$ same as for diatomic molecules (see (a)), except that for stretching vibrations of symmetric linear molecules such as CO_2 , CS_2 , UO_2 , we have $\delta\nu_J' = 4\nu_B$ $\delta\nu_J^Q = (J+1)\Delta\nu_B \left[\int_{\nu=\nu_J-\frac{1}{2}(J+1)\Delta\nu_B}^{\nu=\nu_J+\frac{1}{2}(J+1)\Delta\nu_B} b_J(\nu,\nu_J,\Delta\nu_J)\frac{d\nu}{\Delta\nu_J}\right]^{-1}$ $\Delta\nu_B = \nu_{B_n} - \nu_{B_m}$ $\delta\nu_J^Q = \Delta\nu_J$, if $(J+1)\Delta\nu_B \ll \Delta\nu_J$ $\delta\nu_J^Q = (J+1)\Delta\nu_B$, if $(J+1)\Delta\nu_B \gg \Delta\nu_J$ $\Delta\nu_J = (\Delta\nu_{mn})_D$, $(\Delta\nu_{mn})_C$, $(\Delta\nu_{mn})_N$, or $(\Delta\nu_{mn})_{D,C,N}$
(c) Symmetric-Top Molecules (Sec. 4.7.2, pp. 226-244)	Band: (i) Parallel (//) Bands $b_\nu^{PR} = \frac{2\|\nu-\nu_{mn}\|}{3\Delta\nu_{mn}} \exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2$ $(0 < \nu < \infty)$	$\Delta\nu_{mn} = \left(\frac{4\nu_B kT}{h}\right)^{1/2} = 2.89 \times 10^5\ \nu_B^{1/2}\ T^{1/2}$ (Hz) (°K)

*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$**	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Cont.) (c) Symmetric-Top Molecules (Cont.) (Sec. 4.7.2, pp. 226-244)	$b_\nu^Q = \frac{4\nu_B}{3\xi_B\Delta\nu_{mn}} \exp-\left\{\frac{4\nu_B\lvert\nu_{mn}-\nu\rvert}{\xi_B\Delta\nu_{mn}^2}\right\}$ $\begin{pmatrix} 0 < \nu < \nu_{mn} \text{ , if } \Delta\nu_B > 0 \\ \nu_{mn} < \nu < \infty \text{ , if } \Delta\nu_B < 0 \end{pmatrix}$ $\xi_B = \lvert\Delta\nu_B\rvert/\nu_B = \nu_B^{-1}\left\lvert\sum_\beta \alpha_\beta^B(\nu_{B_m}-\nu_{B_n})\right\rvert$ Values of ν_B and α_β^B are given in Table 3-13, p. 140. (ii) Perpendicular (⊥) Bands b_ν^{PR} = Eq. (4.220), p. 243 b_ν^Q = Eq. (4.221), p. 243	$\Delta\nu_{mn} = \left(\frac{4\nu_B kT}{h}\right)^{1/2} = 2.89 \times 10^5\ \nu_B^{1/2}\ T^{1/2}$ (Hz) (°K)
	Detailed Lines (both // and ⊥ bands): $b_{rov}^{PQR} = \tilde{h}_\nu^{PQR}\ b_{JK}$ $\tilde{h}_\nu^{PQR} = \left(\frac{h\nu_A^{1/2}\nu_B^{1/2}}{3\pi^{1/2}kT}\right)\left[\exp-\left\{\frac{J(J+1)\nu_B+K^2(\nu_A-\nu_B)}{kT/h}\right\}\right]\cdot\left(\frac{\delta\nu_K}{\Delta\nu_{JK}}\right)\cdot$ $\cdot\left[(2J+3)H(J)H(\nu_{mn}-\nu_{JK})H(-\nu_{JK}^Q) + (2J+1)H(J-1)H(\nu_{JK}-\nu_{mn})H(-\nu_{JK}^Q)\right.$ $\left.+ \frac{2J+1}{\xi_B(J+1)} H(J-1)H(-\nu_{JK})\right]$ $b_{JK} = b_D$, b_C , b_N , or b_{DCN} with $\nu_{mn} = \nu_{JK}$ or ν_{JK}^Q ν_{JK} and ν_{JK}^Q are given by Eqs. (4.184a) and (4.184b), p. 226. $\Delta\nu_o$ is given by Eqs. (4.186) or (4.188), p. 227. Values of $\nu_A = cA$, $\nu_B = cB$ and α_β^B are given in Table 3-13, p. 140.	$\delta\nu_K = \delta\nu_K'\left[\int_{\nu_{JK}-\frac{1}{2}\delta\nu_K'}^{\nu_{JK}+\frac{1}{2}\delta\nu_K'} b(\nu,\nu_{JK},\Delta\nu_{JK})\,d\nu\right]^{-1}$ $\delta\nu_K' = 2\Delta\nu_{AC} + (2K+1)(\Delta\nu_A-\Delta\nu_B)$, where $\Delta\nu_{AC}$, $\Delta\nu_A$, and $\Delta\nu_B$ are given by Eqs. (4.187) or (4.189), and (4.192), (4.193); pp. 227 and 228. $\delta\nu_K = \delta\nu_K'$, if $\delta\nu_K' \gg \Delta\nu_{JK}$ $\delta\nu_K = \Delta\nu_{JK}$, if $\delta\nu_K' \ll \Delta\nu_{JK}$ $\Delta\nu_{JK} = (\Delta\nu_{mn})_D$, $(\Delta\nu_{mn})_C$, $(\Delta\nu_{mn})_N$, or $(\Delta\nu_{mn})_{D,C,N}$

*Units and parameters are defined in Chapter 7. **For expressions requiring more than three lines, reference is made to the text.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu, \nu_{mn}, \Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Cont.) (d) Spherical-Top Molecules (Sec. 4.7.3, pp. 244-257)	Band: $b_\nu^{PR} = \left(\frac{4(\nu-\nu_{mn})^2}{3\pi^{1/2}\Delta\nu_{mn}^2}\right) \exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2 \quad (0 < \nu < \infty)$ $b_\nu^Q = \left(\frac{16(1-\zeta_m)^3\nu_B^{3/2}\lvert\nu_{mn}-\nu\rvert^{1/2}}{3\pi^{1/2}\xi_B^{3/2}\Delta\nu_{mn}^2}\right) \cdot \exp-\left\{\frac{4(1-\zeta_m)^2\nu_B\lvert\nu_{mn}-\nu\rvert}{\xi_B\Delta\nu_{mn}^2}\right\} \quad \begin{pmatrix} 0 < \nu < \nu_{mn}, \text{ if } \Delta\nu_B > 0 \\ \nu_{mn} < \nu < \infty, \text{ if } \Delta\nu_B < 0 \end{pmatrix}$ Detailed Lines: $b_{rov}^{PQR} = \tilde{h}_\nu^{PQR}\, b_J$ $\tilde{h}_\nu^{PQR} = \left(\frac{h\nu_B}{3\pi^{1/2}kT}\right)\Big[(2J+3)^2 \left\{\exp-\left(\frac{\nu_B(J+1)(J+2\zeta_m)}{kT/h}\right)\right\} \cdot$ $\cdot \left(\frac{\delta\nu_J}{\Delta\nu_J}\right) H(J)(\nu_{mn}-\nu_J)H(-\nu_J^Q) + (2J-1)^2\left\{\exp-\left(\frac{\nu_B J(J+1-2\zeta_m)}{kT/h}\right)\right\} \cdot$ $\cdot \left(\frac{\delta\nu_J}{\Delta\nu_J}\right) H(J-1)H(\nu_J-\nu_{mn})H(-\nu_J^Q) + \left(\frac{1-\zeta_m}{\xi_B}\right)(2J+1)^2 \left(\frac{\delta\nu_J^Q}{\Delta\nu_J}\right) \cdot$ $\cdot \left\{\exp-\left(\frac{J(J+1)\nu_B}{kT/h}\right)\right\} H(J-1)H(-\nu_J)\Big]$ $b_J = b_D$, b_C , b_N , or $b_{D,C,N}$ with $\nu_{mn} = \nu_J$ or ν_J^Q . ν_J and ν_J^Q are given by Eq. (4.155), p. 217, and (4.180), p. 225. Values of $\nu_B = cB$ and ζ_m are given in Table 3-14, p. 147.	$\Delta\nu_{mn} = \left\{4(1-\zeta_m)^2\nu_B kT/h\right\}^{1/2}$ $\delta\nu_J$ and $\delta\nu_J^Q$ are same as for linear molecules except that $\nu_B = \nu_B \cdot (1-\zeta_m)$ $\Delta\nu_J = (\Delta\nu_{mn})_D$, $(\Delta\nu_{mn})_C$, $(\Delta\nu_{mn})_N$, or $(\Delta\nu_{mn})_{D,C,N}$

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*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$**	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Cont.) (e) Asymmetric-Top Molecules (Sec. 4.7.4; pp. 257-275)	Band: Type-A Bands $b_\nu^{PR} = \frac{2\lvert\nu-\nu_{mn}\rvert}{3\Delta\nu_{mn}} \exp-\left(\frac{\nu-\nu_{mn}}{\Delta\nu_{mn}}\right)^2$ $(0 < \nu < \infty)$ $b_\nu^{Q} = \frac{2(\nu_B+\nu_C)}{3\xi_{BC}\Delta\nu_{mn}} \exp\cdot\left(\frac{2(\nu_B+\nu_C)\lvert\nu_{mn}-\nu\rvert}{\xi_{BC}\Delta\nu_{mn}^2}\right)$ $\begin{pmatrix} 0 < \nu < \nu_{mn}, \text{ if } \Delta\nu_{BC} > 0 \\ \nu_{mn} < \nu < \infty, \text{ if } \Delta\nu_{BC} < 0 \end{pmatrix}$ $\xi_{BC} = 2\lvert\Delta\nu_{BC}\rvert/(\nu_B+\nu_C) = 2\left\lvert\sum_\beta\left[\alpha_\beta^B(\nu_{\beta_m}-\nu_{\beta_n})+\alpha_\beta^C(\nu_{\beta_m}-\nu_{\beta_n})\right]\right\rvert/(\nu_B+\nu_C)$ Values of $\nu_b = cB$, $\nu_C = cC$, and α_β^B, α_β^C are given in Table 4-6, p. 269 (for H_2O), and in Table 3-15, p. 158. Type-B Bands b_ν^{PR} = Eq. (4.277); p. 273 $(0 < \nu < \infty)$ b_ν^{Q} = Eq. (4.278); pp. 273 and 274 $(0 < \nu < \nu_{mn})$ Detailed Lines (both Type-A and Type-B bands): $b_\nu^{PQR} = \tilde{h}_\nu^{PQR}\, b_{JW}$	$\Delta\nu_{mn} = \left\{2(\nu_B+\nu_C)\, kT/h\right\}^{1/2}$

*Units and parameters are defined in Chapter 7. **For expressions requiring more than three lines, reference is made to the text.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
ROTATIONAL (Cont.) (e) Asymmetric-Top Molecules (Cont.) (Sec. 4.7.4; pp. 257-275)	$\tilde{h}^{PQR}_{\nu} = \left\{\frac{\nu_A^{1/2}(\nu_B+\nu_C)^{1/2}}{3(2\pi)^{1/2}kT/h}\right\} H(J^2-W)\cdot\left[\exp-\left\{\frac{J(J+1)(\nu_B+\nu_C)+2W(\nu_A-\nu_B)}{kT/h}\right\}\right]\cdot$ $\cdot\left\{(2J+3)\left(\frac{\delta\nu_W}{\Delta\nu_{JW}}\right)u^{PR}(J,W)H(\nu_{mn}-\nu_{JW})H(-\nu^Q_{JW})H(J)\right. +$ $+\quad(2J+1)\left(\frac{\delta\nu_W}{\Delta\nu_{JW}}\right)u^{PR}(J,W)H(\nu_{JW}-\nu_{mn})H(-\nu^Q_{JW})H(J-1) +$ $+\quad\left.\frac{2J+1}{\xi_{BC}(J+1)}\left(\frac{\delta\nu^Q_W}{\Delta\nu_{JW}}\right)u^Q(J,W)H(-\nu_{JW})H(J-1)\right\}$ $b_{JW} = b_D$, b_C , b_N , or $b_{D,C,N}$ with $\nu_{mn} = \nu_{JW}$ or ν^Q_{JW} ν_{JW} and ν^Q_{JW} are given by Eqs. (4.255), p. 259 and (4.262), p. 260. $u^{PR}(J,W)$ and $u^Q(J,W)$ are given by Eq. (4.268), p. 268 for Type-A bands, and by Eqs. (4.275), (4.276), p. 271 for Type-B bands. Values of $\nu_A = cA$, $\nu_B = cB$, $\nu_C = cC$, and of α^A_B , α^B_B , α^C_B are given in Table 4-6, p. 269 (for H_2O), and in Table 3-15, p. 158.	$\Delta\nu_{mn} = \left\{2(\nu_B+\nu_C)\ kT/h\right\}^{1/2}$ -- $\delta\nu_W$ = Eq. (4.280a), p. 275 $\delta\nu^Q_W$ = Eq. (4.280b), p. 275 $\delta\nu_W = \Delta\nu_{JW}$, if $\nu_{ABC} \gg \Delta\nu_{JW}$ $\delta\nu_W = \nu_{ABC}\big(W(J) - W(J-1)\big)$, if $\nu_{ABC} \ll \Delta\nu_{JW}$ (ν_{ABC} is given by Eq. (4.260), p. 260) $\Delta\nu_{JW} = (\Delta\nu_{mn})_D$, $(\Delta\nu_{mn})_C$, $(\Delta\nu_{mn})_N$, or $(\Delta\nu_{mn})_{D,C,N}$ --

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*Units and parameters are defined in Chapter 7.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu, \nu_{mn}, \Delta\nu_{mn})$**	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
<u>VIBRATIONAL</u> (Vibrational Broadening of Electronic Transitions) (a) Diatomic Molecules (Sec. 4.6.1; pp. 276-298)	<u>Bandsystem:</u> $b_e = (\Delta\nu_{mn}) \times$ (Eq. (4.341) on p. 294) <u>Detailed Bands:</u> $b_{vnc} = \tilde{h}_e\, b_v$ $\tilde{h}_e = \left(\frac{\delta\nu_s}{\Delta\nu^v_{mn}}\right) \times$ (Eq. (4.343) on p. 295) $b_v = b_v^{PR}$, b_v^{Q} as given in this table under "Band" shape functions for rotational broadening with ν_{mn} as given there substituted by ν_s. $\Delta\nu^v_{mn}$ = Spread of vibration band listed as $\Delta\nu_{mn}$ under rotational broadening in this table. $\delta\nu_s$ = Eq. (4.345) on p. 296. ν_s = Eq. (4.344) on p. 296. <u>Detailed Lines:</u> $b_{rvc} = \tilde{h}_e \cdot \tilde{h}_v \cdot b_J$ $\tilde{h}_v = \tilde{h}_v^{PQR}$, or $\tilde{h}_v^{PR}$ as given in this table under rotational broadening with ν_{mn} given there sutstituted by ν_s and ν_J by $\nu_{sJ} = \nu_J(\nu_{mn}=\nu_s)$. $b_J = b_D$, b_C, b_N, or $b_{D,C,N}$ as given in this table under the line-broadening processes, wit: ν_{mn} given there substituted by $\nu_{sJ} = \nu_J(\nu_{mn}=\nu_s)$; the line frequency ν_J (or ν_{JK} or ν_{JW}) is given by the applicable relation discussed under rotational broadening in this table.	$\Delta\nu_{mn} = \frac{2(1-\xi_n^2 B_n^2)kT/h}{1+2B_n/A_n} \cdot \exp\left\{X_n^2 A_n (A_n+2B_n)\left(\frac{h\nu_{d_n}}{kT}\right)\right\}$ $X_n = \frac{\xi_n(1-B_n)}{1-\xi_n^2 B_n^2}$ $A_n = \left\{1 + (1-\xi_n^2)B_n^2\right\}^{1/2}$ $\xi_n = \nu_{e_n} / \nu_{e_m}$ $B_n = \exp -\beta_n (r_{e_m} - r_{e_n})$ $\beta_n = \left(\frac{2\pi^2 \bar{M}_{AB}}{h\nu_{d_n}}\right)^{1/2} \nu_{e_n}$, cm^{-1} $\bar{M}_{AB} = M_A M_B / (M_A + M_B)$ ------------------------------ Values of $\nu_{d_i} = cD_{e_i}$, $\nu_{e_i} (\equiv \omega_{e_i})$, and r_{e_i} are given in Herzberg's tables (Ref. 2). ------------------------------

*Units and parameters are defined in Chapter 7. **For expressions requiring more than three lines, reference is made to the text.

TABLE 5-3. SHAPE FUNCTIONS AND SPREADS OF MOLECULAR LINE AND BAND BROADENING PROCESSES IN PHOTON EMISSION OR ABSORPTION* (Cont.)

BROADENING PROCESS	LINE-, BAND-, OR BANDSYSTEM-SHAPE FUNCTION $b(\nu,\nu_{mn},\Delta\nu_{mn})$**	LINE-, BAND-, OR BANDSYSTEM-SPREAD $\Delta\nu_{mn}$, Hz
<u>VIBRATIONAL</u> (Cont.)	<u>Bandsystem:</u>	
(b) Polyatomic Molecules (Sec. 4.8.2; pp. 298-309)	b_e = Eq. (4.366), p. 308.	$\Delta\nu_{mn}$ = Eq. (4.361), p. 306.
	<u>Detailed Bands:</u> $b_{vnc} = \tilde{h}_e \, b_{v\alpha}$ $\tilde{h}_e = \left(\frac{\delta\nu_{\alpha s}}{\Delta\nu_{mn}^{v\alpha}}\right) \times \left[\text{Eq. (4.366), p. 308 with } \nu = \nu_{\alpha s}\right]$ $b_{v\alpha} = b_v^{PR}$, b_v^{Q} as given in this table under "Band" shape functions for rotational broadening with ν_{mn} as given there substituted by $\nu_{\alpha s}$. $\Delta\nu_{mn}^{v\alpha}$ = Spread of α-vibration band listed as $\Delta\nu_{mn}$ under rotational broadening in this table. $\delta\nu_{\alpha s}$ = Eq. (4.368), p. 308. $\nu_{\alpha s}$ = Eq. (4.367), p. 308.	
	<u>Detailed Lines:</u> $b_{rvc} = \tilde{h}_e \cdot \tilde{h}_{v\alpha} \cdot b_J$ $\tilde{h}_{v\alpha} = \tilde{h}_v^{PQR}$, or $\tilde{h}_v^{PR}$ as given in this table under rotational broadening with ν_{mn} given there substituted by $\nu_{\alpha s}$, and ν_J by $\nu_{sJ} = \nu_J(\nu_{mn} = \nu_{\alpha s})$. $b_J = b_D$, b_C, b_N, or $b_{D,C,N}$ as given in this table under the line-broadening processes, with ν_{mn} given there substituted by $\nu_{sJ} = \nu_J(\nu_{mn} = \nu_{\alpha s})$; the line frequency ν_J (or ν_{JK} or ν_{JW}) is given by the applicable relation discussed under rotational broadening in this table.	

*Units and parameters are defined in Chapter 7. **For expressions requiring more than three lines, reference is made to the text.

As discussed in Chapter 2, the most convenient parameter to use in photon emission problems is the spectral rate $\left(\frac{dA_{mn}}{d\nu}\right)^o$ sec^{-1} Hz^{-1}, and/or the total rate A^o_{mn} sec^{-1} or decay time $\tau^o_{mn} = (A^o_{mn})^{-1}$ sec. In absorption or stimulated emission problems on the other hand the cross-section σ^o_{nm} cm^2 or σ^o_{mn} cm^2 is more appropriate. Microscopic absorption and emission are interrelated by the following equations:

$$\underset{\text{(absorption)}}{\sigma^o_{nm}} = \frac{\lambda^2_{mn}}{8\pi}\left(\frac{w_m}{w_n}\right)\left(\frac{dA_{mn}}{d\nu}\right)^o = \frac{\lambda^2_{mn}}{8\pi}\left(\frac{w_m}{w_n}\right)A^o_{mn}\, g_o(\nu,\nu_{mn},\Delta\nu_{mn}) \qquad (5.1)$$

$$\underset{\text{(stim. emission)}}{\sigma^o_{mn}} = \left(\frac{w_n}{w_m}\right)\underset{\text{(absorption)}}{\sigma^o_{nm}} = \frac{\lambda^2_{mn}}{8\pi}\left(\frac{dA_{nm}}{d\nu}\right)^o =$$

$$= \frac{\lambda^2_{mn}}{8\pi} A^o_{mn}\, g_o(\nu,\nu_{mn},\Delta\nu_{mn}) \text{ , cm}^2 \qquad (5.2)$$

Here the sub- or superscript o stands for o = elc, o = vib, or o = rot, as the case may be, while m indicates the upper excited level of the molecule and n designates the lower level. In addition, for the function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ the subscript o may stand for o = rov (= rovibrational), o = vnc (= vibronic), and o = rvc (= rovibronic).

Any one of the parameters A^o_{mn}, σ^o_{mn}, or σ^o_{nm} are completely determined by four subsidiary parameters, namely the matrix element $(R^2_{mn})^o$, the statistical weights w_m and w_n (or alternatively the connection factor C_{mn} and either w_m or w_n), and the contour function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$, for which analytic expressions are tabulated in Tables 5-2 and 5-3. In Table 5-3, analytic expressions for the function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ are given in two parts, namely by $b_o(\nu,\nu_{mn},\Delta\nu_{mn})$ tabulated in the middle column, and $\Delta\nu_{mn}$ which is given in the right-hand column. In all cases of course:

$$g_o(\nu,\nu_{mn},\Delta\nu_{mn}) = \frac{b_o(\nu,\nu_{mn},\Delta\nu_{mn})}{\Delta\nu_{mn}} \text{ , Hz}^{-1} \qquad (5.3)$$

The "spread" $\Delta\nu_{mn}$ is defined such that:

$$\int_{\nu = 0}^{\infty} g_o(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = 1 \text{ ,} \qquad (5.4)$$

or:

$$\int_{\nu = 0}^{\infty} b_o(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = \Delta\nu_{mn} \text{ ,} \qquad (5.5)$$

which has the advantage that for a function $f(\nu)$ that varies slowly in the frequency region $\nu_{mn} - \frac{1}{2}\Delta\nu_{mn} < \nu < \nu_{mn} + \frac{1}{2}\Delta\nu_{mn}$:

$$\int_{\nu = 0}^{\infty} f(\nu)\, g_o(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = f(\nu{=}\nu_{mn}) \qquad (5.6)$$

$$\int_{\nu = 0}^{\infty} f(\nu)\, b_o(\nu,\nu_{mn},\Delta\nu_{mn})\, d\nu = \Delta\nu_{mn}\; f(\nu{=}\nu_{mn}) \qquad (5.7)$$

The spread $\Delta\nu_{mn}$ is not quite the same as the "width-at-half-height" $\bar{\Delta}\nu_{mn}$ widely used in the current literature. For a "gaussian" line- or band-shape function $b_G = \exp - \frac{1}{\pi}\left\{(\nu-\nu_{mn})/\Delta\nu_{mn}\right\}^2$, the spread $\Delta\nu_{mn}$ and width-at-half-height $\bar{\Delta}\nu_{mn}$ are related by (see section 2.1):

$$\underset{\text{(Gaussian)}}{\Delta\nu_{mn}} = \left(\frac{\pi}{\ln 2}\right)^{\frac{1}{2}} \bar{\Delta}\nu_{mn} \text{ , Hz ,} \tag{5.8}$$

while for "lorentzian" line- or band-shape functions $b_L = (\Delta\nu_{mn}/\pi)^2\left[(\nu-\nu_{mn})^2 + (\Delta\nu_{mn}/\pi)^2\right]^{-1}$, the relation is (see section 2.1):

$$\underset{\text{(Lorentzian)}}{\Delta\nu_{mn}} = \pi\, \bar{\Delta}\nu_{mn} \text{ , Hz} \tag{4.9}$$

For vibrational combination-band transitions, the parameters R^2_{mn}, w_m, and w_n can be directly obtained from Table 5-2. However in some cases, it may not be immediately clear which band-contour function $g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ must be chosen from Table 5-3 for a combination-band transition in which the initial level m (or n) has different symmetry properties from the final level n (or m). For example the important $\nu_3 \rightarrow 2\nu_2$ transition in CO_2 connects the asymmetric-stretch vibrational level ν_3 which possesses only rotational sublevels with even J (J = 0, 2, 4,.....), to the $2\nu_2$ bending vibration which can support rotational sublevels of both even and odd J (J = 0, 1, 2, 3,....). Transitions within the ν_3 vibrational band moreover show only P- and R-Branches, whereas transitions within the ν_2 band have a Q-Branch as well. Thus the question arises whether only b_v^{PR}, or both b_v^{PR} and b_v^{Q} apply in the case $\nu_3 \rightarrow 2\nu_2$. In this case the detailed transition selection rules must be examined, which show that only transitions with even J can take place and that Q-Branch transitions ($\Delta J=0$) are forbidden just like for pure ν_3 band transitions. Thus the expression for the b_v function (and thus the g_v function) to be used for the $\nu_3 \leftrightarrow 2\nu_2$ transition is the one that also applies to transitions for the pure ν_3 vibration band. That is for the $\nu_3 \leftrightarrow 2\nu_2$ transition, the shape function that has only a P- and R-Branch is applicable, and furthermore $\delta\nu_J' = 4\nu_B$ in this case as a consequence of the fact that $J = 0, 2, 4, \ldots.$ for vibrational level ν_3 .

In Tables 5-1, 5-2, and 5-3, consistent units of cm² for R^2_{mn} , cm for λ_{mn} , Hz for ν, ν_{mn} , etc., and sec^{-1} for A°_{mn} were used. In many applications the frequency ν is expressed in cm^{-1} or "wavenumbers." Of course the conversions are simply:*

$$1 \text{ Hz} \equiv 1 \text{ sec}^{-1} = 3.33563 \times 10^{-11} \text{ cm}^{-1} \equiv 3.33563 \times 10^{-11} \text{ Hb}$$

$$1 \text{ cm}^{-1} \equiv 1 \text{ Hb} = 2.99793 \times 10^{10} \text{ Hz} = 2.99793 \times 10^{10} \text{ sec}^{-1}$$

Since frequencies in the visible and infrared are on the order of 10^{12} to 10^{15} Hz, a frequency unit that is often used is the teraherz = THz = 10^{12} Hz. Thus:

$$1 \text{ THz} = 33.3563 \text{ cm}^{-1} \equiv 33.3563 \text{ Hb}$$

$$1 \text{ cm}^{-1} \equiv 1 \text{ Hb} = 0.0299793 \text{ THz}$$

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*The author would like to propose here that 1 cm^{-1} ≡ 1 Hb ≡ 1 Herzberg be adopted, named after Nobel laureate Gerhard Herzberg. This new name provides much more clarity in expressions such as the ones given for $g(\nu,\nu_{mn},\nu_{mn})$ whose units are Hz^{-1} or $(\text{cm}^{-1})^{-1} \equiv \text{Hb}^{-1}$. Confusion often arises if one gave $g_v(\nu,\nu_{mn},\Delta\nu_{mn})$ in units of cm = $(\text{cm}^{-1})^{-1}$.

In Table 5-3, the Heaviside unit step function $H(x)$ appears often. It is defined by:

$$H(x) = 1 \quad , \quad \text{for } x = 0 \text{ , and } x > 0 \tag{5.10a}$$

$$H(x) = 0 \quad , \quad \text{for } x < 0 \tag{5.10b}$$

In the expressions for rotational broadening (Table 5-3), the functions h_v^{PQR} have the factors $H(-\nu_J^Q)$ and $H(-\nu_J)$. These factors, and the factors $H(\nu_{mn}-\nu_J)$ and $H(\nu_J-\nu_{mn})$, merely insure that only one of three possible weighting terms respectively for the P-, Q-, and R-Branch, is nonzero for each rotational line with frequency ν_J or ν_J^Q that is being considered. If only P- and R-Branches existed, the factors $H(-\nu_J^Q)$ and $H(-\nu_J)$ would not be necessary since the frequencies ν_J in the P- and R-Branches do not overlap, and the factors $H(\nu_{mn}-\nu_J)$ and $H(\nu_J-\nu_{mn})$ would keep the appropriate weighting terms separated. However the ν_J^Q frequencies of the Q-Branch can overlap with the P-Branch, hence it was necessary to add the "on-off" factors $H(-\nu_J)$ and $H(-\nu_J^Q)$. It is assumed in these expressions that $\nu_J^Q = 0$ if a line in the P- or R-Branch with frequency ν_J is considered, and vice versa $\nu_J = 0$ if the strength of a line in the Q-Branch with frequency ν_J^Q is being calculated. For symmetric-top rotors the parameters ν_J , ν_J^Q change to ν_{JK} , ν_{JK}^Q , while for asymmetric-top rotors they become ν_{JW} , ν_{JW}^Q . The same comments in these cases apply for the factors $H(-\nu_{JK})$, $H(-\nu_{JK}^Q)$, $H(-\nu_{JW})$, and $H(-\nu_{JW}^Q)$ of course.

In the sections that follow, we give for illustrative purposes, some examples of applications in contemporary applied physics in which photon absorption cross-sections or emission rates are used. In addition some other general relations are given that are pertinent in photonics work.

5.2 INFRARED EMISSION RATES OF ROCKET PLUME MOLECULES

Some of the main combustion products created by reactions of rocket fuel with oxidizer are listed in Table 5-4. Of these, H_2O, CO_2, and CO usually contribute most to radiations in the infrared via vibrational transitions. Though H_2 is also quite abundant in rocket exhausts, it does not radiate in the infrared. This is because the vibrational dipole charge z_1 of H_2 is zero because of this molecule's atomic symmetry.

Many molecular species present in rocket exhausts are also the major species produced by the usual combustion processes in aircraft and automobile engines. They furthermore represent major infrared-active species of importance in the earth's biosphere. Thus the formulas which we shall obtain below for these species may be used also in such diverse applications as aircraft exhaust radiation and atmospheric pollution monitoring.

From the relations given in Tables 5-1 and 5-3, we find that for fundamental vibrational infrared transitions between $v_\alpha = 0$ and $v_\alpha = 1$, for both diatomic and polyatomic molecules, we get for the spontaneous emission rate A^{o}_{1-0} :*

$$\boxed{\left(A^{o}_{1-0}\right)_{vib} = \frac{8}{3}\,\frac{\pi^2 e^2}{c^3}\,\underset{(Hz^2/gm)}{\left(\frac{\nu_\alpha^2 z_\alpha^2}{M_\alpha}\right)} = 1.219 \times 10^{-4}\,\underset{\left((Hb)^2/amu\right)}{\left(\frac{\nu_\alpha^2 z_\alpha^2}{M_\alpha}\right)}\ ,\ \sec^{-1}} \qquad (5.11)$$

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*We only give properties of the fundamentals here. The (much weaker) emission rates for overtones and combination-band transitions can also be readily calculated from the equations given in Chapters 2, 3, and 4.

TABLE 5-4. FUNDAMENTAL ($v_\alpha = 0 \longleftrightarrow v_\alpha = 1$) VIBRATIONAL INFRARED BAND PARAMETERS OF IMPORTANT MOLECULES IN ROCKET PLUMES AND IN THE EARTH ATMOSPHERE (See also Table 3-6, p. 90; Table 3-7, p. 106; Table 3-11, p. 116; Table 3-12, p. 124; Table 3-15, p. 158; and Table 4-6, p. 269)

MOLECULE	TYPE OF VIBRATOR	TYPE OF ROTOR	NORMAL VIBRATION FREQUENCY (Hb)	TYPE OF NORMAL VIBRATION	VIBRATION DIPOLE CHARGE z_1	VIBRATION MASS M_α (amu)	VIBRATIONAL DECAY TIME* τ^v_{1-0} (ms)	FUNDAMENTAL ROTATION FREQUENCY (Hb)	VIBRATIONAL BAND SPREAD $(\Delta\nu_{mn})_n$ (Hb)	ξ_B OR ξ_{BC} (LISTED ONLY FOR BANDS WITH Q-BRANCH)	APPLICABLE b_v FUNCTIONS
H_2	Linear	Linear	$\nu_e = 4395$	Stretch	0	0.5041	∞	$\nu_B = 60.80$	$13.020T^{1/2}$	—	Eq. (5.15)
OH	Linear	Linear	$\nu_e = 3735$	Stretc	0.106	0.9484	4.401	$\nu_B = 18.87$	$7.254T^{1/2}$	—	Eq. (5.15)
HCℓ	Linear	Linear	$\nu_e = 2990$	Stretch	0.0826	0.9799	29.028	$\nu_B = 10.59$	$5.434T^{1/2}$	—	Eq. (5.15)
HF	Linear	Linear	$\nu_e = 4139$	Stretch	0.0533	0.9573	161.363	$\nu_B = 20.94$	$7.641T^{1/2}$	—	Eq. (5.15)
CO	Linear	Linear	$\nu_e = 2170$	Stretch	0.630	6.858	30.102	$\nu_B = 1.93$	$2.320T^{1/2}$	—	Eq. (5.15)
NO	Linear	Linear	$\nu_e = 1904$	Stretch	0.973	7.4	17.853	$\nu_B = 1.70$	$2.177T^{1/2}$	—	Eq. (5.15)
N_2	Linear	Linear	$\nu_e = 2360$	Stretch	0	7.004	∞	$\nu_B = 2.01$	$2.367T^{1/2}$	—	Eq. (5.15)
O_2	Linear	Linear	$\nu_e = 1580$	Stretch	0	8.000	∞	$\nu_B = 1.45$	$2.011T^{1/2}$	—	Eq. (5.15)
H_2O $(O^{\diagup H \diagdown}O)$	Planar	Asym. Top	$\nu_1 = 3657$	Symm. In$^{(a)}$	0.105	0.1905	11.141	$\nu_A = 27.88$	$5.760T^{1/2}$	0.03342	Eqs. (5.24), (5.25)
"	"	"	$\nu_2 = 1595$	Symm. Out$^{(a)}$	0.273	1.0438	45.161	$\nu_B = 14.51$	$5.760T^{1/2}$	0.00183	Eqs. (5.24), (5.25)
"	"	"	$\nu_3 = 3756$	Asymmetric$^{(a)}$	0.153	0.9271	23.030	$\nu_C = 9.29$	$5.760T^{1/2}$	0.02026	Eqs. (5.21), (5.22)
CO_2 (O-C-O)	Linear (Sym.)	Linear	$\nu_1 = 1388$	Sym. Stretch$^{(b)}$	0	16.000	∞	$\nu_B = 0.390$	$1.475T^{1/2}$	—	Eq. (5.15)
"	"	"	$\nu_2 = 667$	Bending$^{(b)}$	0.21[illegible]	2.182	86.237	$\nu_B = 0.390$	$1.475T^{1/2}$	0.001846	Eqs. (5.17), (5.18)
"	"	"	$\nu_3 = 2349$	Asym. Stretch$^{(b)}$	1.308	4.364	3.792	$\nu_B = 0.390$	$1.475T^{1/2}$	—	Eq. (5.15)

(a) See Figure B-6 on p. B-52; (b) See Figure B-3 on p. B-28; (c) See Figure B-5, p. B-40 of Appendix B.

*This is the radiative lifetime. At ordinary pressures the excitation lifetime is determined by collisions.

TABLE 5-4. FUNDAMENTAL ($v_\alpha = 0 \longleftrightarrow v_\alpha = 1$) VIBRATIONAL INFRARED BAND PARAMETERS OF IMPORTANT MOLECULES IN ROCKET PLUMES AND IN THE EARTH ATMOSPHERE (See also Table 3-6, p. 90; Table 3-7, p. 106; Table 3-11, p. 116; Table 3-12, p. 124; Table 3-15, p. 158; and Table 4-6, p. 269) (Cont.)

MOLECULE	TYPE OF VIBRATOR	TYPE OF ROTOR	NORMAL VIBRATION FREQUENCY (Hb)	TYPE OF NORMAL VIBRATION	VIBRATION DIPOLE CHARGE z_1	VIBRATION MASS M_α (amu)	VIBRATIONAL DECAY TIME* τ^{v}_{1-0} (ms)	FUNDAMENTAL ROTATION FREQUENCY (Hb)	VIBRATIONAL BAND SPREAD $(\Delta\nu_{mn})_v$ (Hb)	ξ_B OR ξ_{BC} (LISTED ONLY FOR BANDS WITH Q-BRANCH)	APPLICABLE b_v FUNCTIONS
N_2O (N-N-O)	Linear (Asym.)	Linear	ν_1 = 1285	Sym. Stretch[(c)]	0.0738	8.272	7,545.5	ν_B = 0.419	$1.081T^{1/2}$	—	Eq. (5.15)
"	"	"	ν_2 = 589	Bending[(c)]	0.1602	1.625	1,497.2	ν_B = 0.419	$1.081T^{1/2}$	0.001337	Eqs. (5.17), (5.18)
"	"	"	ν_3 = 2224	Asym. Stretch[(c)]	0.5726	2.312	11.695	ν_B = 0.419	$1.081T^{1/2}$	—	Eq. (5.15)
NO_2 ($O^{\diagup N \diagdown}O$)	Planar	Asym. Top	ν_1 = 1320	Symm. In[(a)]	0.8852	1.6239	9.757	ν_A = 3.001	$1.085T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_2 = 750	Symm. Out[(a)]	0.8360	5.3535	111.712	ν_B = 0.434	$1.085T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_3 = 1618	Asymmetric[(a)]	1.6861	5.8947	6.497	ν_C = 0.410	$1.085T^{1/2}$		Eqs. (5.21), (5.22)
O_3 ($O^{\diagup O \diagdown}O$)	Planar	Asym. Top	ν_1 = 1110	Symm. In[(a)]				ν_A = 3.554	$1.082T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_2 = 705	Symm. Out[(a)]				ν_B = 0.445	$1.082T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_3 = 1042	Antisymm.[(a)]				ν_C = 0.395	$1.082T^{1/2}$		Eqs. (5.21), (5.22)
SO_2 ($O^{\diagup S \diagdown}O$)	Planar	Asym. Top	ν_1 = 1151	Symm. In[(a)]	0.3139	2.1460	134.863	ν_A = 2.027	$0.943T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_2 = 519	Symm. Out[(a)]	0.3271	10.8291	3,082.43	ν_B = 0.344	$0.943T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_3 = 1361	Antisymm.[(a)]	0.5543	9.1429	131.79	ν_C = 0.294	$0.943T^{1/2}$		Eqs. (5.21), (5.22)
H_2S ($H^{\diagup S \diagdown}H$)	Planar	Asym. Top	ν_1 = 2615	Symm. In[(a)]	0.0703	0.2025	49.155	ν_A = 10.37	$4.373T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_2 = 1183	Symm. Out[(a)]	0.0692	0.9310	1,139.631	ν_B = 3.99	$4.373T^{1/2}$		Eqs. (5.24), (5.25)
"	"	"	ν_3 = 2628	Antisymm.[(a)]	0.1079	0.9687	98.883	ν_C = 4.73	$4.373T^{1/2}$		Eqs. (5.21), (5.22)

(a) See Figure B-6 on p. B-52; (b) See Figure B-3 on p. B-28; (c) See Figure B-5, p. B-40 of Appendix B.

*This is the radiative lifetime. At ordinary pressures the excitation lifetime is determined by collisions.

or for the decay time $\tau^{v}_{1-0} = \left(A^{\circ}_{1-0}\right)^{-1}_{vib}$:

$$\boxed{\tau^{v}_{1-0} = 8203 \; \frac{M_{\alpha}}{\nu^{2}_{\alpha} z^{2}_{\alpha}} \; , \text{ sec} \quad \left(\text{amu}/(\text{Hb})^{2}\right)} \tag{5.12}$$

In Table 5-4, values of τ^{v}_{1-0} are listed for the various normal vibrations.

The spectral emission rate for 0-1 transitions is of course given by:

$$\boxed{\left(\frac{dA_{0-1}}{d\nu}\right)_{vib} = \left(A^{\circ}_{0-1}\right)_{vib} \; g_{v}(\nu,\nu_{0-1},\Delta\nu_{0-1}) \; , \text{ sec}^{-1} \cdot \text{Hz}^{-1} \; ,} \tag{5.13}$$

where g_{v} is the vibrational band contour function discussed in section 4.7, and listed in Table 5-3. For all diatomic molecules and for the ν_{1} and ν_{3} vibrations of all linear molecules* we have only a P- and R-Branch. Thus we have:

$$\boxed{\underset{\text{(all molecules)}}{g^{PR}_{v}(\nu,\nu_{0-1},\Delta\nu_{0-1})} = \frac{b^{PR}_{v}(\nu,\nu_{0-1},\Delta\nu_{0-1})}{\Delta\nu_{0-1}} \; , \text{ Hz}^{-1}} \tag{5.14}$$

---

*The ν_{1} vibration of symmetric CO_2 is not infrared-active however because $z_{1} = 0$.

where:

$$\underset{\left(\begin{array}{c}\text{all diatomic molecules;}\\ CO_2 - \nu_3\\ N_2O - \nu_1\ ,\ \nu_3\end{array}\right)}{b_v^{PR}(\nu,\nu_{0-1},\Delta\nu_{0-1})} = \frac{|\nu - \nu_\alpha|}{\Delta\nu_{0-1}}\ \exp-\left(\frac{\nu - \nu_\alpha}{\Delta\nu_{0-1}}\right)^2 \qquad (0 < \nu < \infty) \tag{5.15}$$

$$\begin{aligned}\underset{\left(\begin{array}{c}\text{all diatomic molecules;}\\ CO_2\ ;\ N_2O\end{array}\right)}{\Delta\nu_{0-1}} &= (4\nu_B kT/h)^{1/2} = 5.006 \times 10^{10}\ \underset{(Hb)(^\circ K)}{(\nu_B \cdot T)^{1/2}},\ Hz =\\ &= 1.6698\ \underset{(Hb)(^\circ K)}{(\nu_B \cdot T)^{1/2}}\ ,\quad Hb\end{aligned}$$

(5.16)*

Values of $\Delta\nu_{0-1}$ (in Hb) are listed in Table 5-4. The transition frequency $\nu_{mn} = \nu_{1-0} = \nu_\alpha$ since $\Delta v_\alpha = 1$; values of ν_α are listed in Table 5-4 ($\nu_\alpha = \nu_e$ for diatomic molecules and $\nu_\alpha = \nu_1$, ν_2 , ν_3 for triatomic molecules).

For the ν_2 (bending) normal vibrations of CO_2 and N_2O, there is a Q-Branch in addition to the P- and R-Branches (see Eqs. (4.176) and (4.177)), and in this case we have for the P- and R-Branch:

$$\underset{\left(\begin{array}{c}CO_2 - \nu_2\\ N_2O - \nu_2\end{array}\right)}{b_v^{PR}(\nu,\nu_{0-1},\Delta\nu_{0-1})} = \frac{2}{3}\,\frac{|\nu - \nu_\alpha|}{\Delta\nu_{0-1}}\ \exp-\left(\frac{\nu - \nu_\alpha}{\Delta\nu_{0-1}}\right)^2 , \qquad (0 < \nu < \infty) \tag{5.17}$$

---

*For CO_2 , $\Delta\nu_{0-1}$ is $\sqrt{2}$ times the value given here, that is $(\Delta\nu_{0-1})_{CO_2} = 2.3615\ \nu_B^{1/2} T^{1/2}$, Hb ; see footnotes on pp. 215 and 223.

while for the Q-Branch:

$$\boxed{\begin{aligned} & b_\nu^Q(\nu,\nu_{0-1},\Delta\nu_{0-1}) = \left(\frac{4\nu_B}{3\xi_B\Delta\nu_{0-1}}\right)\exp-\left(\frac{4\nu_B|\nu-\nu_\alpha|}{\xi_B\Delta\nu_{0-1}^2}\right) \\ & \begin{pmatrix} CO_2 - \nu_2 \\ N_2O - \nu_2 \end{pmatrix} (\nu_\alpha < \nu < \infty) \end{aligned}} \tag{5.18}$$

For the Q-Branch $\nu_\alpha < \nu < \infty$, since $\Delta\nu_B < 0$ for the ν_2 vibrations of CO_2 and N_2O. Also we neglect ν_B^Q which is small compared to $\nu_{mn} = \nu_\alpha$ (see Eq. (4.177)). Equation (5.16) for $\Delta\nu_{0-1}$ still holds for the ν_2 normal vibrations of N_2O and CO_2, as does of course Eq. (5.14) which holds for all molecules.

The parameter ξ_B in Eq. (5.18) is (for ν_2 vibrations) given by (see Eq. (4.93), p. 195):

$$\boxed{\xi_B = \left(\xi_B\right)_{0-1} = \frac{\left|\left(\Delta\nu_B\right)_{0-1}\right|}{\nu_B} = \frac{|\alpha_2|}{\nu_B}} , \tag{5.19}$$

since for 0-1 transitions $(v_m - v_n) = 1 - 0 = 1$.

For CO_2, $\xi_B = 0.00072/0.390 = 0.001846$, while for N_2O, $\xi_B = 0.00056/0.419 = 0.001337$, according to the data in Herzberg's tables (Ref. 11). Values of ξ_B are listed in Table 5-4 for vibrations with Q-Branches, if values of α_B are available from Ref. 11.

For the nonlinear triatomic molecules H_2O, NO_2, O_3, SO_2, and H_2S which are asymmetric-top rotors, the spread $\Delta\nu_{0-1}$ is instead of (5.16), given by:

$$\Delta\nu_{0-1} = \Big(2(\nu_B+\nu_C)kT/h\Big)^{1/2} = 3.5398 \times 10^{10}\Big\{\underset{(\mathrm{Hb})(^{\circ}\mathrm{K})}{(\nu_B+\nu_C)\ \ T}\Big\}^{1/2}, \ \mathrm{Hz} =$$

$$= 1.1807\Big\{\underset{(\mathrm{Hb})(^{\circ}\mathrm{K})}{(\nu_B+\nu_C)\ \ T}\Big\}^{1/2}, \quad \mathrm{Hb} \tag{5.20}$$

The shape function $b_v(\nu,\nu_{mn},\Delta\nu_{mn})$ for the ν_3 (asymmetric) vibration bands of these molecules is given by (see Eqs. (4.273) and (4.274)):

$$\underset{\left(\begin{array}{c}\nu_3\text{-Bands of } H_2O\\ NO_2,\ O_3,\ SO_2,\ \text{and } H_2S;\\ 0<\nu<\infty\end{array}\right)}{b_v^{PR}} = \frac{2}{3}\frac{|\nu-\nu_3|}{\Delta\nu_{0-1}}\exp-\left(\frac{\nu-\nu_3}{\Delta\nu_{0-1}}\right)^2 \tag{5.21}$$

$$\underset{\left(\begin{array}{c}\nu_3\text{-Bands of } H_2O,\\ NO_2,\ O_3,\ SO_2,\ \text{and } H_2S;\\ 0<\nu<\nu_3\end{array}\right)}{b_v^{Q}} = \frac{2(\nu_B+\nu_C)}{3\xi_{BC}\Delta\nu_{0-1}}\exp-\left\{\frac{2(\nu_B+\nu_C)|\nu_3-\nu|}{\xi_{BC}\Delta\nu_{0-1}^2}\right\} \tag{5.22}$$

Here ξ_{BC} for $\Delta v_3 = 1$ transitions is given by (see Eq. (4.269)):

$$\left(\xi_{BC}\right)_3 = \left(\frac{2c}{\nu_B+\nu_C}\right)|\Delta\nu_{BC}|_3 = \frac{2c|\alpha_3^B + \alpha_3^C|}{\nu_B + \nu_C} \tag{5.23}$$

Values of ξ_{BC} are listed in Table 5-4 for molecules whose α_3^B and α_3^C parameters are known.

For the ν_1 and ν_2 vibrations of the asymmetric-top molecules H_2O , NO_2 , O_3 , SO_2 , and H_2S, the band shape functions are given by (see Eqs. (4.277) and (4.278)):

$$
\begin{aligned}
\underset{\left(\begin{array}{c}\nu_1 \text{ and } \nu_2 \text{ Bands of} \\ H_2O\ ,\ NO_2\ ,\ O_3\ ,\ SO_2\ ,\text{ and } H_2S; \\ 0 < \nu < \infty\end{array}\right)}{b_\nu^{PR}} = {} & \frac{2}{3\Delta\nu_{1-0}}\left(\frac{\nu_B+\nu_C}{2\pi\nu_A}\right)^{1/2}\left[\exp-\left(\frac{\nu-\nu_{1-0}}{\Delta\nu_{1-0}}\right)^2 + \right. \\
& \left. - \exp-\left\{\frac{\nu_B+\nu_C}{2\nu_A}\left(\left(\frac{\nu_B+\nu_C}{\Delta\nu_{1-0}}\right)^2\left(\frac{\nu_A}{|\nu_B+\nu_C-\nu_A|}-1\right)^2+1\right)\right\}\right] + \\
& + \frac{2|\nu-\nu_{1-0}|}{3\Delta\nu_{1-0}}\left(\frac{\nu_B+\nu_C}{2\nu_A}\right)\left(\frac{\nu_B+\nu_C}{2\nu_A-\nu_B-\nu_C}\right)^{1/2}\left[\exp-\left\{\frac{\nu_B+\nu_C}{2\nu_A}\left(\frac{\nu-\nu_{1-0}}{\Delta\nu_{1-0}}\right)^2\right\}\right] \cdot \\
& \cdot \left[\operatorname{erf}\left\{\left(\frac{\nu_A}{|\nu_B+\nu_C-\nu_A|}-1\right)\left(\frac{(\nu_B+\nu_C)^2}{2\nu_A(2\nu_A-\nu_B-\nu_C)}\right)\left(\frac{|\nu-\nu_{1-0}|}{\Delta\nu_{1-0}}\right)\right\}\right. \\
& \left. - \operatorname{erf}\left\{\left(\frac{\nu_A-\nu_B}{\nu_A}\right)^{1/2}\left(\frac{|\nu-\nu_{1-0}|}{\Delta\nu_{1-0}}\right)\right\}\right]
\end{aligned}
\qquad (5.24)
$$

$$
\begin{aligned}
\underset{\left(\begin{array}{c}\nu_1 \text{ and } \nu_2 \text{ Bands of} \\ H_2O\ ,\ NO_2\ ,\ O_3\ ,\ SO_2\ ,\text{ and } H_2S; \\ 0 < \nu < \nu_{1-0} \text{ for } \nu_1 \text{ Band;} \\ \nu_{1-0} < \nu < \infty \text{ for } \nu_2 \text{ Band}\end{array}\right)}{b_\nu^{Q}} = {} & \frac{\nu_B+\nu_C}{3\xi_{BC}\Delta\nu_{1-0}}\left(\frac{2\nu_A}{2\nu_A-\nu_B-\nu_C}\right)^{1/2} \cdot \\
& \cdot \left[\exp-\left\{\frac{(\nu_B+\nu_C)\left(2\xi_{BC}|\nu-\nu_{1-0}| - 2\nu_A+\nu_B+\nu_C\right)}{\xi_{BC}^2\ \Delta\nu_{1-0}^2}\right\}\right] \cdot
\end{aligned}
$$

$$\cdot \left[\operatorname{erf}\left\{ \left(\frac{(\nu_B+\nu_C)(2\nu_A-\nu_B-\nu_C)}{\xi_{BC}^2 \, \Delta\nu_{1-0}^2} \right)^{1/2} \cdot \left(\frac{2\nu_A-\nu_B-\nu_C}{\nu_B+\nu_C} \left(\left(\frac{2\xi_{BC}(\nu_B+\nu_C)\,|\nu_{1-0}-\nu|}{(2\nu_A-\nu_B-\nu_C)^2} + 1 \right)^{1/2} - 1 \right) - 1 \right) \right\} + \right.$$

$$\left. + \operatorname{erf}\left\{ \left(\frac{(\nu_B+\nu_C)(2\nu_A-\nu_B-\nu_C)}{\xi_{BC}^2 \, \Delta\nu_{1-0}^2} \right)^{1/2} \cdot \left(\frac{2\nu_A-\nu_B-\nu_C}{\nu_B+\nu_C} \left(\left(\frac{2\xi_{BC}(\nu_B+\nu_C)\,|\nu_{1-0}-\nu|}{(2\nu_A-\nu_B-\nu_C)^2} + 1 \right)^{1/2} + 1 \right) + 1 \right) \right\} \right] \tag{5.25}$$

The parameter ξ_{BC} for $0 \longleftrightarrow 1$ transitions of the ν_1 vibration is given by (see Eq. (4.269)):

$$\boxed{ (\xi_{BC})_1 = \left(\frac{2\,|\Delta\nu_{BC}|}{\nu_B + \nu_C} \right)_1 = \frac{2c\,|\alpha_1^B + \alpha_1^C|}{\nu_B + \nu_C} \,, } \tag{5.26}$$

and for $0 \longleftrightarrow 1$ transitions of the ν_2 vibration:

$$\boxed{ (\xi_{BC})_2 = \left(\frac{2\,|\Delta\nu_{BC}|}{\nu_B + \nu_C} \right)_2 = \frac{2c\,|\alpha_2^B + \alpha_2^C|}{\nu_B + \nu_C} } \tag{5.27}$$

Values of $(\xi_{BC})_i$ for molecules whose α_1^B, α_1^C, and α_2^B, α_2^C parameters are known are listed in Table 5-4.

5.3 LIFETIMES OF EXCITED MOLECULES

The average time that it takes for an excited molecule to decay and emit a photon is of course given by the inverse of the Einstein emission coefficient $\tau^o_{mn} = (A^o_{mn})^{-1}$. In general however the lifetime τ^* of an excited molecule is not solely determined by the photon emission decay time τ^o_{mn} (which can be calculated from the formulas in the tables), but also by the rates of other processess such as molecular collision excitation and deexcitation (so-called "V-T" exchanges), or by electron collision excitation or deexcitation rates ("V-E" exchanges) if an electronic discharge or other electron source is present in the gas. In addition to the V-T and/or V-E processes, resonance transfer of excited energy between molecules can occur (so-called "V-V" exchanges), and excitations or deexcitations by the gas containing walls or other energetic material particles (protons, fission fragments, etc.) can take place. Finally population (and depopulation) of a particular excited level m can also occur after a molecular or atomic ion recombines with a free electron, and the newly-formed neutral molecule or ion relaxes via a number of intermediate excitation levels (among which is level m) to the ground state.

Considering only VT, VE, and VV processes (besides the photon interactions), the lifetime τ^*_m of the level m of an excited molecule can be expressed by the relation:

$$\boxed{\tau^*_m = \left[\sum_n \left(\frac{1}{\tau^o_{mn}} - \frac{1}{\tau^o_{nm}}\right) + \left(\frac{1}{\tau_{VT}} - \frac{1}{\tau_{TV}}\right) + \left(\frac{1}{\tau_{VE}} - \frac{1}{\tau_{EV}}\right) + \left(\frac{1}{\tau_{V_1V_2}} - \frac{1}{\tau_{V_2V_1}}\right)\right]^{-1}, \text{ sec}} \tag{5.28}$$

Here the photon-molecule parameters τ^{o}_{mn} and τ^{o}_{nm} are determinable from the expressions given in this monograph, but the other time constants for molecule-molecule and electron-molecule interactions must be obtained from other sources. Though a sum over n appears in (5.28), in practice there is usually only one or a few other levels n with which the level m can connect, because of the selection rules for photonic transitions.

In Eq. (5.28), the subscript VT refers to intermolecular collisions in which potential energy or excitation energy (V) is converted to translational energy (T), and conversely subscript TV refers to collisions in which translation energy (T) is converted to excitation energy (V). Similarly subscript VE refers to the transfer of excitation energy (V) to electron kinetic energy (E) and subscript EV to the reverse process, while V_1V_2 indicates the process in which excitation energy (V_1) from the molecule in question is transferred to excitation energy (V_2) of a second, possibly different kind of molecule, and again V_2V_1 refers to the reverse process.

The potential excitation energy V in all these processes can refer to either electronic, vibrational or rotational energy levels. For any one of the three processes VT, VE, and V_1V_2 , or the reverse processes TV, EV, and V_2V_1 , the rates $K_{P_iQ_j}$ or time constants $\tau_{P_iQ_j}$ are given by the general relation:

$$\boxed{\begin{aligned} K_{P_iQ_j} &= \frac{1}{\tau_{P_iQ_j}} = \int_{\epsilon_i=0}^{\infty} \frac{dn_{Q_i}}{d\epsilon_i} \left(\frac{2\epsilon_i (M_i + M_j)}{M_i + M_j} \right)^{1/2} \sigma_{P_iQ_j}(\epsilon_i) d\epsilon_i = \\ &= n_{Q_i} \bar{v}_{ij} \bar{\sigma}_{P_iQ_j} = F_{Q_i} \bar{\sigma}_{P_iQ_j} , \quad \sec^{-1} \end{aligned}} \qquad (5.29)$$

where:

n_{Q_i} = Density of molecules (or electrons), with potential or translational energy Q , cm^{-3}

ϵ_i = Kinetic energy of a molecule i , ergs

$\bar{v}_{ij}$ = Mean relative velocity between molecules (electrons) i and molecules (electrons) j , cm/sec

$\bar{\sigma}_{P_iQ_j}$ = Mean energy exchange cross-section for velocity $\bar{v}_{ij}$, cm^2

F_{Q_i} = $n_{Q_i} \bar{v}_{ij}$ = Omnidirectional fluence of molecules (electrons) i carrying energy Q (Q = V or Q = T) as observed by molecules (electrons) j , $cm^{-2} \cdot sec^{-1}$

The mean velocity $\bar{v}_{12}$ between two molecules 1 and 2 of mass M_1 and M_2 in a gas is:

$$\boxed{v_{12} = \sqrt{\frac{4kT(M_1+M_2)}{\pi M_1 M_2}} = 1.029 \times 10^4 \underset{(^\circ K)}{T^{1/2}} \underset{(amu)}{\left(\frac{M_1 M_2}{M_1+M_2}\right)^{-1/2}} , \text{ cm/sec ,}} \qquad (5.30)$$

where M_1 and M_2 are in atomic mass units (amu= mol. wt.) and T is the temperature in °K. Similarly the mean electron velocity of electrons with kinetic energy E (electron-volts) is:

$$\boxed{v_e = \left(\frac{2E}{me}\right)^{-1/2} = 5.931 \times 10^7 \underset{(eV)}{E^{1/2}} , \text{ cm/sec}} \qquad (5.31)$$

Thus if the density n_{Q_1} and the temperature T_1 or energy E are specified, only the microscopic cross-sections $\bar{\sigma}_{P_iQ_j}$ needs to be know in order to obtain values for $K_{P_iQ_j}$ or $\tau_{P_iQ_j}$.

Analytical expressions for $\bar{\sigma}_{P_iQ_j}$ for electron-molecule interactions (that is $Q = Q_e = T_e$) are available for some atoms and molecules, but a good general theory is still lacking (Refs. 43 to 48). For this reason one usually relies on experimental measurements of $\bar{\sigma}_{P_iQ_e}$ as a function of electron energy.

Theoretical expressions for cross-sections $\bar{\sigma}_{P_1Q_2}$ and $\bar{\sigma}_{P_1Q_1}$, that is for VT and VV exchanges between different and like molecules have also been derived, but agreement between theory and experiment is even worse (Refs. 49 and 50), so that reliance on experimental data for these cross-sections again prevails.

One general result may be derived however for cross-sections $\bar{\sigma}_{V_iT_j}$ and $\bar{\sigma}_{T_jV_i}$ by considering so-called local thermodynamic equilibrium (LTE) conditions according to which one must have:*

$$\text{Excitation Rate per cm}^3 = \text{Deexcitation Rate per cm}^3 , \qquad (5.32a)$$

in order to preserve equilibrium, or:

$$n_{V_1} n_{T_2} \bar{v}_{12} \bar{\sigma}_{V_1T_2} = n_{T_2} n_{T_1} \bar{v}_{21} \bar{\sigma}_{T_2V_1} , \ \text{cm}^{-3} \cdot \text{sec}^{-1} \qquad (5.32b)$$

Now $\bar{v}_{21} = \bar{v}_{12}$ according to (5.30), and therefore it follows from (5.32b) that in a gas where LTE exists:

$$n_{V_1} \bar{\sigma}_{V_1T_2} = n_{T_1} \bar{\sigma}_{T_2V_1} \qquad (5.33)$$

---

*Of course this condition does not hold for gases that react chemically with each other.

From the theory of statistics of equilibrium gases we can write next that:

$$\frac{\bar{\sigma}_{T_2V_1}}{\bar{\sigma}_{V_1T_2}} = \frac{n_{V_1}}{n_{T_1}} = Z_o^{-1}\exp-\left(\frac{V_1}{kT}\right) \quad , \tag{5.34}$$

where Z_o is the appropriate normalization or sum-over-states factor (electronic, vibrational or rotational). Since we can write expression (5.34) in the presence of any second molecule (labeled 3, 4, etc.), this result can be generalized to:

$$\boxed{\bar{\sigma}_{TV}/\bar{\sigma}_{VT} = Z_o^{-1}\exp-\left(\frac{V}{kT}\right)} \tag{5.35}$$

for any pair of molecules. Thus if a measurement or analytical expression for one cross-section, say $\bar{\sigma}_{TV}$ is available, the cross-section $\bar{\sigma}_{VT}$ can also be obtained via Eq. (5.35).

Note also that since:

$$K_{V_1T_2} = \tau^{-1}_{V_1T_2} = n_2\, v_{21}\, \bar{\sigma}_{V_1T_2} \quad , \tag{5.36}$$

and:

$$K_{T_2V_1} = \tau^{-1}_{T_2V_1} = n_2\, v_{12}\, \bar{\sigma}_{T_2V_1} \tag{5.37}$$

we have that:

$$\boxed{\tau_{VT}/\tau_{TV} = \bar{\sigma}_{TV}/\bar{\sigma}_{VT} = Z_o^{-1}\exp-\left(\frac{V}{kT}\right)} \tag{5.38}$$

Thus again, if one time constant, say τ_{VT} , is known, the other, τ_{TV} , can also be obtained from Eq. (5.38).

5.4 PHOTON ATTENUATION COEFFICIENTS AND TRANSMISSION IN GASES

Once the microscopic photon absorption cross-section σ_{abs} has been determined from the appropriate combination of the expressions given in Tables 5-1 through 5-3, it is a simple matter to calculate the attenuation coefficient α_{abs} or mean free path λ_{abs} of course. The attenuation coefficient, which is also often called the macroscopic absorption cross-section,* is given by (see for example Ref. 52):

$$\boxed{\alpha_{abs_i} = n_i \, \sigma_{abs_i} \, , \ \mathrm{cm}^{-1} \, ,} \tag{5.39}$$

and the photon mean free path:

$$\boxed{\lambda_{abs_i} = \alpha_{abs_i}^{-1} = \left(n_i \, \sigma_{abs_i}\right)^{-1} \, , \ \mathrm{cm}} \tag{5.40}$$

Here n_i is the number density of molecules i per cm^3 which have absorption cross-section σ_{abs_i} cm^2 .

A beam of photons of $\Gamma(\nu)$ photons · cm^{-2} will be attenuated by a gas due to absorption according to the relation:

$$\frac{d\Gamma(\nu)}{dx} = \sum_i \alpha_{abs_i}(\nu) \, \Gamma(\nu) = \sum_i n_i \, \sigma_{abs_i}(\nu) \, \Gamma(\nu) \, , \tag{5.41}$$

which leads to:

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*In neutronics theory the symbol used for the macroscopic cross-section is Σ instead of α . However α is used in photonics work by most authors.

$$\Gamma(\nu,x) = \Gamma(\nu,x{=}o)\ \exp-\left[x \sum_i n_i\ \sigma_{abs_i}(\nu)\right] \tag{5.42}$$

Here x is the distance of travel into the gas by the beam.

If we add photon scattering to photon absorption, the total attenuation or transmission at frequency ν is:

$$\boxed{Tr(\nu,x) = \frac{\Gamma(\nu,x)}{\Gamma(\nu,x{=}o)} = \exp-\left[x\sum_i \left\{\left(\sigma_{abs_i}(\nu) + \sigma_{sc_i}(\nu)\right)\right\} n_i\right]} \tag{5.43}$$

Note that we can write the total transmission as:

$$Tr(\nu,x) = Tr_a(\nu,x) \cdot Tr_s(\nu,x)\ , \tag{5.44}$$

where:

$$Tr_a(\nu,x) = \exp-\left[x \sum_i n_i\ \sigma_{abs_i}(\nu)\right] \tag{5.45}$$

$$Tr_s(\nu,x) = \exp-\left[x \sum_i n_i\ \sigma_{sc_i}(\nu)\right] \tag{5.46}$$

The photon scattering cross-section of molecules is usually much weaker than the photon absorption cross-section. It is given by "Rayleigh's Law" (Ref. 5):

$$\frac{d\sigma_{sc}}{d\Omega} = \frac{8\pi}{3}\left(\frac{e^2h^2}{m}\right)^2\left(\frac{1}{\lambda^4}\right)\left(\frac{1}{E_{ion}^4}\right)\left(\frac{1+\cos^2\theta}{16\pi/3}\right) =$$

$$= 5.4224 \times 10^{-29}\ \lambda_{(\mu m)}^{-4}\ \zeta(E_{ion})\left(\frac{1+\cos^2\theta}{16\pi/3}\right),\ cm^2/ster\ , \tag{5.47}$$

where:

$$\zeta(E_{ion}) = \frac{z_{outer}}{2}\left(\frac{15.576}{E_{ion(eV)}}\right)^4 \qquad (5.48)$$

Here z_{outer} is the number of outer electron, with average ionization energy E_{ion}, in eV. For the N_2 molecule, we have $z_{outer} = 2$, and $E_{ion} = 15.576$ eV, so that $\zeta = 1$.

The total cross-section is obtained by integrating Eq. (5.47) over all angles θ:

$$\boxed{\sigma_{sc} = 5.4224 \times 10^{-29}\ \lambda_{(\mu m)}^{-4}\ \zeta(E_{ion})\ ,\ \text{cm}^2} \qquad (5.49)$$

The parameter $\lambda = c/\nu$ in Eqs. (5.47) and (5.49) is of course the photon wavelength (in μm).

Equations (5.42) and (5.45) are most useful for monochromatic photon beams which do not have a distribution of frequencies. For example for a laser beam of photons with frequency $\nu = \nu_L$, we can use Eq. (5.42) directly yielding:

$$\boxed{\underset{\text{(Laser Beam)}}{\Gamma_L(x)} \equiv \Gamma_L(x,\nu=\nu_L) = \Gamma_L(x=o)\ \exp-\left[x\sum_i n_i\ \sigma_{abs_i}(\nu=\nu_L)\right]} \qquad (5.50)$$

Similarly using Eq. (5.45), we get for the absorptive transmission:

$$\boxed{\underset{\text{(Laser Beam)}}{Tr_a(x,\nu=\nu_L)} = \frac{\Gamma_L(x)}{\Gamma_L(x=o)} = \exp-\left[x\sum_i n_i\sigma_{abs_i}(\nu=\nu_L)\right]} \tag{5.51}$$

If we have a beam of photons with a frequency distribution $d\Gamma/d\nu$, Eqs. (5.41) and (5.42) are not too useful and it is more convenient to work with the differential beam intensity $d\Gamma/d\nu$ instead of $\Gamma(\nu)$. In place of (5.41) we can write in this case:

$$\frac{d\Gamma_{tot}}{dx} = \frac{d}{dx}\int_\nu \left(\frac{d\Gamma}{d\nu}\right) d\nu = \int_\nu -\sum_i n_i \ \sigma_{abs_i}(\nu)\left(\frac{d\Gamma}{d\nu}\right) d\nu \ , \tag{5.52}$$

which yields:

$$\boxed{\Gamma_{tot}(x) = \int_\nu \left(\frac{d\Gamma}{d\nu}\right)_x \ d\nu = \int_\nu \left(\frac{d\Gamma}{d\nu}\right)_{x=o} \left[\exp-\left(x\sum_i n_i \ \sigma_{abs_i}(\nu)\right)\right] d\nu} \tag{5.53}$$

Usually the differential intensity of $d\Gamma/d\nu$ varies slowly with fraquency in the absorption regions of the molecules i , and in this case Eq. (5.52) can be written (see section 2.3, Eq. (2.20), and Eq. (4.9)):

$$\frac{d\Gamma_{tot}}{dx} = -\sum_i \left(\frac{d\Gamma(x)}{d\nu}\right)_{\nu=\nu_{mn_i}} n_i \ \Delta\nu_{mn_i} \ \sigma_{abs_i} = -\sum_i n_i \ \sigma_{abs_i} \ \Delta\Gamma_i(x) \ , \ \frac{\text{photons}}{\text{cm}^3\cdot\text{sec}} \tag{5.54}$$

where:

$$\boxed{\Delta\Gamma_i(x) \equiv \Delta\nu_{mn_i}\left(\frac{d\Gamma(x)}{d\nu}\right)_{\nu=\nu_{mn_i}} \ , \ \frac{\text{photons}}{\text{cm}^2\cdot\text{sec}}} \tag{5.55}$$

Here the total cross-section σ_{abs_i} is given by (see Eq. (2.20) and Eq. (4.9)):

$$\boxed{\sigma_{abs_i} = \frac{8\pi^3 e^2}{3hc} \frac{\nu_{mn_i}}{\Delta\nu_{mn_i}} \left(\frac{C_{mn_i}}{w_{n_i}}\right)_o (R^2_{mn})_o \text{ , cm}^2} \tag{5.56}$$

If photon losses are only due to absorption by the molecules i, we can rewrite the left-hand side of (5.54), and obtain:

$$\sum_i \frac{d\left(\Delta\Gamma_i(x)\right)}{dx} = -\sum_i n_i\,\sigma_{abs_i}\,\Delta\Gamma_i(x) \tag{5.57}$$

Since the i absorptions are uncoupled (even if the absorption regions overlap), we finally have:

$$\boxed{\sum_i \Delta\Gamma_i(x) = \sum_i \left[\Delta\Gamma_i(x=o)\ \exp-\left(x\ n_i\ \sigma_{abs_i}\right)\right] , \frac{\text{photons}}{\text{cm}^2 \cdot \text{sec}}} \tag{5.58}$$

This result can be expressed also by the relation:

$$\boxed{Tr_a(x) = \frac{\Gamma_{tot}(x)}{\Gamma_{tot}(x=o)} = \left[1 - \sum_i f_i \left\{1 - \exp-\left(x\ n_i\ \sigma_{abs_i}\right)\right\}\right] , \frac{\text{photons}}{\text{cm}^2 \cdot \text{sec}} ,} \tag{5.59}$$

where:

$$\boxed{f_i = \frac{\Delta\Gamma_i(x=o)}{\Gamma_{tot}(x=o)} \simeq \left(\frac{\Delta\nu_{mn_i}}{\Gamma_{tot}(x=o)}\right)\left(\frac{d\Gamma}{d\nu}\right)_{\nu=\nu_{mn_i}}} \tag{5.60}$$

5.5 STIMULATED EMISSION CROSS-SECTIONS AND GAIN OF THE CO_2 LASER

In this section we shall develop expressions for the stimulated emission cross-section and gain coefficient of the CO_2 laser, which involves an interband transition namely $\nu_3 \rightarrow \nu_1$ ($\lambda_{mn} = 10.6\ \mu$) as illustrated in Figure 5-1. We shall limit our analysis to the $\nu_3 \rightarrow \nu_1$ transition here. A similar treatment for the other $\nu_3 \rightarrow 2\nu_2$ ($\lambda_o = 9.4\ \mu m$) laser transition is readily carried out however.

In this application, analytic expressions for photon-molecule, molecule-molecule, and electron-molecule interactions are all needed. Whereas we have the apparatus now for obtaining photon-molecule parameters, relations for the other interactions must be obtained from other sources.

In the CO_2 lasing scheme, the ν_3 vibrational level is continuously being excited or "pumped" via V-V exchange collisions (see section 5.3) with excited ($v = 1$) N_2 molecules which are intermixed with the CO_2 . The N_2 molecules are in turn continuously excited to the $v = 1$ level by electrons in V-E collisions (see section 5.3), if the laser is driven by an electron discharge, (Electron Discharge Laser = EDL), or they are excited thermally by molecular T-V collisions at high temperatures. In the latter case, the N_2-CO_2 mixture after being heated, is supersonically expanded through a nozzle to lower pressures and temperatures, causing a transient excess population of ν_3 levels of CO_2 due to the different relaxation mechanisms of N_2 and CO_2 ($N_2^*(v=1)$ cannot radiate and relaxes by collisions with CO_2; CO_2 however can relax via radiation). Laser action can then be induced in the downstream region of the expanding gas. This type of laser is called the Gas Dynamic Laser (GDL). In what follows we shall restrict ourselves to the EDL pumping scheme. However similar calculations can be readily carried out for a GDL system.

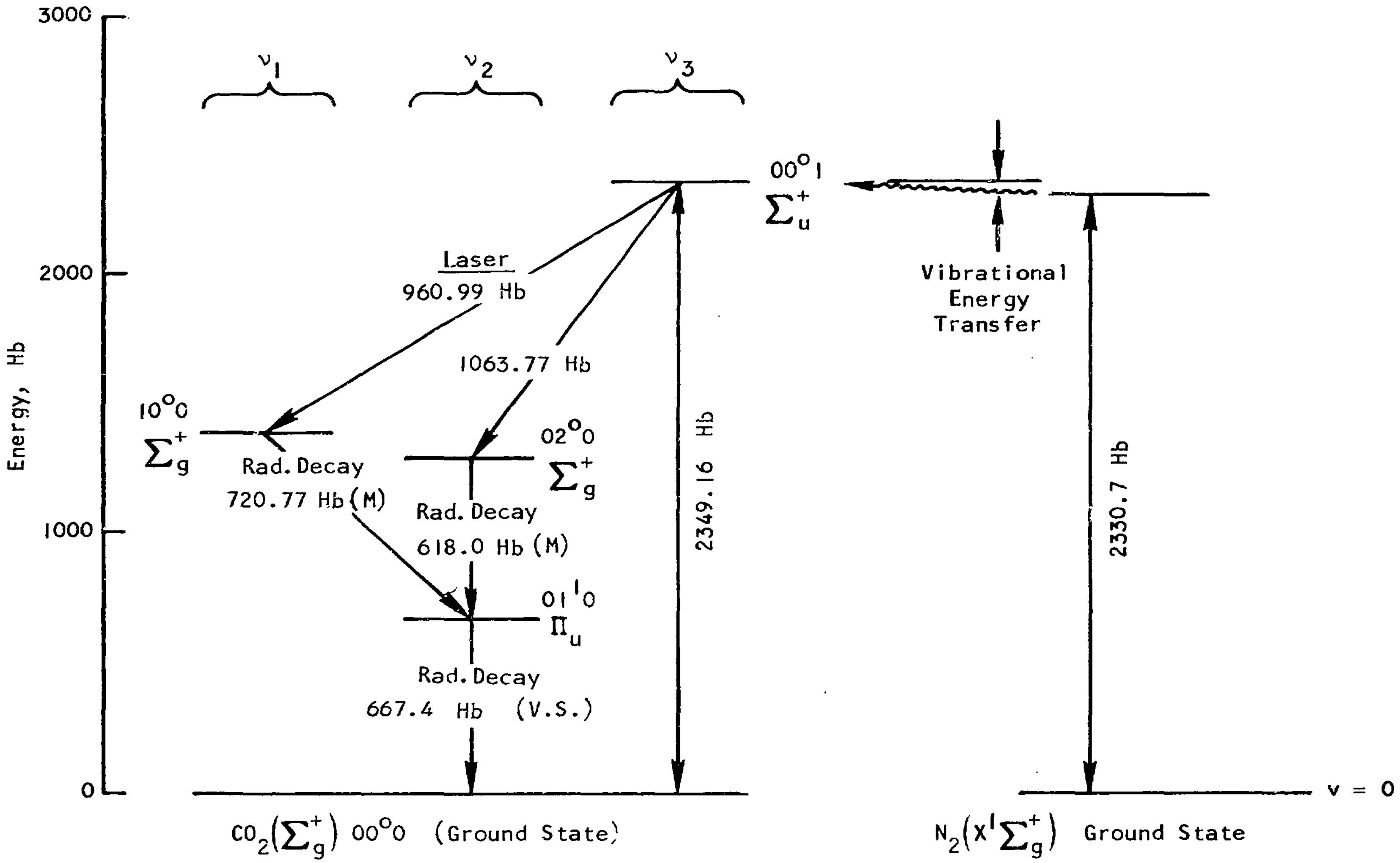

FIGURE 5-1. ENERGY-LEVEL DIAGRAM SHOWING PERTINENT VIBRATIONAL LEVELS OF CO_2 AND N_2
(After Patel, Ref. 56)

The gain in intensity of a beam of laser photons passing through a gaseous laser medium is given by:

$$G(x) = I(x)/I(x=o) = \Gamma(x)/\Gamma(x=o) = \exp-(\alpha_G x) \qquad (5.61)$$

Here x (cm) is the distance traveled, I(x) is the beam intensity (watts/cm^2), and α_G is the gain coefficient given by:*

$$\alpha_G = \sigma_{s.e.} (n_U - n_L) \text{ , cm}^{-1} \qquad (5.62)$$

in which:

$\sigma_{s.e.}$ = Cross-section for stimulated emission, cm^2.

n_U, n_L = Population density of excited molecules in the upper (U) and lower (L) lasing levels, cm^{-3}. For the λ = 10.6 μm laser transition in CO_2, U = ν_3 level, and L = ν_1 vibrational level.

In Eq. (5.62), we can readily provide an expression for $\sigma_{s.e.}$ but the population densities of the upper and lower laser levels n_U and n_L must be obtained from molecular kinetics theory. We shall write out an expression for $\sigma_{s.e.}$ later on, but first turn to the problem of solving for n_U and n_L.

To determine the population densities n_U and n_L in the CO_2 gas, we write the kinetic rate equations:

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*Note that α_G is like a negative attenuation or transmission factor Tr discussed in the previous section. For lasing to be possible α_G must be positive, which means that $(n_U - n_L) > 0$. If $(n_U - n_L) < 0$, the photon beam will be attenuated, i.e., there is no gain.

$$\frac{\partial n_U}{\partial t} = n_e \bar{v}_e \bar{\sigma}_{e\text{-}001} \left[CO_2\right] + \left[N_2^{v1}\right] \bar{v}_{N_2\text{-}CO_2} \, \bar{\sigma}_{v1\text{-}001} \left[CO_2\right] - A_U^{\circ} n_U \; +$$

$$- \left\{1 - \exp\text{-}(V_{001}/kT)\right\} \sum_X \, [X] \; \bar{v}_{X\text{-}CO_2} \; \bar{\sigma}_{X\text{-}001} \; n_U - \Gamma \sigma_{s.e.}(n_U - n_L) \qquad (5.63)$$

$$\frac{\partial n_L}{\partial t} = n_e \bar{v}_e \bar{\sigma}_{e\text{-}100} \left[CO_2\right] + \Gamma \sigma_{s.e.} \; (n_U - n_L) - A_L^{\circ} n_L - \left\{1 - \exp\text{-}\left(\frac{V_{010}}{kT}\right)\right\} \cdot$$

$$\cdot \left\{1 - 0.20 \exp\text{-}\left(\frac{V_{100} - V_{010}}{kT}\right)\right\} \sum_X \, [X] \; \bar{v}_{X\text{-}CO_2} \; \bar{\sigma}_{X\text{-}010} \; n_L \qquad (5.64)$$

$$\frac{\partial \left[N_2^{v1}\right]}{\partial t} = n_e \bar{v}_e \bar{\sigma}_{e\text{-}v1} \left[N_2\right] - \left[CO_2\right] \bar{v}_{CO_2\text{-}N_2} \; \bar{\sigma}_{v1\text{-}001} \left[N_2^{v1}\right] \qquad (5.65)$$

The various parameters in the above expressions are defined as follows:

I = Bidirectional (total) Laser Beam Intensity in Laser Medium, Watts $\cdot$ cm^{-2}

Γ = Total Laser Beam Fluc in Laser Medium, photons $\cdot$ $sec^{-1} \cdot cm^{-2}$

$$\Gamma = I/h\nu_L \text{ , photons} \cdot cm^{-2} \cdot sec^{-1} \qquad (5.66)$$

ν_L = Laser Frequency, Hz

h = Planck's Constant = 6.6252×10^{-34} joules $\cdot$ Hz^{-1}

k = Boltzmann's Constant = 1.3804×10^{-23} joules $\cdot$ $^{\circ}K^{-1}$

T = Gas temperature, °K

$\bar{v}_e$ = Mean kinetic velocity of electrons in gas, $cm \cdot sec^{-1}$

n_e = Electron density, cm^{-3}

$\bar{v}_{X-CO_2}$ = Mean relative kinetic velocity between molecules X and CO_2 in gas, $cm \cdot sec^{-1}$

A^o_U, A^o_L = Spontaneous radiative emission rates of upper (U) and lower (L) laser levels of CO_2, sec^{-1}

$\bar{\sigma}_{e-001}$; $\bar{\sigma}_{e-100}$; $\bar{\sigma}_{e-v1}$ = Mean cross-section for average relative electron velocity $\bar{v}_e$ for the E-V excitation of a ground-state molecule by electron impact to the 001, 100 vibrational states* of CO_2 and the v = 1 vibrational state of N_2 respectively, cm^2

$\bar{\sigma}_{v1-001}$ = Mean cross-section for a VV transfer resulting in the excitation of a ground-state CO_2 molecule to the 001 level, by an excited N_2 molecule in the v = 1 level, and the N_2 molecule's deexcitation to the ground state, cm^2

$\bar{\sigma}_{X-001}$, $\bar{\sigma}_{X-010}$ = Mean VT cross-sections for the deexcitation of CO_2 species excited to the 001 and 010 state respectively by molecules X, cm^2

V_{100}, V_{010}, V_{001} = Vibrational energy levels of the 100, 010, and 001 states of CO_2 ; V_{100} = 1388.1 Hb ; V_{010} = 667.4 Hb , V_{001} = 2349.2 Hb

$[Y]$ = Concentration of molecular species Y, $molecules \cdot cm^{-3}$

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*For CO_2 , the notation (v_1, v_2, v_3) denotes the level of excitation of the ν_1 , ν_2 , and ν_3 normal vibrations. Thus (001) denotes that the ν_3 vibration is excited to the first level (v_3=1), while the ν_1 and ν_2 normal vibrations are unexcited (v_1=0, v_2=0). The designation (121) means that the ν_1 vibration is singly excited (v_1=1), the ν_2 vibration is doubly excited (v_2=2), and the ν_3 vibration is singly excited (v_3=1).

Only the first-order highest-valued rate terms are included in Eqs. (5.63), (5.64), and (5.65). For example, the deexcitation rate of N_2^{vI} species by collisions with electrons could have been included in (5.65), but since $N_2^{vI} << N_2$ this reverse rate term is negligible in comparison with the forward excitation term represented by the first member on the right-hand side of Eq. (5.65). Similarly, deexcitation of N_2^{vI} by collisions with the atoms present in the laser gas mixture could have been included in (5.65) but the cross-section for this V-T interaction is several orders of magnitude smaller than the nearly resonant V-V interaction represented by the second member on the right-hand side of Eq. (5.65).

The factor $\left\{1 - 0.25 \exp-\left(\frac{V_{100} - V_{010}}{kT}\right)\right\}$ in the last member of Eq. (5.64) is an approximation to account for the temperature effect on the detailed balancing between the 100, 020, and 010 levels. It assumes that $V_{100} \approx V_{020}$ and that the 100 state is sharp but that the 020 level has three states. (The ν_2 vibration is doubly degenerate.) Furthermore, it is assumed that the 010 level is controlling the deexcitation rates of the 100 and 020 levels (Refs. 56 and 57).*

Now, under steady-state conditions, we may set:

$$\partial n_U/\partial t = \partial n_L/\partial t = \partial\left[N_2^{vI}\right]/\partial t = 0 \qquad (5.67)$$

With these conditions, Eqs. (5.63) and (5.64) reduce to:

$$n_U = \frac{R_2\tau_2 + (R_2+R_1)\,\Gamma\sigma_{s.e.}\,\tau_1\tau_2}{1 + \Gamma\sigma_{s.e.}\,(\tau_1+\tau_2)}\ ,\ \text{cm}^{-3} \qquad (5.68)$$

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*A more precise approach is to replace the average velocity $\bar{v}_i$ and cross-sections $\bar{\sigma}_{ij}$ in (5.63) through (5.65) by $v(\epsilon_i)$ and $\sigma_{ij}(\epsilon_i)$, and to perform integrations over the energy ϵ_i, using Boltzman or other distribution functions of the molecules i, that is $dn_i/d\epsilon_i$.

$$n_L = \frac{R_1\tau_1 + (R_1+R_2)\,\Gamma\sigma_{s.e.}\,\tau_1\tau_2}{1 + \Gamma\sigma_{s.e.}\,(\tau_1+\tau_2)} \tag{5.69}$$

$$(n_U - n_L) = \frac{R_2\tau_2 - R_1\tau_1}{1 + \Gamma\sigma_{s.e.}\,(\tau_1+\tau_2)} \quad , \; cm^{-3} \; , \tag{5.70}$$

where we defined for convenience:

$$R_1 = n_e\bar{v}_e\bar{\sigma}_{e-100}\left[CO_2\right] \quad , \; sec^{-1} \tag{5.71}$$

$$R_2 = n_e\bar{v}_e\left\{\bar{\sigma}_{e-001}\left[CO_2\right] + \bar{\sigma}_{e-v1}\left[N_2\right]\right\}, \; sec^{-1} \tag{5.72}$$

$$\tau_1 = \left[A^o_L + \sum_X \bar{v}_{X-CO_2}\,\bar{\sigma}_{X-010}\,[X]\left\{1 - \exp-\left(\frac{V_{010}}{kT}\right)\right\}\cdot\right.$$

$$\left.\cdot\left\{1 - 0.25\,\exp-\left(\frac{V_{100} - V_{010}}{kT}\right)\right\}\right]^{-1} \quad , \; sec \tag{5.73}$$

$$\tau_2 = \left[A^o_U + \sum_X \bar{v}_{X-CO_2}\,\bar{\sigma}_{X-001}\,[X]\left\{1 - \exp-\left(\frac{V_{001}}{kT}\right)\right\}\right]^{-1}, \; sec \tag{5.74}$$

Usually CO_2 lasers are operated at pressures above a few Torr and in this case the spontaneous radiative deexcitation constants A^o_L and A^o_U in (5.73) and (5.74) can be neglected in comparison with the collisional deexcitation terms.

If the laser gas is moving through a laser cavity at hold-up times (τ_f) comparable to or shorter than the relaxation times τ_1 and τ_2, Eqs. (5.63) and (5.64) must be modified to:

$$\frac{\partial N_U}{\partial t} = R_2 - \tau_2^{-1} n_U - \Gamma\sigma_{s.e.} (n_U - n_L) + \tau_f^{-1} \left(n_{U_o} - n_U\right) \tag{5.75}$$

$$\frac{\partial N_L}{\partial t} = R_1 - \tau_1^{-1} n_L + \Gamma\sigma_{s.e.} (n_U - n_L) + \tau_f^{-1} \left(n_{L_o} - n_L\right) , \tag{5.76}$$

Here we introduce the parameters:

$$\tau_f = \frac{S}{U} , \text{ sec} \tag{5.77}$$

S = Distance of gas flow travel through cavity, cm

U = Laser Gas flow Velocity, cm/sec

n_{U_o}, n_{L_o} = Population density of species in the upper (U) and lower (L) lasing levels in the upstream entrance region where the laser gas enters the lasing cavity, cm^{-3}

Under steady state, with $\partial n_U/\partial t = \partial n_L/\partial t = 0$, the population densities (assuming significant convective-flow deexcitation) then become:

$$n_U = \frac{\left(R_2 + \tau_f^{-1} n_{U_o}\right) \tau_2^1 + \left\{R_1 + R_2 + \tau_f^{-1} \left(n_{U_o} + n_{L_o}\right)\right\} \Gamma\sigma_{s.e.} \tau_1^1 \tau_2^1}{1 + \Gamma\sigma_{s.e.} \left(\tau_1^1 + \tau_2^1\right)} , \text{ cm}^{-3} \tag{5.78}$$

$$n_L = \frac{\left(R_1 + \tau_f^{-1} n_{L_o}\right)\tau'_1 + \left\{R_1 + R_2 + \tau_f^{-1}\left(n_{U_o} + n_{L_o}\right)\right\}\Gamma\sigma_{s.e.}\,\tau'_1\,\tau'_2}{1 + \Gamma\sigma_{s.e.}\left(\tau'_1 + \tau'_2\right)}, \ \mathrm{cm}^{-3}, \tag{5.79}$$

and thus:

$$(n_U - n_L) = \frac{R_2\tau'_2 - R_1\tau'_1 + \tau_f^{-1}\left(n_{U_o}\tau'_2 - n_{L_o}\tau'_1\right)}{1 + \Gamma\sigma_{s.e.}\left(\tau'_1 + \tau'_2\right)}, \ \mathrm{cm}^{-3}, \tag{5.80}$$

where:

$$\tau'_1 = \frac{\tau_1\,\tau_f}{\tau_1 + \tau_f}, \ \mathrm{sec} \tag{5.81}$$

$$\tau'_2 = \frac{\tau_2\,\tau_f}{\tau_2 + \tau_f}, \ \mathrm{sec} \tag{5.82}$$

Note that Eq. (5.80) reduces to Eq. (5.70) if $\tau_f >> \tau_1, \tau_2$ as expected.

Returning to Eq. (5.62), and substituting Eq. (5.80) or (5.70), we can rewrite it in the convenient form:

$$\boxed{\alpha_G = \frac{\alpha_o}{1 + (I/I_s)}, \ \mathrm{cm}^{-1},} \tag{5.83}$$

where the so-called "zero-power gain coefficient" α_o is given by:

$$\boxed{\alpha_o = \sigma_{s.e.}\left\{R_2\tau'_2 - R_1\tau'_1 + \tau_f^{-1}\left(n_{U_o}\tau'_2 - n_{L_o}\tau'_1\right)\right\}, \ \mathrm{cm}^{-1},} \tag{5.84}$$

and the "saturation intensity" I_s is:

$$\boxed{I_s = \left(\frac{h\nu_L}{\sigma_{s.e.}}\right)\left(\tau_2' + \tau_1'\right)^{-1} \;,\; \frac{\text{Watts}}{\text{cm}^2}} \tag{5.85}$$

Note that if $\tau_f \gg \tau_1, \tau_2$ as is often the case, the primes on τ_1 and τ_2 in (5.85) can be dropped, and (5.84) reduces to:

$$\boxed{\alpha_o = \sigma_{s.e.}\,(R_2\tau_2 - R_1\tau_1) \;,\; \text{cm}^{-1}} \tag{5.86}$$

Measured values for the collisional deexcitation cross-sections $\bar{\sigma}_{X-001}$ and $\bar{\sigma}_{X-010}$ to be used in the calculation of τ_1 and τ_2 (or τ_1' and τ_2') from Eqs. (5.73) and (5.74) are listed in Table 5-5. The mean relative velocity $\bar{v}_{X-CO_2}$ to be used in these equations is given by (see Eq. (5.53)):

$$\bar{v}_{X-CO_2} = 1.03 \times 10^4\, T^{1/2} \left(\frac{44 + m_X}{44 m_X}\right)^{1/2} \;,\; \text{cm/sec} \;, \tag{5.87}$$

where:

m_X = Mass of molecule X , a.m.u.

With Eq. (5.87) and the ideal gas-law relation:

$$[X] = 7.244 \times 10^{21}\, y_X\, p\, T^{-1} \;,\; \text{cm}^{-3} \;, \tag{5.88}$$

TABLE 5-5. MEASURED VT COLLISIONAL DEEXCITATION LIFETIMES AND CROSS-SECTIONS FOR THE UPPER AND LOWER CO_2 LASING LEVELS IN $X\text{-}CO_2$ GAS MIXTURES

Mixing Gas X	UPPER LEVEL 00°1				LOWER LEVEL 10°0**			
	Reference 57		Reference 58		Reference 57		Reference 58	
	$p\tau_{001}$* (atm · μs)	$\bar{\sigma}_{001\text{-}X}$ (10^{-20} cm^2)	$p\tau_{001}$* (atm · μs)	$\bar{\sigma}_{001\text{-}X}$ (10^{-20} cm^2)	$p\tau_{010}$* (atm · μs)	$\bar{\sigma}_{010\text{-}X}$ (10^{-20} cm^2)	$p\tau_{010}$* (atm · μs)	$\bar{\sigma}_{010\text{-}X}$ (10^{-20} cm^2)
CO_2	3.42 (1.0)	26.85	3.76 (1.0)	24.60	0.61 (1.0)	154	6.8 (1.0)	13.6
N_2	11.45 (0.88)	4.57	12.4 (0.891)	4.56	1.84 (0.80)	20.7	3 (0.80)	30.2
He	26.3 (0.89)	0.273	15.5 (0.978)	2.19	2.80 (0.88)	6.52	0.39 (0.786)	10.5
H_2	0.292 (0.50)	173	0.343 (0.818)	92.9	0.044 (0.25)	2,266	0.0172 (0.50)	3,075
H_2O	0.0313 (0.20)	10,880	0.055 (0.047)	26,100	0.001 (0.025)	2,726,000	0.0030 (0.01)	911,500
CO	6.82 (0.71)	17.4	—	—	0.320 (0.71)	283.8	--	—
Xe	26.3 (0.90)	1.20	—	—	0.0523 (0.14)	13,930	—	—

*All data are normalized to T = 400°K; the mole fraction y_X is given in parentheses.

**It is assumed that deexcitation from the 010 level is rate controlling.

in which:

y_X = Mole fraction of gas X in the laser gas mixture,

p = Gas pressure, atm ,

T = Gas temperature, °K ,

we can write (5.73) and (5.74) in the form:

$$\tau_1 = \frac{2.288 \times 10^{-26}\, T^{1/2}}{p} \left[\left\{ 1 - \exp-(961.0/T) \right\} \cdot \left\{ 1 - 0.25 \exp-(1037.8/T) \right\} \sum_X y_X \, \sigma_{010-X} \left(\frac{44 + m_X}{44 m_X} \right)^{1/2} \right]^{-1} , \text{ sec} \qquad (5.89)$$

$$\tau_2 = \frac{2.288 \times 10^{-26}\, T^{1/2}}{p} \left[\left\{ 1 - \exp-(1998.5/T \right\} \cdot \sum_X y_X \, \bar{\sigma}_{001-X} \left(\frac{44 + m_X}{44 m_X} \right)^{1/2} \right]^{-1} , \text{ sec} \qquad (5.90)$$

Here we have neglected the spontaneous radiation rates A_U° and A_L° since the collisional rates are much higher in most practical CO_2 lasers.

For the usual laser gas mixture containing CO_2 , N_2 , and He , we find for τ_1 and τ_2 , using the cross-sections for N_2 and He given in Table 5-6:

$$\boxed{\tau_1 = \frac{0.752 \times 10^{-7}\, T^{1/2}}{y_{CO_2}\, p \left\{ 1 - \exp-(961/T) \right\} \left\{ 1 - 0.2 \exp-(1038/T) \right\}} \cdot \left(1 - 0.654\, y_{N_2} - 0.655\, y_{He} \right)^{-1} , \text{ sec}} \qquad (5.91)$$

TABLE 5-6. SUMMARY OF "BEST ESTIMATE" COLLISIONAL DEEXCITATION CROSS-SECTIONS BASED ON DATA GIVEN IN TABLE 5-5

Mixing Gas X	$\bar{\sigma}_{001-X}$ (cm^2)	$\bar{\sigma}_{010-X}$ (cm^2)
CO_2	0.2572×10^{-18}	0.836×10^{-18}
N_2	0.0456×10^{-18}	0.255×10^{-18}
He	0.012×10^{-18}	0.085×10^{-18}
H_2	1.33×10^{-18}	26.71×10^{-18}
H_2O	184.9×10^{-18}	$18,188 \times 10^{-18}$
CO	0.17×10^{-18}	2.84×10^{-18}
Xe	0.01×10^{-18}	139.3×10^{-18}

$$\boxed{\tau_2 = \frac{2.444 \times 10^{-7}\, T^{1/2}}{y_{CO_2}\, p\left\{1 - \exp\text{-}(1999/T)\right\}\left(1 - 0.799\, y_{N_2} - 0.842\, y_{He}\right)}\ ,\ \text{sec}} \qquad (5.92)$$

Here we also used the conservation relation:

$$y_{CO_2} + y_{N_2} + y_{He} = 1 \qquad (5.93)$$

To obtain expressions for R_2 and R_2 as a function of n_e , p , T , and gas composition, we need values for the electron excitation cross-sections $\bar{\sigma}_{e-100}(\bar{v}_e)$, $\bar{\sigma}_{e-001}(\bar{v}_e)$, $\bar{\sigma}_{e-v1}(\bar{v}_e)$, and the electron velocity $\bar{v}_e$. Now the average electron energy and therefore the velocity varies in general as a function of the applied electric field strength E. For the pumping of the CO_2 laser gas mixtures, Ref. 48 indicates that an average electron kinetic energy of $\bar{E}_e = 0.9$ eV is optimum. For a self-maintained electron plasma produced by an electric discharge, it is usually not possible to operate the discharge in such a manner that $\bar{E}_e = 0.9$ eV, but a value of $\bar{E}_e \sim 3$ eV is usually required. On the other hand for a plasma whose electron density is independently controlled via a high-energy electron beam or radioisotope source, there is no difficulty for operations at $\bar{E}_e = 0.9$ eV.

With the understanding that the value of $\bar{E}_e$ may not be quite correct for all EDL CO_2 lasers, we shall nevertheless assume $\bar{E}_e$ to have the value:

$$\bar{E}_e = 0.9 \text{ eV} \qquad (5.94a)$$

and therefore according to Eq. (5.54):

$$\bar{v}_e = 5.6 \times 10^7 \text{ cm/sec} \tag{5.94b}$$

From the data given in Ref. 48, we then estimate that the electron-energy-spectrum averaged cross-sections are:

$$\bar{\sigma}_{e-v1}\,(\bar{\varepsilon} = 0.9 \text{ eV}) = 1.0 \times 10^{-16} \text{ cm}^2 \tag{5.95}$$

$$\bar{\sigma}_{e-001}(\bar{\varepsilon} = 0.9 \text{ eV}) = 1.0 \times 10^{-16} \text{ cm}^2 \tag{5.96}$$

$$\bar{\sigma}_{e-100}(\bar{\varepsilon} = 0.9 \text{ eV}) = 0.6 \times 10^{-16} \text{ cm}^2 \tag{5.97}$$

With the values (5.95) to (5.97) substituted, we get finally for R_1 and R_2 according to Eqs. (5.71) and (5.72):

$$\boxed{R_1 = 2.42 \times 10^{13}\, n_e\, p\, y_{CO_2}\, T^{-1}\,, \quad \text{sec}^{-1}\cdot \text{cm}^{-3}} \tag{5.98}$$

$$\boxed{R_2 = 4.00 \times 10^{13}\, n_e\, p\, (y_{CO_2} + y_{N_2})\, T^{-1}\,, \quad \text{sec}^{-1}\cdot \text{cm}^{-3}\,,} \tag{5.99}$$

where we used relation (5.88), and where:

n_e = Electron density (independently controlled by electron gun or radioisotope), cm^{-3}

p = Total gas pressure, atm

T = Gas temperature, °K

Having obtained expressions for τ_1 , τ_2 , R_1 , and R_2 from kinetic theory to be used in Eqs. (5.84) through (5.86), we now turn to obtaining an expression for the stimulated photon emission cross-section $\sigma_{s.e.}$ using the equations developed in this monograph. From Table 5-1, we have that:

$$\sigma_{\substack{s.e.\\001-100}} = 0.0960\ \nu_{\substack{001-\\100(Hz)}} \left(\frac{C_{001-100}}{w_{001}}\right) R^2_{\substack{001-\\100(cm^2)}}\ g_{rov}\left(\nu, \nu_{\substack{001-\\100}}, \Delta\nu_{\substack{001-\\100}}\right) \text{ , cm}^2 \tag{5.100}$$

For the 001 → 100 or $\nu_3 \rightarrow \nu_1$ transition in CO_2 we have that $\nu_{001-100} = \nu_t =$ $= 961$ Hb $= 2.883 \times 10^{13}$ Hz, while $w_{001} = w_{100} = 1$, so that $C_{001-100} = 1$. Thus:

$$\sigma_{\substack{s.e.\\001-100}} = 2.7677 \times 10^{12}\ R^2_{\substack{001-\\100\\(cm^2)}}\ g_{\substack{rov\\001-\\100}}(\nu,\nu_t,\Delta\nu_t)_{(Hz^{-1})} \text{ , cm}^2 \tag{5.101}$$

Here we abbreviate $\nu_{001-100} \equiv \nu_t$ and $\Delta\nu_{001-100} \equiv \Delta\nu_t$ for convenience.

From Table 5-2, we find that for the interband 001 → 100 transition:

$$R^2_{001-100} = 5.0548 \times 10^{-5}\ \underset{(amu)(Hz)}{\frac{z_t^2}{M_t \nu_t x_t}} \prod_{\alpha} \left(\frac{v_{\alpha_m}!}{v_{\alpha_n}!}\right)^{\delta_\alpha} \left(\frac{x_\alpha^{|v_{\alpha_m} - v_{\alpha_n}|}}{\left(|v_{\alpha_m} - v_{\alpha_n}| + 1\right)^2}\right) =$$

$$= 5.0548 \times 10^{-5} \underset{(amu)(Hz)}{\left(\frac{z_t^2}{M_t \nu_t x_t}\right)} \left(\frac{x_1}{4}\right)\left(\frac{x_3}{4}\right) = 1.8330 \times 10^{-23} \text{ , cm}^2 \tag{5.102}$$

Here:

$$M_t \equiv M_{001-100} = \left[\frac{1}{M_1^{1/2}} + \frac{1}{M_3^{1/2}}\right]^{-2} = 1.883 \quad \text{amu} \, , \tag{5.103}$$

$$x_t \equiv x_{001-100} = \left[\frac{1}{x_1^{1/2}} + \frac{1}{x_3^{1/2}}\right]^{-2} = 0.001252 \tag{5.104}$$

$$z_t \equiv z_{001-100} = \sqrt{\nu_t M_t x_t}\left|\sum_{\alpha}\left(\frac{|\nu_{\alpha_m} - \nu_{\alpha_n}| + 1}{|\nu_{\alpha_m} - \nu_{\alpha_n}|}\right)\left(\frac{z_\alpha \vec{e}_\alpha}{M_\alpha^{1/2}\,\nu_\alpha^{1/2}\,x_\alpha^{1/2}}\right)\right| =$$

$$= \sqrt{\nu_t M_t x_t}\left(\frac{2z_1}{M_1^{1/2}\,\nu_1^{1/2}\,x_1^{1/2}} + \frac{2z_3}{M_3^{1/2}\,\nu_3^{1/2}\,x_3^{1/2}}\right) = 0.3521 \tag{5.105}$$

Here we used the values $\nu_1 =$ 1388.2 Hb $= 41.646$ THz, $\nu_3 = 2349.2$ Hb $=$ $= 70.476$ THz, $M_1 = 16.000$ amu, $M_3 = 4.364$ amu, $x_1 = 0.00281$, $x_3 = 0.01132$, $z_1 = 0$, $z_3 = 1.26$. Thus:

$$\sigma_{\substack{\text{s.e.}\\ 001-100}} = 5.0732 \times 10^{-10} \underset{(\text{Hz}^{-1})}{g_{\substack{\text{rov}\\ 001-\\ 100}}(\nu, \nu_t, \Delta\nu_t)} \; , \; \text{cm}^2 \tag{5.106}$$

For the band contour function $g_{\text{rov}}(\nu, \nu_t, \Delta\nu_t)$ we obtain finally from Table 5-3:

$$g_{\substack{\text{rov}\\ 001-100}}(\nu, \nu_t, \Delta\nu_t) = \left(\frac{b_{\substack{\text{rov}\\ 001-100}}(\nu, \nu_t, \Delta\nu_t)}{\Delta\nu_t}\right) = \hat{h}^{PR}_{\substack{001-\\ 100}}(\nu, \nu_t, \Delta\nu_t) \cdot \left(\frac{b_J(\nu, \nu_J, \Delta\nu_J)}{\Delta\nu_t}\right) , \; \text{Hz}^{-1} \tag{5.107}$$

Here:

$$\Delta\nu_t \equiv \Delta\nu_{001\text{-}100} = 2.89 \times 10^5 (2\underset{(\mathrm{Hz})}{\nu_B})^{1/2} \underset{(^\circ\mathrm{K})}{T^{1/2}} = 4.421 \times 10^{10} \underset{(^\circ\mathrm{K})}{T^{1/2}}, \ \mathrm{Hz} \tag{5.108}$$

$$\underset{(J=0,2,4,6,\ldots)}{\hat{h}^{PR}_{001\text{-}100}} = \left(\frac{h\nu_B}{kT}\right)^{1/2} \left\{\exp-\left(\frac{J(J+1)\ h\nu}{kT}\right)\right\}\left\{\frac{\delta\nu_J}{\Delta\nu_t}\right\} \cdot \Big\{(J+\tfrac{3}{2})\ H(J)\ H(\nu_c-\nu_J) +$$

$$+ \ (J-\tfrac{1}{2})\ H(J-1)\ H(\nu_J-\nu_c)\Big\} =$$

$$\underset{(J=0,2,4,6,\ldots)}{\hat{h}^{PR}_{001\text{-}100}} = \frac{0.7933}{\underset{(^\circ\mathrm{K})}{T}} \left\{\exp-\left(\frac{0.5615J(J+1)}{T_{(^\circ\mathrm{K})}}\right)\right\}\Big\{(J+\tfrac{3}{2})\ H(J)\ H(961-\nu_J) +$$

$$+ \ (J-\tfrac{1}{2})\ H(J-1)\ H(\underset{(\mathrm{cm}^{-1})}{\nu_J}-961)\Big\} \tag{5.109}$$

For p ≲ 5 Torr:

$$\underset{\left(\begin{smallmatrix} p \gtrsim 5 \text{ Torr} \\ T \sim 400\ ^\circ\mathrm{K}\end{smallmatrix}\right)}{b_J(\nu,\nu_J,\Delta\nu_J)} = b_C(\nu,\nu_J,\Delta\nu_C) = \frac{(\Delta\nu_J/\pi)^2}{(\nu-\nu_J)^2 + (\Delta\nu_J/\pi)^2} \tag{5.110}$$

$$\Delta\nu_J = \Delta\nu_C = 3.384 \times 10^{26} \frac{\sigma_{1-2}p}{\sqrt{\mu_{1-2}T}} = 7.2150 \times 10^{11} \underset{(\mathrm{atm})}{p} \underset{(^\circ\mathrm{K})}{T^{-1/2}} \left(\frac{1-0.48y_{N_2} - 0.85y_{He}}{\sqrt{1-0.222y_{N_2} - 0.913y_{He}}}\right) =$$

$$= 9.4933 \times 10^8 \underset{(\mathrm{Torr})}{p} \underset{(^\circ\mathrm{K})}{T^{-1/2}} \left(\frac{1-0.48y_{N_2} - 0.85y_{He}}{\sqrt{1-0.22y_{N_2} - 0.91\ y_{He}}}\right), \ \mathrm{Hz} \tag{5.111}$$

while for p ≲ 0.2 Torr:

$$b_J(\nu,\nu_J,\Delta\nu_J) = b_D(\nu,\nu_J,\Delta\nu_D) = \exp-\left(\frac{\nu-\nu_J}{\Delta\nu_J\ \pi^{1/2}}\right)^2 \qquad (5.112)$$

$(p \lesssim 0.2$ Torr)

$$\Delta\nu_J = \Delta\nu_D = \nu_J\left(\frac{2\pi kT}{Mc^2}\right)^{1/2} = 3.3116\times 10^6\ T^{1/2}\ ,\ \text{Hz} \qquad (5.113)$$

For the P-Branch:

$$\nu_J = \nu_J^P = \nu_{mn} - 2\nu_B(J_m+1) - \Delta\nu_B\ J_m^2 =$$

$(J = 0,2,4,6,\ldots)$

$$= 961 - 0.780(J+1) - 0.00188\ J^2\ ,\ \text{cm}^{-1} =$$

$$= 3\times 10^{10}\left[961 - 0.780(J+1) - 0.00188\ J^2\right]\ ,\ \text{Hz}\ , \qquad (5.114a)$$

while for the R-Branch:

$$\nu_J = \nu_J^R = \nu_{mn} + 2\nu_B J_m - \Delta\nu_B J_m^2 = 961 + 0.780 - 0.00188\ J^2\ ,\ \text{cm}^{-1} =$$

$(J = 2,4,6,\ldots)$

$$= 3\times 10^{10}\left[961 + 0.780\ J - 0.00188\ J^2\right]\ ,\ \text{Hz} \qquad (5.114b)$$

In the above equations we used the following values or relations applicable to $CO_2/N_2/He$ laser gas mixture:

$\nu_B = 0.390$ Hb $= 1.17\times 10^{10}$ Hz (see Table 3-12, p. 123)

$\Delta\nu_B = \alpha_3 - \alpha_1 = 1.88\times 10^{-3}$ Hb $= 5.64\times 10^{7}$ Hz (see Table 3-12, p. 123)

$\delta\nu_J = \delta\nu_J^{I} = 4\nu_B$, since $\delta\nu_J^{I} = 4\nu_B \gg \Delta\nu_J$

$M = M_{CO_2} = 44$ amu

$$\mu_{1-2} = y_{CO_2}\left(\frac{44 \times 44}{44 + 44}\right) + y_{N_2}\left(\frac{44 \times 28}{44 + 28}\right) + y_{He}\left(\frac{44 \times 2}{44 + 2}\right) =$$

$$= 22\, y_{CO_2} + 17.11\, y_{N_2} + 1.91\, y_{He} =$$

$$\boxed{\mu_{1-2} = 22 - 4.89\, y_{N_2} - 20.09\, y_{He}\text{ , amu}} \qquad (5.115)$$

$$y_{CO_2} = 1 - y_{N_2} - y_{He} \qquad (5.116)$$

$$\sigma_{1-2} = y_{CO_2}\, \sigma_{CO_2-CO_2} + y_{N_2}\, \sigma_{CO_2-N_2} + y_{He}\, \sigma_{CO_2-He} \qquad (5.117)$$

$\sigma_{CO_2-CO_2} \approx 100 \times 10^{-16}$ cm^2
(see Table 4-1, p. 176, and consider that
$\sigma_{Hg-CO_2} = 98.4 \times 10^{-16}$, $\sigma_{Hg-CO} = 44.5 \times 10^{-16}$;
$\sigma_{CO-CO} = 40.4 \times 10^{-16}$ cm^2)

$\sigma_{CO_2-N_2} \approx 52 \times 10^{-16}$ cm^2
(see Table 4-1, p. 176, and consider that
$\sigma_{Hg-CO_2} = 98.4 \times 10^{-16}$, $\sigma_{Hg-N_2} = 51.0 \times 10^{-16}$ cm^2)

$\sigma_{CO_2-He} \approx 15 \times 10^{-16}$ cm^2
(see Table 4-1, p. 176, and consider that
$\sigma_{Hg-CO_2} = 98.4 \times 10^{-16}$, $\sigma_{Hg-He} = 15.0 \times 10^{-16}$ cm^2)

$$\boxed{\begin{aligned}\sigma_{1-2} &= \left(y_{CO_2} + 0.51\, y_{N_2} + 0.15\, y_{He}\right) \times 10^{-14}\ \text{cm}^2 = \\ &= \left(1 - 0.48\, y_{N_2} - 0.85\, y_{He}\right) \times 10^{-14}\ \text{cm}^2\end{aligned}} \qquad (5.118)$$

Actually the line-shape functions b_J given by (5.110) and (5.112) are the limiting cases where pressure-broadening and temperature-broadening prevail, respectively. The exact line-shape function is a mixture of the two and must be used at pressures where both line-broadening processes are important. Thus for pressures p such that $0.2 \lesssim p \lesssim 5$ Torr (and at moderate temperatures $T \approx 300$ to 400°K) the function $b_J/\Delta\nu_J$ in Eq. (5.107) is instead of (5.110)/(5.111), or (5.112)/(5.113) given by (see section 4.5, p. 177):

$$\underset{(0.2 \lesssim p \lesssim 5 \text{ Torr})}{b_J(\nu,\nu_J,\Delta\nu_J)} = b_{D,C}(\nu,\nu_J,\Delta\nu_J) = \frac{I(a,\xi)}{I(a,o)} \tag{5.119}$$

$$\Delta\nu_J = \left(\Delta\nu_{mn}\right)_{D,C} = \frac{\Delta\nu_D}{I(a,o)} = \frac{3.3116 \times 10^6\ T^{1/2}}{I(a,o)}\ ,\ \text{Hz} \tag{5.120}$$

$$a = \frac{1}{\pi^{1/2}}\left(\frac{\left(\Delta\nu_{mn}\right)_C}{\left(\Delta\nu_{mn}\right)_D}\right) = 161.736\ \frac{p(\text{Torr})}{T(^\circ K)}\left(\frac{1-0.48\ y_{N_2} - 0.85\ y_{He}}{\sqrt{1-0.22\ y_{N_2} - 0.91\ y_{He}}}\right) \tag{5.121}$$

$$\xi = \pi^{1/2}\frac{(\nu-\nu_J)}{\left(\Delta\nu_{mn}\right)_D} = 5.35226 \times 10^{-7}\ \underset{(^\circ K)}{T^{-1/2}}\underset{(\text{Hz})}{(\nu-\nu_J)} = 16056.77\ \underset{(^\circ K)}{T^{-1/2}}\underset{(\text{Hb})}{(\nu-\nu_J)} \tag{5.122}$$

$I(a,\xi)$ = Function plotted in Figure 4-2, p. 183 and tabulated in Table 4-2, p. 182.

Because it is tedious to calculate b_J in the transition region ($0.2 \lesssim p \lesssim 5$ Torr), since tabulated values of the function $I(a,\xi)$ must be looked up, the following analytical approximation which gives reasonable results may be used in Eq. (5.107), if great accuracy is not required (sufficient for most preliminary laser design problems):

$$\boxed{\begin{aligned} b_J(\nu,\nu_J,\Delta\nu_J) &= b_C(\nu,\nu_J,\Delta\nu_C)\ \Omega_C + b_D(\nu,\nu_J,\Delta\nu_D)\ \Omega_D \ = \\ &= \left(\frac{k_y^2\ p^2\ T^{-1}}{k_y^2\ p^2\ T^{-1} + 99.28\ (\nu-\nu_J)^2}\right)\Omega_C + \Omega_D\ \exp-\left\{\frac{16{,}056.5\ \underset{(\mathrm{Hb})}{(\nu-\nu_J)}}{\underset{(^\circ\mathrm{K})}{T^{1/2}}}\right\}^2 \end{aligned}}$$

(5.123)

and:

$$\Delta\nu_J = \Delta\nu_C\ \Omega_C + \Delta\nu_D\ \Omega_D = 9.4933 \times 10^8\ \underset{(\mathrm{Torr})(^\circ\mathrm{K})}{p\ T^{-1/2}}\ k_y\ \Omega_C\ +$$

$$+\ 3.312 \times 10^6\ \underset{(^\circ\mathrm{K})}{T^{1/2}}\ \Omega_D\ ,\ \mathrm{Hz} =$$

$$= 0.03165\ \underset{(\mathrm{Torr})(^\circ\mathrm{K})}{p\ T^{-1/2}}\ k_y\ \Omega_C + 0.0001104\ \underset{(^\circ\mathrm{K})}{T^{1/2}}\ \Omega_D\ ,\ \mathrm{Hb} \qquad (5.124)$$

where we abbreviate for convenience:

$$k_y = \frac{1 - 0.48\ y_{N_2} - 0.85\ y_{He}}{\sqrt{1 - 0.22\ y_{N_2} - 0.91\ y_{He}}} \qquad (5.125)$$

$$\Omega_C = \cos^2\left\{\frac{\pi}{2}\ \exp-\left(\frac{\Delta\nu_C}{\Delta\nu_D}\right)\right\} = \cos^2\left\{\frac{\pi}{2}\ \exp-\left(\frac{286.7\ k_y\ p}{T}\right)\right\} \qquad (5.126a)$$

$$\Omega_D = \sin^2\left\{\frac{\pi}{2}\exp-\left(\frac{\Delta\nu_C}{\Delta\nu_D}\right)\right\} = \sin^2\left\{\frac{\pi}{2}\exp-\left(\frac{286.7\;k_y\;p}{T}\right)\right\} \qquad (5.126b)$$

Approximations (5.123) and (5.124) obey the conservation laws and tend to the proper limits at high and low pressures p. The advantage of Eqs. (5.123) and (5.124) over (5.119) and (5.120) is of course that they can be readily used in a computer program, without the need for a lengthy compilation of tabulated values and the requirement for interpolation.

Returning to our expression for $\sigma_{s.e.}$ given by Eq. (5.106), we can now write down the final relation for this cross-section as a function of gas pressure p , temperature T , gas composition (y_{CO_2} , y_{N_2} , y_{He}), and line center frequency ν_J (or J number):

$$\begin{aligned}
\underset{001-100}{\sigma_{s.e.}} &= 4.2393 \times 10^{-19}\,T^{-1}\left[\left\{\exp-\frac{0.5615\;J(J+1)}{T}\right\}\cdot\right.\\
&\cdot\left.\left\{(J+\tfrac{3}{2})\;H(J)\;H(961-\nu_J) + (J-\tfrac{1}{2})\;H(J-1)\;H(\nu_J-961)\right\}\right]\cdot\\
&\cdot\left[\frac{\Omega_C\,k_y^2\,p^2\,T^{-1}}{k_y^2\,p^2\,T^{-1} + 99.26\,(\nu-\nu_J)^2} + \Omega_D\exp-\left\{\frac{16{,}056.5\,(\nu-\nu_J)}{T^{1/2}}\right\}^2\right]\\
&\cdot\left[\Omega_C\,k_y\,p\,T^{-1/2} + \Omega_D\,0.00349\,T^{1/2}\right]^{-1}\quad,\quad \text{cm}^2\quad, \qquad (5.127a)
\end{aligned}$$

which can be further factored and reduced to:

$$\boxed{\begin{aligned}
\sigma_{\substack{\text{s.e.}\\ 001-100\\ (J=0,2,4,6,\ldots)}} &= 4.2393\times 10^{-19}\,T^{-1/2}\cdot\left\{\Omega_C\,p\,k_y+\Omega_D\,\frac{T}{286.6}\right\}^{-1}\cdot\\
&\cdot\left\{\frac{\Omega_C\,k_y^2\,p^2\,T^{-1}}{k_y^2\,p^2\,T^{-1}+9{,}856\,(\nu-\nu_J)^2}+\Omega_D\,\exp-\left(\frac{16{,}056.5\,(\nu-\nu_J)}{T^{1/2}}\right)^2\right\}\cdot\\
&\cdot\left[\left\{\exp-\left(\frac{J(J+1)}{1.78\,T}\right)\right\}\left\{\underbrace{(J+\tfrac{3}{2})\,H(J)\,H(961-\nu_J)}_{\text{(P-Branch)}}+\underbrace{(J-\tfrac{1}{2})\,H(J-1)\,H(\nu_J-961)}_{\text{(R-Branch)}}\right\}\right],\ \text{cm}^2
\end{aligned}}$$

(5.127b)

Here p is in Torr, T is in °K, and ν_J is in Hb(=cm^{-1}) throughout Eq. (5.127), and:

$$\boxed{\nu_{\substack{J\\(J=0,2,4,\ldots)}} = \nu_J^P = 961-0.780\,(J+1)-0.00188\,J^2\,,\quad \text{Hb}} \tag{5.128a}$$

$$\boxed{\nu_{\substack{J\\(J=2,4,6,\ldots)}} = \nu_J^R = 961+0.780\,J-0.00188\,J^2\,,\quad \text{Hb}} \tag{5.128b}$$

In Eq. (5.127) we have used the approximations (5.123) and (5.124) which gives accurate results for $p \gtrsim 5$ Torr and $p \lesssim 0.2$ Torr, and approximate results for $0.2 \lesssim p \lesssim 5$ Torr.

Using Eqs. (5.91), (5.92), (5.98), (5.99), and (5.127) for substitution in (5.85) and (5.86) finally yields for the two key laser parameters α_o and I_s :

$$\boxed{\begin{aligned}
\alpha_o = {} & 5.861\left(\frac{1}{T}\right)\left(\frac{n_e}{10^{12}}\right) \cdot \left[\Omega_C\, k_y\, p + \Omega_D\left(\frac{T}{286.6}\right)\right]^{-1} \cdot \\
& \cdot \left[\frac{\Omega_C\, k_y^2\, p^2\, T^{-1}}{k_y^2\, p^2\, T^{-1} + 33{,}804(\nu-\nu_J)^2} + \Omega_D \exp-\left(\frac{16{,}057(\nu-\nu_J)}{T^{1/2}}\right)^2\right] \cdot \\
& \cdot \left[\left\{\exp-\left(\frac{J(J+1)}{1.781\, T}\right)\right\}\left\{\underbrace{(J+\tfrac{3}{2})\, H(J)\, H(961-\nu_J)}_{\text{(P-Branch)}} + \underbrace{(J-\tfrac{1}{2})\, H(J-1)\, H(\nu_J-960)}_{\text{(R-Branch)}}\right\}\right] \cdot \\
& \cdot \left[\left(1 + \frac{y_{N_2}}{y_{CO_2}}\right)\left\{1 - \exp-\left(\frac{1999}{T}\right)\right\}^{-1}\left\{1-0.799\, y_{N_2} - 0.842\, y_{He}\right\}^{-1} + \right. \\
& - 0.1846\left\{1-0.654\, y_{N_2} - 0.655\, y_{He}\right\}^{-1}\left\{1 - \exp-\left(\frac{961}{T}\right)\right\}^{-1} \cdot \\
& \left. \cdot \left\{1-0.25\exp-\left(\frac{1038}{T}\right)\right\}^{-1}\right], \quad \text{cm}^{-1}
\end{aligned}} \tag{5.129}$$

where:

p = Total gas pressure, Torr

n_e = Electron density, electrons/cm^3

T = Gas temperature, °K

k_y = Given by Eq. (5.125)

Ω_C, Ω_D = Parameters given by Eq. (5.126)

$y_{CO_2}, y_{N_2}, y_{He}$ = Mole fractions of CO_2 , N_2 , and He in the laser gas

ν_J = Center frequency of a line in P- or R-Branch given by Eq. (5.128), Hb

and, with the same units:

$$\boxed{\begin{aligned}
I_s = {} & 242.58\, y_{CO_2}\, p \left[\Omega_C\, k_y\, p + \Omega_D \left(\frac{T}{286.6} \right) \right] \cdot \\
& \cdot \left[\frac{\Omega_C\, k_y\, p^2\, T^{-1}}{p^2\, T^{-1} + 33{,}803.5(\nu-\nu_J)^2} + \Omega_D \exp-\left\{ \frac{16{,}056.5(\nu-\nu_J)}{T^{1/2}} \right\}^2 \right] \cdot \\
& \cdot \left[\left\{ \exp-\left(\frac{J(J+1)}{1.781\, T} \right) \right\} \cdot \left\{ \underset{\text{(P-Branch)}}{(J+\tfrac{3}{2})\, H(J)\, H(961-\nu_J)} + \underset{\text{(R-Branch)}}{(J-\tfrac{1}{2})\, H(J-1)\, H(\nu_J-961)} \right\} \right]^{-1} \cdot \\
& \cdot \left[\left\{ 1 - \exp-\left(\frac{1999}{T} \right) \right\}^{-1} \left\{ 1-0.799\, y_{N_2} - 0.842\, y_{He} \right\}^{-1} + 0.3068 \cdot \right. \\
& \left. \cdot \left\{ 1-0.654\, y_{N_2} - 0.655\, y_{He} \right\}^{-1} \left\{ 1-\exp-\left(\frac{961}{T} \right) \right\}^{-1} \left\{ 1-0.25 \exp-\left(\frac{1038}{T} \right) \right\}^{-1} \right]^{-1} , \ \frac{\text{Watts}}{\text{cm}^2}
\end{aligned}}$$

(5.130)

Note that the values of α_o and I_s depend on $(\nu-\nu_J)^2$, and that the peak value of α_o and minimum value of I_s are given by:

$$
\begin{aligned}
\alpha_o^{peak}(\nu=\nu_J) = {} & \left(\frac{4.144}{T}\right)\left(\frac{n_e}{10^{12}}\right)\left[\Omega_C\, k_y\, p + \Omega_D\left(\frac{T}{286.6}\right)\right]^{-1} \cdot \\
& \cdot\left[\left\{\exp-\left(\frac{J(J+1)}{1.781\ T}\right)\right\}\left\{\underset{\text{(P-Branch)}}{(J+\tfrac{3}{2})\ H(J)\ H(961-\nu_J)} + \underset{\text{(R-Branch)}}{(J-\tfrac{1}{2})\ H(J-1)\ H(\nu_J-961)}\right\}\right] \cdot \\
& \cdot\left[\left(1+\frac{y_{N_2}}{y_{CO_2}}\right)\left\{1-\exp-\left(\frac{1999}{T}\right)\right\}^{-1}\left\{1-0.799\ y_{N_2}-0.842\ y_{He}\right\}^{-1} - 0.1846 \cdot \right. \\
& \left. \cdot\left\{1-0.654\ y_{N_2}-0.655\ y_{He}\right\}^{-1}\left\{1-\exp-\left(\frac{961}{T}\right)\right\}^{-1}\cdot\left\{1-0.2\ \exp-\left(\frac{1038}{T}\right)\right\}^{-1}\right],\ \text{cm}^{-1}
\end{aligned}
\tag{5.131}
$$

$$
\begin{aligned}
I_s^{min}(\nu=\nu_J) = {} & 242.58\ y_{CO_2}\ p\left[\Omega_C\, k_y\, p + \Omega_D\left(\frac{T}{286.6}\right)\right] \cdot \\
& \cdot\left[\left\{\exp-\left(\frac{J(J+1)}{1.781\ T}\right)\right\}\cdot\left\{\underset{\text{(P-Branch)}}{(J+\tfrac{3}{2})\ H(J)\ H(961-\nu_J)} + \underset{\text{(R-Branch)}}{(J-\tfrac{1}{2})\ H(J-1)\ H(\nu_J-961)}\right\}\right]^{-1} \cdot \\
& \cdot\left[\left\{1-\exp-\left(\frac{1999}{T}\right)\right\}^{-1}\left\{1-0.799\ y_{N_2}-0.842\ y_{He}\right\}^{-1} + 0.3068 \cdot \right. \\
& \left. \cdot\left\{1-0.654\ y_{N_2}-0.655\ y_{He}\right\}^{-1}\left\{1-\exp-\left(\frac{961}{T}\right)\right\}^{-1}\cdot\left\{1-0.2\ \exp-\left(\frac{1038}{T}\right)\right\}^{-1}\right]^{-1},\ \frac{\text{Watts}}{\text{cm}^2}
\end{aligned}
\tag{5.132}
$$

Plots of expressions (5.131) and (5.132) are given in Figures 5-2 and 5-3.

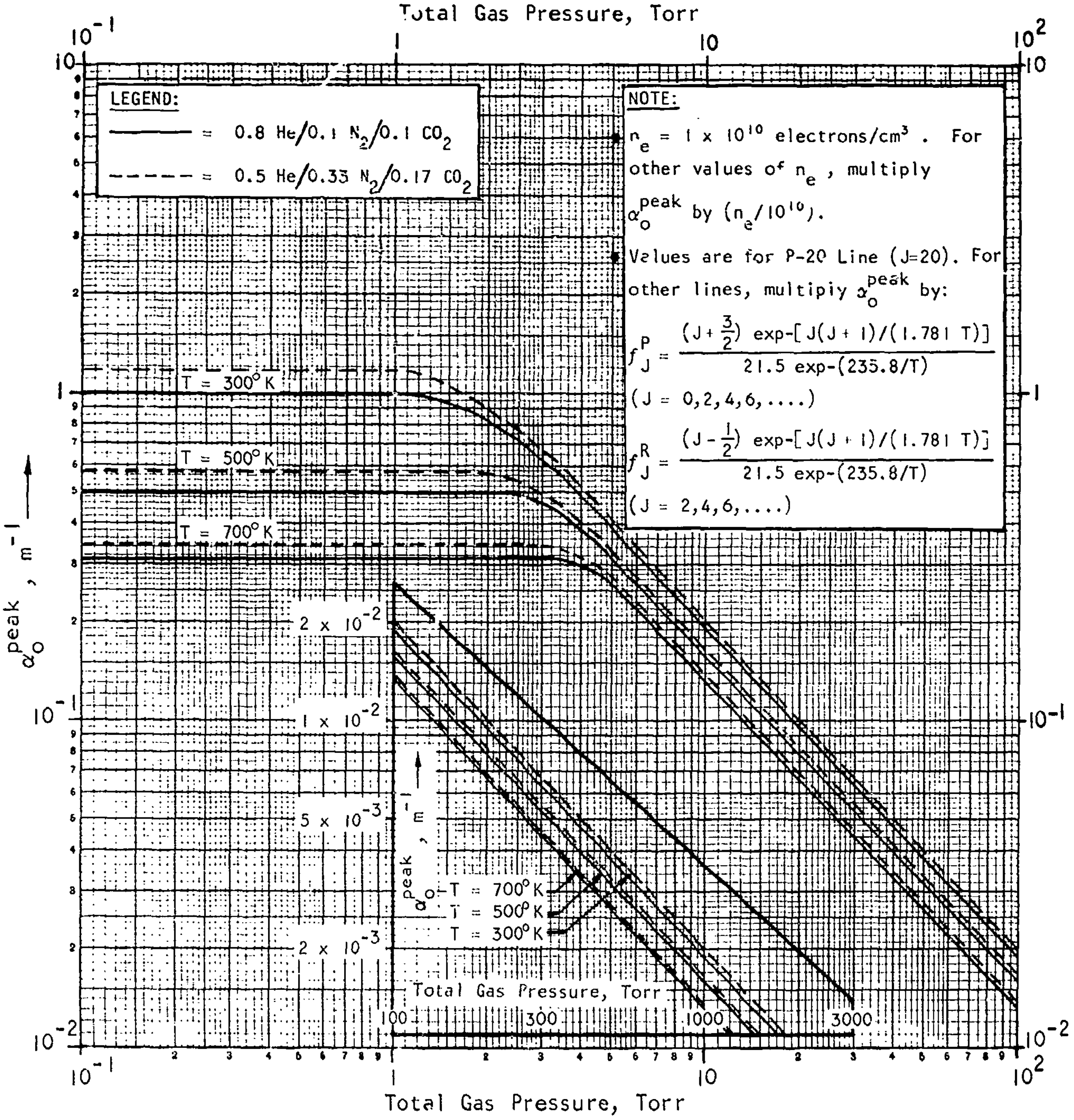

FIGURE 5-2. ZERO-POWER GAIN AT LINE-CENTER ($\nu = \nu_J = \nu_{20}$)
FOR A CO_2 LASER GAS

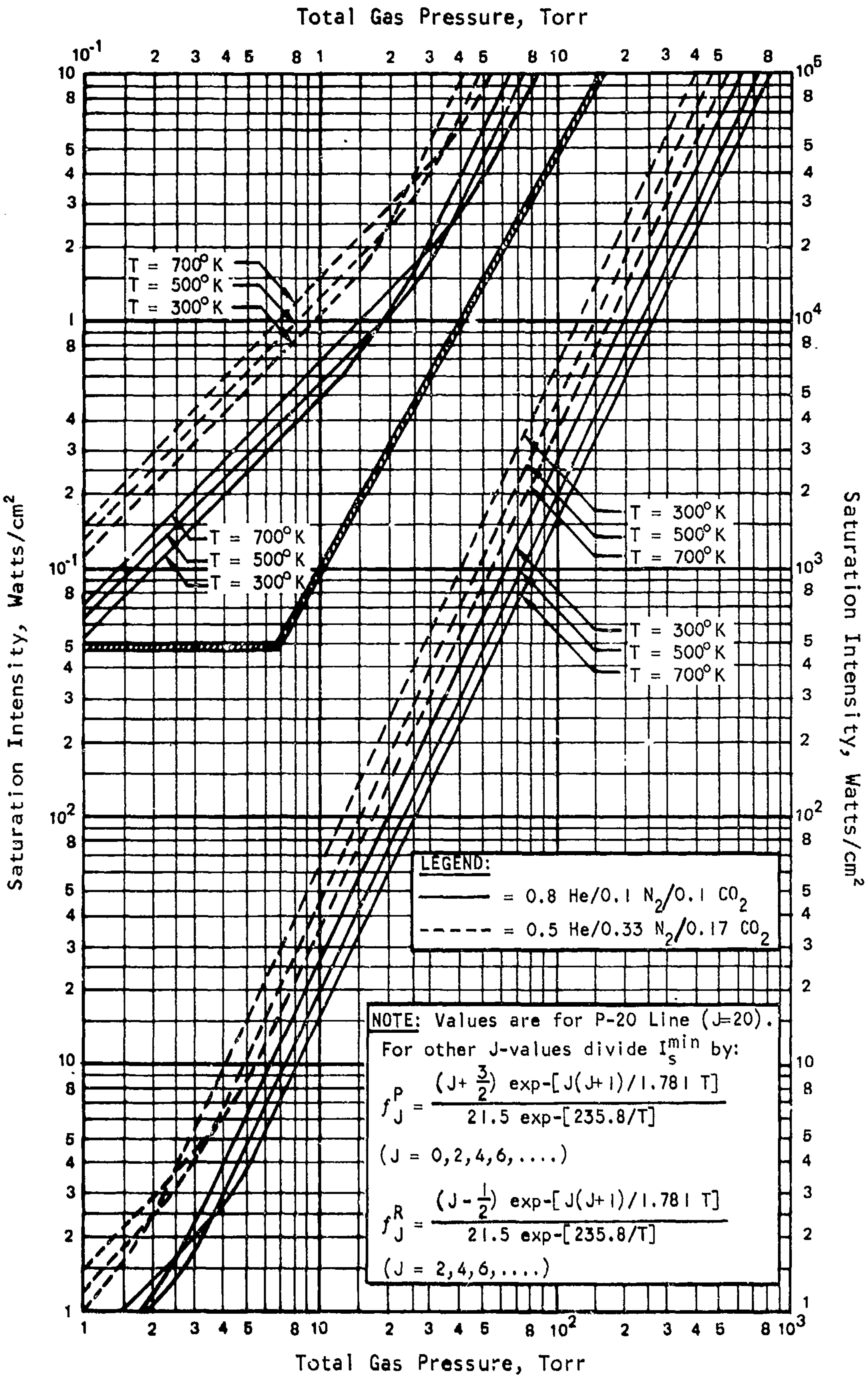

FIGURE 5-3. SATURATION INTENSITY I_s^{min} AT LINE-CENTER ($\nu = \nu_J = \nu_{20}$) FOR A CO_2 LASER GAS

Note that with the definitions (5.131) and (5.132), we can write Eqs. (5.129) and (5.130) in the form:

$$\boxed{\alpha_o = \alpha_o^{peak} b_J(\nu,\nu_J,\Delta\nu_J) , \text{ cm}^{-1}} \tag{5.133}$$

$$\boxed{I_s = I_s^{min} b_J^{-1}(\nu,\nu_J,\Delta\nu_J) , \frac{\text{Watts}}{\text{cm}^2}} \tag{5.134}$$

where $b_J(\nu,\nu_J,\Delta\nu_J)$ is given by Eq. (5.123).

In Ref. 59, a value of $\alpha_o^{peak} = 0.011 \text{ cm}^{-1}$ was measured for the P-20 line (J=20) for example, with $p_{tot} = 4.95$ Torr, and $y_{CO_2} = 0.1313$, $y_{N_2} = 0.2828$, $y_{He} = 0.5859$, $T = 340$ °K. Substituting these values into Eq. (5.131), we obtain $\alpha_o^{peak} = 0.4957 \ (n_e/10^{12}), \text{ cm}^{-1} = 0.011 \text{ cm}^{-1}$, if $n_e = 2.22 \times 10^{10}$ electrons/cm³. The latter value for the electron density is about what one would expect for the operating conditions discussed in Ref. 59 (Current = 0.015 amps; Discharge volume ≈ 500 cm³).

Equation (5.129) gives an analytical expression for the detailed stimulated emission line spectrum of the $\nu_1 - \nu_3$ band (for a pumped CO_2 laser gas) which is very similar to the absorption spectrum shown in Figure 5-4. The figure also shows the $\nu_3 - 2\nu_2$ band and indicates (with arrows) the P-lines on which Patel (Ref. 56) first observed laser action. Lasing on R-lines has also been observed in the meantime.

To determine the precise spectrum of the possible laser emission frequencies for a given laser, consider Eq. (5.83) again. In a laser

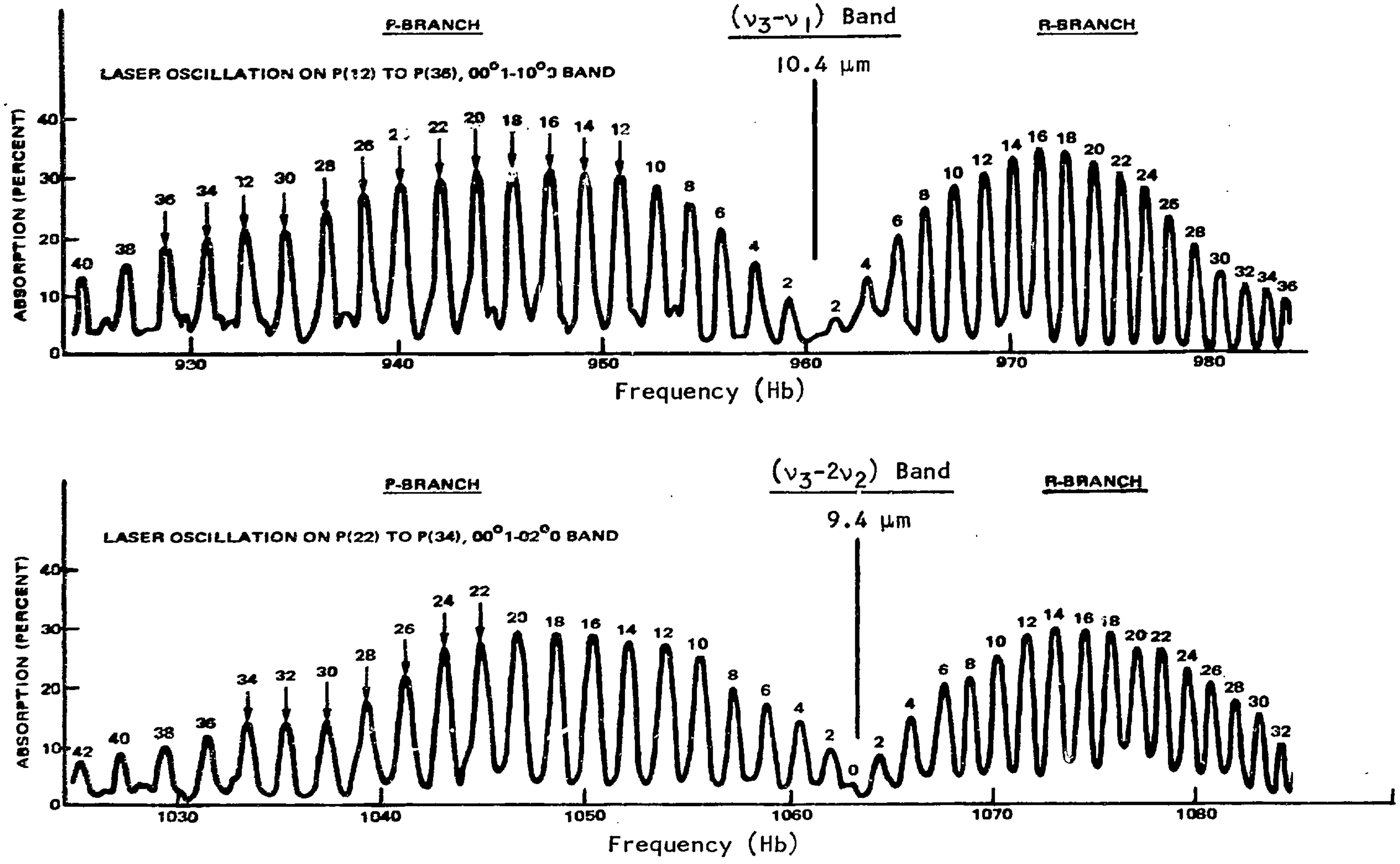

FIGURE 5-4. ABSORPTION SPECTRUM AT $p = 1$ atm FOR THE $00^01 - 10^00$ BAND (TOP) AND THE $00^01 - 02^00$ BAND (BOTTOM) AS MEASURED BY BARKER AND ADEL. The frequency scale is corrected in both cases to read vacuum wave numbers. Observed laser wavelengths are indicated by arrows on the particular transitions responsible. (After Ref. 56.)

oscillator with composed of an optical resonator with laser end-mirrors, the laser intensity I in the laser gas is related to the laser output I_{out} by:

$$I = \frac{2}{\delta} I_{out} \quad , \quad \frac{\text{Watts}}{\text{cm}^2} \tag{5.135}$$

where:

δ = Fractional photon loss (transmission per roundtrip pass through laser cavity).

We have further the laser balance equation (conservation of photons):

$$\left\{ \exp(2\alpha_G L) \right\} (1-\delta)\left(1-A_{a_1}\right)\left(1-A_{a_2}\right) = 1 \ , \tag{5.136}$$

or:

$$\alpha_G = \frac{\ell n \left[(1-\delta)\left(1-A_{a_1}\right)\left(1-A_{a_2}\right) \right]^{-1}}{2L} \ , \quad \text{cm}^{-1} \tag{5.137}$$

where:

L = Laser cavity length, cm

A_{a_1}, A_{a_2} = Non-useful absorption loss on mirrors 1 and 2 of the resonator.

Usually one laser mirror is totally reflecting and the other partially transmitting and reflecting so that $\delta = Tr_1$, where Tr_1 is the useful output transmission of the "transmirror" or "output mirror" 1.

For a steadily operating continuous wave laser, Eq. (5.137) which relates α_G to the laser hardware parameters, must equal α_G given by Eq. (5.83) which relates α_G to the physical parameters of the laser medium. From these two equations, and making use of (5.135), (5.133), and (5.134), we can write:

$$\boxed{\frac{I_{out}(\nu)}{I_s^{min}} = \frac{\delta}{2}\left[\frac{2L\,\alpha_o^{peak}}{\ln\left[(1-\delta)\left(1-A_{a_1}\right)\left(1-A_{a_2}\right)\right]^{-1}} - \frac{1}{b_J(\nu,\nu_J,\Delta\nu_J)}\right]} \qquad (5.138)$$

Note from Eq. (5.138), that $I_{out}(\nu) = 0$ when $\left[b_J(\nu,\nu_J,\Delta\nu_J)\right]^{-1}$ equals or exceeds the value $2L\,\alpha_o^{peak}/\ln\left\{(1-\delta)(1-A_{a_1})(1-A_{a_2})\right\}^{-1}$ (a negative output is of course unphysical).

Equation (5.138) gives then the actual laser output line frequency profiles. Since $b_J(\nu,\nu_J,\Delta\nu_J)$ has a maximum value of 1 at $\nu = \nu_J$, and is less than 1 for $\nu \neq \nu_J$, $I_{out}(\nu)$ will also peak at $\nu = \nu_J$ and become less for $\nu \neq \nu_J$ as expected. If $p \gtrsim 5$ Torr, Eq. (5.110) may be used for $b_J(\nu,\nu_J,\Delta\nu_J)$ and (5.138) becomes:

$$\boxed{\begin{aligned}\frac{I_{out}(\nu)}{I_s^{min}} &= \frac{\delta}{2}\left[\frac{(U-1)(\Delta\nu_J/\pi)^2 - (\nu-\nu_J)^2}{(\Delta\nu_J/\pi)^2}\right] = \\ &= \frac{\delta}{2}\left[\frac{(U-1)\,p^2\,T^{-1} - 33{,}803.5\,(\nu-\nu_J)^2}{p^2\,T^{-1}}\right] \\ &p \gtrsim 5 \text{ Torr})\end{aligned}} \qquad (5.139)$$

Here:

$$\boxed{U = \frac{2L\,\alpha_o^{peak}}{\ln\left[(1-\delta)\left(1-A_{a_1}\right)\left(1-A_{a_2}\right)\right]^{-1}}\ ,} \qquad (5.140)$$

and $\Delta\nu_J$ is given by Eq. (5.110), ν_J by (5.128), and I_s^{min} by (5.132). Units of p is in Torr, T is in °K, and ν, ν_J is in Hb as before. Of course U must be larger than 1 for lasing to be possible.

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7. CONSTANTS, UNITS, AND NOMENCLATURE

7.1 CONSTANTS OF MOLECULAR PHYSICS

7.1.1 Basic Constants

Avogadro's Number	A_o	$= 6.02471 \times 10^{23}$ molecules $\cdot$ (mole)$^{-1}$
Atomic Mass Unit	amu	$= A_o^{-1} = 1.65983 \times 10^{-24}$ g
Boltzmann Constant	k	$= 1.3804 \times 10^{-16}$, erg $\cdot$ (°K)$^{-1}$
		$= 1.3804 \times 10^{-23}$, Joule $\cdot$ (°K)$^{-1}$
		$= 0.86167 \times 10^{-4}$, eV $\cdot$ (°K)$^{-1}$
Gas Constant	R	$= 8.317 \times 10^{7}$ erg $\cdot$ (°K)$^{-1}$ $\cdot$ (mole)$^{-1}$
		$= 1.987$ cal $\cdot$ (°K)$^{-1}$ $\cdot$ (mole)$^{-1}$
		$= 83.17$ bar $\cdot$ cm^{3} $\cdot$ (°K)$^{-1}$ $\cdot$ (mole)$^{-1}$
		$= 82.08$ atm $\cdot$ cm^{3} $\cdot$ (°K)$^{-1}$ $\cdot$ (mole)$^{-1}$
Planck's Constant	h	$= 6.6252 \times 10^{-27}$ erg/Hz
		$= 6.6252 \times 10^{-34}$ Joules/Hz
		$= 1.9862 \times 10^{-16}$ ergs/Hb
		$= 1.9862 \times 10^{-23}$ Joules/Hb
Velocity of Light	c	$= 2.99793 \times 10^{10}$ cm/sec
		$= 2.99793 \times 10^{8}$ m/sec
Electronic Charge Squared	e^2	$= 2.3068 \times 10^{-19}$ erg $\cdot$ cm
		$= 2.3068 \times 10^{-28}$ Joule $\cdot$ m
		$= 1.440 \times 10^{-7}$ eV $\cdot$ cm

Electronic Charge $e = 4.8029 \times 10^{-10}\ \mathrm{erg}^{1/2} \cdot \mathrm{cm}^{1/2}$

$= 4.8029 \times 10^{-10}$ esu

Electronic Mass $m_e = 0.54875 \times 10^{-3}$ amu

$= 0.91083 \times 10^{-27}$ g

$= 0.91083 \times 10^{-30}$ kg

Proton Mass $m_p = 1.00759$ amu

$= 1836.2\ m_e$

$= 1.67243 \times 10^{-24}$ g

$= 1.67243 \times 10^{-27}$ kg

Neutron Mass $m_n = 1.00898$ amu

$= 1838.7\ m_e$

$= 1.67474 \times 10^{-24}$ g

$= 1.67474 \times 10^{-27}$ kg

Hydrogen Atom Mass $m_H = 1.00814$ amu

$= 1837.1\ m_e$

$= 1.67334 \times 10^{-24}$ g

$= 1.67334 \times 10^{-27}$ kg

Earth Gravitational Constant $\tilde{g} = 980.665\ \mathrm{cm/sec}^2 = 9.80665\ \mathrm{m/sec}^2$

$g_{pole} = 983\ \mathrm{cm/sec}^2 = 9.83\ \mathrm{m/sec}^2$

$g_{equator} = 978\ \mathrm{cm/sec}^2 = 9.78\ \mathrm{m/sec}^2$

7.1.2 Derived Constants

Bohr Orbit (Hydrogen Atom) Radius	a_o	$= a_H = h^2/(4\pi^2 m_e e^2) =$
		$= 0.52917 \times 10^{-8}$ cm
		$= 0.52917 \times 10^{-10}$ m
Classical Electron Radius	a_e	$= e^2/(m_e c^2) =$
		$= 0.28178 \times 10^{-12}$ cm
		$= 0.28178 \times 10^{-14}$ m
Compton Electron Wavelength	λ_c	$= h/m_e c = 2.42626 \times 10^{-10}$ cm
		$= 2.42626 \times 10^{-12}$ m
Fine Structure Constant	α	$= \frac{2\pi e^2}{hc} = \frac{1}{137.04}$
Planck/Boltmann Ratio	h/k	$= 1.43886$, $(^\circ K) \cdot Hb^{-1}$
		$= 4.79948 \times 10^{-11}$, $(^\circ K) \cdot Hz^{-1}$
Rydberg Energy (Ionization Energy of Hydrogen Atom)	Ry	$= \frac{e^2}{2a_o} = \frac{2\pi^2 m_e e^4}{h^2} = 13.605$ eV
		$= 2.1797 \times 10^{-11}$ erg
		$= 2.1797 \times 10^{-18}$ Joules
Electron Rest Mass Energy	ϵ_e	$= m_e c^2 = 0.51098 \times 10$ eV
		$= 8.1864 \times 10^{-7}$ erg
		$= 8.1864 \times 10^{-14}$ Joules
Electron Velocity in Bohr Orbit	v_H	$= \frac{2\pi e^2}{h} = 2.188 \times 10^8$ cm/sec
		$= 2.188 \times 10^6$ m/sec
Thomson Electron Cross-Section	σ_T	$= \frac{8}{3}\pi a_e^2 = \frac{8\pi e^2}{3 m_e c^2}$
		$= 0.6652 \times 10^{-24}$ cm^2
		$= 0.6652 \times 10^{-28}$ m^2

Bohr Orbit (Hydrogen Atom) Cross-Section

$$\sigma_B = \pi a_o^2 = \frac{h^2}{4\pi\ me^2} =$$

$$= 0.8798 \times 10^{-16}\ \text{cm}^2$$

$$= 0.8798 \times 10^{-20}\ \text{m}^2$$

Stefan-Boltzmann (Radiation) Constant

$$\sigma_{SB} = \frac{2\pi^5 k^4}{15\ h^3 c^2} =$$

$$= 4.6687 \times 10^{-12}\ \text{W} \cdot \text{cm}^{-2} \cdot (^\circ\text{K})^{-4}$$

Photon Parameter Conversions (Energy ϵ, Frequency ν, Wavelength λ)

(1 Hz = 1 sec^{-1} ; 1 Hb = 1 cm^{-1})

$$\nu = c \cdot \lambda^{-1}$$

$$\nu = \epsilon \cdot h^{-1}$$

$$\nu(\text{Hz}) = 2.99793 \times 10^{10} \cdot \lambda^{-1}\ (\text{cm})$$

$$\nu(\text{Hb}) = \lambda^{-1}\ (\text{cm})$$

$$\nu(\text{Hz}) = 1.5094 \times 10^{26} \cdot \epsilon\ (\text{erg})$$

$$\nu(\text{Hb}) = 5.0347 \times 10^{15} \cdot \epsilon\ (\text{erg})$$

$$\nu(\text{Hz}) = 2.4182 \times 10^{14} \cdot \epsilon\ (\text{eV})$$

$$\nu(\text{Hb}) = 8066.166 \cdot \epsilon\ (\text{eV})$$

7.2 UNITS AND CONVERSION FACTORS

7.2.1 Prefix Scaling Values

T = Tera- = 10^{12}

G = Giga- = 10^{9}

M = Mega- = 10^{6}

k = Kilo- = 10^{3}

h = hecto- = 10^{2}

da = deca- = 10

Basic Unit = 1

d = deci- = 10^{-1}

c = centi- = 10^{-2}

m = milli- = 10^{-3}

μ = micro- = 10^{-6}

n = nano- = 10^{-9}

p = pico- = 10^{-12}

f = femto- = 10^{-15}

a = atto- = 10^{-18}

Examples: 1 pm = 10^{-12} meters; 1 MJ = 10^{6} Joules; 1 heV = 100 electronvolts; 1 mTorr = 10^{-3} Torr; etc.

7.2.2 Length

1 m = 1 meter = 100 cm

1 cm = 1 centimeter = 0.01 m

1 ft = 1 foot = 30.48 cm

1 in = 1 inch = 2.54 cm

1 nm = 10^{-9} m = 10^{-7} cm

1 Å = 1 Angstrom = 10^{-8} cm = 10^{-10} m

1 μm = 1 micrometer = 1 micron = 10^{-4} cm = 10^{-6} m

1 km = 10^{3} meter = 0.6215 mile

1 mi. = 1 mile = 5280 foot = 1.609 km

1 n.mi. = 1 nautical mile = 1.853 km

7.2.3 Area

1 barn = 10^{-24} cm^{2} = 10^{-28} m^{2}

1 a = 1 are = 10^{2} m^{2} = 10^{6} cm^{2}

1 ha = 1 hectare = 10^{4} m^{2} = 10^{8} cm^{2}

1 acre = 43,560 ft^{2} = 0.4047 ha = 4046.8564 m^{2}

7.2.4 Volume

1 ℓ = 1 liter = 1000 cm^{3} = 1.057 quart

1 mℓ = 1 milliliter = 1 cm^{3}

1 gal = 1 gallon = 4 quarts = 3.785 ℓ

1 qrt = 1 quart = 0.9461 ℓ

1 cu.ft. = 1 ft^{3} = 7.481 gal. = 28.32 ℓ

1 cu.in. = 1 in^{3} = 16.387 cm^{3}

7.2.5 Time

1 s = 1 sec = 1 second

1 ms = 1 millisecond = 10^{-3} s

1 μs = 1 microsecond = 10^{-6} s

1 ns = 1 nanosecond = 10^{-9} s

1 year = 365 days = 8760 hours =

1 year = 525,600 minutes = 3.1536 × 10^{7} seconds

7.2.6 Mass

1 g = 1 gm = 1 gram = 10^{-3} kg

1 kg = 1 kilogram = 10^{3} g

1 lb = 1 pound = 453.59 g = 0.45359 kg

1 slug = 32.174 lb = 14.594 kg

1 metric ton = 10^{3} kg = 10^{6} g = 2205 lb

1 British ton = 2000 lb = 907.2 kg

1 amu = 1 atomic mass unit = 1.65983×10^{-24} g

7.2.7 Photon Frequency

1 Hz = 1 hertz = 1 s^{-1} = 1 cps = 1 cycle per second

1 Hz = 33.356 pHb = 3.3356×10^{-11} Hb

1 MHz = 1 megaherz = 10^{6} Hz = 0.033 mHb

1 GHz = 10^{9} Hz = 33 mHb = 0.033 Hb

1 THz = 1 terahertz = 10^{12} Hz = 33.36 Hb

1 Hb = 1 herzberg = 1 cm^{-1} = 1 wavenumber

1 Hb = 0.03 THz = 30 GHz

1 mHb = 1 milliherzberg = 10^{-3} Hb = 10^{-3} cm^{-1}

1 pHb = 1 picoherzberg = 10^{-12} Hb

1 mHb = 30 MHz

7.2.8 Energy

1 erg = 1 dyne-cm = 1 $g \cdot cm^{2} \cdot s^{-2}$ = 10^{-7} J =

= 6.2418×10^{11} eV

1 J = 1 Newton-m = 1 $kg \cdot m^{2} \cdot s^{-2}$ = 10^{7} erg =

= 6.2418×10^{18} eV

1 eV = 1 electron-volt = 1.6021×10^{-12} erg =

= 1.6021×10^{-19} Joules

1 cal = 1 calorie = 4.18 J = 4.18×10^7 ergs

1 kcal = 1 Cal = 1 kilocaloric = 1000 cal = 4,180 J

1 eV/molecule = 23.06 kcal/mole

1 BTU = 252 cal = 778 ft · lb = 1055 J

7.2.9 Power

1 W = 1 watt = $1\ \mathrm{J \cdot s^{-1}} = 10^7\ \mathrm{erg \cdot s^{-1}}$

1 kW = 1 Kilowatt = 10^3 W

1 HP = 1 Horse Power = 0.746 kW

1 BTU/hr = 0.29306 W

7.2.10 Pressure

1 atm = 1 atmosphere = 760 Torr = 1.0133 bar = 14.696 psi

1 Torr = 1 mm Hg = 1.3158×10^{-3} atm = $1333.2\ \mathrm{dyne \cdot cm^{-2}}$

1 bar = 0.9869 atm = 750 Torr = $10^6\ \mathrm{dyne \cdot cm^{-2}} = 10^3$ pascal

1 pascal = $1\ \mathrm{Newton \cdot m^{-2}} = 10^{-2}$ mbar = $10\ \mathrm{dyne \cdot cm^{-2}}$

1 psi = $1\ \mathrm{lb \cdot in^{-2}} = 6.895 \times 10^4\ \mathrm{dyne \cdot cm^{-2}}$

1 psf = $1\ \mathrm{lb \cdot ft^{-2}} = 478.8\ \mathrm{dyne \cdot cm^{-2}}$

7.2.11 Force

1 dyne = 10^{-5} newton = $1\ \mathrm{g \cdot cm \cdot s^{-2}}$

1 newton = $1\ \mathrm{kg \cdot m \cdot s^{-2}} = 10^5$ dyne = 7.2330 poundal

1 poundal = 0.031081 lbs-force

7.2.12 Temperature

1 °K = 1 degree Kelvin = $\frac{9}{5}$ °R

1 °R = 1 degree Rankine = $\frac{5}{9}$ °K

x °C = (x + 273.16) °K

x °F = (x + 459.7) °R

7.2.13 Electrical

1 C = 1 coulomb = 6.242×10^{18} electrons

1 Faraday = 96,520.1 C = 6.0247×10^{23} electron charges

1 A = 1 amp = 1 ampere = $1\ \mathrm{C} \cdot \mathrm{s}^{-1}$ =

= 6.242×10^{18} electrons $\cdot\ \mathrm{s}^{-1}$

1 V = 1 volt = $1\ \mathrm{W} \cdot \mathrm{A}^{-1} = 1\ \mathrm{J} \cdot \mathrm{C}^{-1}$

1 Ω = 1 ohm = $1\ \mathrm{V} \cdot \mathrm{A}^{-1}$

1 F = 1 farad

1 H = 1 henry

1 esu = 1 electrostatic charge unit = $1\ \mathrm{erg}^{1/2}\ \mathrm{cm}^{1/2}$ =

= 1.6021×10^{-19} C

1 debye = 1 dipole moment unit = $10^{-18}\ \mathrm{erg}^{1/2}\ \mathrm{cm}^{3/2}$

7.3 NOMENCLATURE AND UNITS

a = Special parameter defined by Eq. (4.58), used in combined collision and doppler line-broadening calculations.

a = $\left\{9\,\pi^2/(128Z)\right\}^{1/3} a_o$ = Effective Bohr radius for a multi-electronic atom.

$\vec{a}$ = Unit vector along principal axis of a molecule (defined by Eq. (4.54)).

$a_o = a_H$ = Bohr radius = 0.52917×10^{-8} cm = 0.52917 Å.

a_m = Special quantum number used in Eq. (3.45a) or (3.47a), defined by Eq. (3.45b) or (3.47b).

A = Special constant used in vibrational calculations of a linear molecule, defined by Eq. (3.134) or (B.85).

$A, A', A'', A_1, A_2, A_g, A_u$ = Certain group-theoretical symmetry species designations (non-degenerate) for a molecule, defined in Refs. 10 and 11.

$A_{mn} = A_{m\rightarrow n}$ = Spontaneous photon emission rate of a molecule for transitions from state or level m to n.

A^o_{mn} = $\int_{\nu=0}^{\infty} (dA_{mn}/d\nu)\,d\nu$ = Total spontaneous photon emission rate constant (Einstein "A" coefficient) of a molecule for transitions from state or level m to n, $\sec^{-1}$.

$dA_{mn}/d\nu$ = Spontaneous photon emission rate constant per unit frequency range of a molecule for transitions from state or level m to n, $\sec^{-1}$ Hz^{-1} or $\sec^{-1}$ Hb^{-1}.

$A^o_{mn\ elc}$ = Total spontaneous photon emission rate constant (Einstein "A" coefficient) of a molecule for electronic transitions from electronic level m to electronic level n, $\sec^{-1}$.

$A^o_{mn\ vib}$ = Total spontaneous Photon emission rate constant (Einstein "A" coefficient) of a molecule for vibrational transitions from vibrational level m to vibrational level n, $\sec^{-1}$.

$A^{o}_{mn\,\mathrm{rot}}$ = Total spontaneous photon emission rate constant (Einstein "A" coefficient) of a molecule for rotational transitions from rotational level m to rotational level n , sec^{-1} .

A_m, A_n ; A_{v_m}, A_{v_n} = Rotational constants of symmetric-top and asymmetric-top molecules along direction $\vec{e}_a$ for vibrationally (or vibronic) excited states m and n respectively, Hb (cm^{-1}) .

A = Rotational constant of symmetric-top and asymmetric-top molecules along direction $\vec{e}_a$, in units of Hb (cm^{-1}).

A_o = Rotational constant along principal axis $\vec{e}_a$ of a polyatomic molecule in the ground vibrational state , Hb .

ΔA = $A_{v_n} - A_{v_m} = A_n - A_m$ = Difference between excited vibrational upper (m) and lower (n) state's rotational constants of symmetric-top and asymmetric-top molecules along direction $\vec{e}_a$, Hb .

ΔA_ζ = Difference in rotational levels between upper (m) and lower (n) vibrational states due to Coriolis (ζ) interactions by degenerate vibrations (see Eq. (4.167)), Hb .

A_n = Special constant used in vibronic transition calculations, defined by Eq. (4.440).

A_{a_1}, A_{a_2} = Absorption (fractional) of laser photons by laser end mirrors 1 and 2.

b = a/π = Molecular radius used in molecular dipole calculations, in cm or Å .

b = Special constant defined by Eq. (3.194) for asymmetric-top rotor equations.

b_n = Special quantum number used in Eq. (3.45a) or (3.47a), defined by Eq. (3.45c) or (3.47c).

$b(\nu,\nu_{mn},\Delta\nu_{mn})$ = Dimensionless shape function of line, band, or bandsystem frequency spectrum for molecular transitions between levels m and n. The shape function is related to the contour function $g(\nu,\nu_{mn},\Delta\nu_{mn})$ by $b(\nu,\nu_{mn},\Delta\nu_{mn}) =$ $= \Delta\nu_{mn} \cdot g(\nu,\nu_{mn},\Delta\nu_{mn})$.

$b_G(\nu,\nu_{mn},\Delta\nu_{mn})$ = Gaussian line-shape function defined by Eq. (4.10) or (4.16).

$b_L(\nu,\nu_{mn},\Delta\nu_{mn})$ = Lorentzian line-shape function defined by Eq. (4.11) or (4.17).

$b_N(\nu,\nu_{mn},\Delta\nu_{mn})$ = Natural-broadened line-shape function defined by Eq. (4.34).

$b_D = b_D(\nu) = b_D(\nu,\nu_{mn},\Delta\nu_{mn})$ = Dopper-broadened line-shape function defined by Eq. (4.43).

$b_C = b_C(\nu) = b_C(\nu,\nu_{mn},\Delta\nu_{mn})$ = Collision-broadened line-shape function defined by Eq. (4.45).

$b_S = b_S(\nu) = b_S(\nu,\nu_{mn},\Delta\nu_{mn})$ = Stark-broadened line-shape function defined by Eq. (4.73).

$b_{C,N} = b_{C,N}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Combined collision- and natural-broadened line-shape function, defined by Eq. (4.51).

$b_{C,N,D} = b_{C,N,D}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Combined collision-, doppler-, and natural-broadened line-shape function defined by Eq. (4.59).

$b_v^{PR}(\nu) = b_v^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Band-shape function for the P- and R-Branch of a vibrational band.

$b_v^{Q}(\nu) = b_v^{Q}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Band-shape function for the Q-Branch of a vibrational band.

$b_e(\nu, \nu_{mn}, \Delta\nu_{mn})$ = Band-system shape function for electronic transitions.

B = Special constant used in the calculation of vibrational parameters of planar symmetric triatomic molecules, defined by Eq. (B.128).

B^o_{nm} = Einstein "B" coefficient for induced absorption, in units of $cm^3 \cdot Hz \cdot erg^{-1} \cdot sec^{-1}$.

B, B_1, B_2, B_u, B_g = Certain group-theoretical symmetry species designations (non-degenerate) for a molecule, defined in Refs. 10 and 11.

B_e = ν_B/c = Fundamental equilibrium rotational constant of a diatomic molecule, Hb .

B = Rotational constant of a polyatomic molecule along its principal axis $\vec{e}_b$, Hb .

B_v = Rotational constant of a polyatomic molecule along its main axis which includes vibrational effects (see Eq. (3.138)), Hb .

$\Delta B = B_{v_n} - B_{v_m} = B_n - B_m$ = Difference between rotational constants for upper vibrationally (or vibronic) excited state m and lower vibrationally (or vibronic) excited state n , Hb .

$\bar{B} = (B_m + B_n)/2$ = Average value of rotational constants for upper vibrational (or vibronic) state m and lower vibrational (or vibronic) state n , Hb .

B_o = Rotational constant along principal axis $\vec{e}_b$ of a polyatomic molecule in the ground vibrational state, Hb .

B_n = Special parameter used in vibronic transition calculations defined by Eq. (4.328).

c = Velocity-of-light constant = 2.9958×10^{10} cm/sec .

c = Special quantum number used in Eqs. (3.19a), (3.45a), or (3.47a), defined by (3.19d), (3.45d), or (3.47d).

$\cosh(x)$ = Hyperbolic cosine function of quantity x .

$\cos(x)$ = Cosine function of quantity x .

$\cos(a,b)$ = Cosine of angle between lines a and b or directions $\vec{e}_a$ and $\vec{e}_b$.

C = Special constant used in the calculation of vibrational parameters of planar molecules, defined by Eq. (B.144).

$C^{elc}_{mn}, C^{vib}_{mn}, C^{rot}_{mn}$ = Connection factors for respectively electronic, vibrational, and rotational main transitions from upper molecular level m to lower molecular level n, defined by Eqs. (1.10), (1.15), and (1.16).

C_{nm}, C_{mn} = General connection factors for respectively transitions from internal lower molecular level n to upper level m, and from upper level m to lower level n .

$C_{m_i n_k} = C_{n_k m_i}$ = Component connection factor between states i and k for transitions between levels m and n .

C = Third rotational constant of an asymmetric-top molecule due to moment of inertia I_C about principal axis $\vec{e}_c$, Hb .

C_v = Third rotational constant of an asymmetric-top molecule in a vibrational excited state due to the moment of inertia I_C about principal axis $\vec{e}_c$, Hb .

C_o = Third rotational constant of an asymmetric-top molecule in the ground vibrational state, due to the moment of inertia I_C about principal axis $\vec{e}_c$, Hb.

C_m = Stark coefficient for electronic level m of an atom or molecule (see Table 4-3), in $\mathrm{Hz} \cdot \mathrm{m} \cdot \mathrm{V}^{-1}$.

${}^{\circ}C_{mn}^{vib} = {}^{\circ}C_{mn}^{vib}(\nu_m, \nu_n; \Lambda_m, \Lambda_n)$ = Connection factor for the vibrational levels in an electronic transition from the upper molecular electronic state m to the lower molecular electronic state n , defined by Eq. (1.11).

${}^{\circ}C_{mn}^{rot} = {}^{\circ}C_{mn}^{rot}(J_m, J_n; \Lambda_m, \Lambda_n; v_m, v_n)$ = Connection factor for the rotational levels in an electronic $(\Lambda_m \neq \Lambda_n)$ or vibrational $(\Lambda_m = \Lambda_n)$ transition from the upper molecular energy state m to the lower molecular energy state n, defined by Eq. (1.12).

d_{X_k} = General designation of the degeneracy of a molecule in excited state k , of symmetry species X , where X = A, B, E, or F ; we have $d_{A_k} = 1$; $d_{B_k} = 1$, $d_{E_k} = 2$, and $d_{F_k} = 3$.

$d_\beta, d_\alpha = d_{X_\alpha}$ = General symbol for the degeneracy of the normal vibration β , or α of a polyatomic molecule with symmetry species X_α , where X_α = A, B, E, or F ; we have $d_A = 1$, $d_B = 1$, $d_E = 2$, $d_F = 3$.

$d, d_o = \mu_o/e = z_o r_e$ = Effective "length" of axis of permanent dipole moment, in units of cm or Å .

$d_{M.D.} = \mu_{M.D.}/e$ = Effective "length" of permanent magnetic dipole moment, in units of cm or Å .

${}^{g}d_o$ = Effect dipole "length" of permanent dipole moment along direction g , where g = a, b, or c are the principal moment-of-inertia axes of an asymmetric-top molecule, in units of cm or Å .

dip(p) = Special function used in dipole charge calculations defined by Eq. (B.44).

D = Special constant used in the calculation of vibrational parameters of pyramidal molecules, defined by Eq. (B.167).

D^{o}_{mn} = Total stimulated emission or deactivation rate for molecular transitions from level m to n , $\sec^{-1}$.

D_e = Equilibrium vibrational dissociation energy of a diatomic molecule in the ground electronic state, in eV, ergs, or Hb .

D_α = Vibrational dissociation energy for the normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule, in the ground electronic state, in units of eV , ergs, or Hb .

D_{e_i} = Equilibrium vibrational dissociation energy of a diatomic molecule in electronic state i in eV, ergs, or Hb .

D_{α_i} = Vibrational dissociation energy of the normal vibration α of a polyatomic molecule in electronic state i , in units of eV, ergs, or Hb .

$D(A-B), D_{XY}$ = Dissociation energy of the bond between A and B, or X and Y, in units of eV , ergs , or Hb.

e = Used as subscript, meaning: electronic.

elc = Used as subscript or superscript, meaning: electronic.

e, e^2 = Electron charge or square of the electron charge respectively equal to 4.8029×10^{-10} $\text{erg}^{1/2} \cdot \text{cm}^{1/2}$ (esu), and 2.3068×10^{-19} erg · cm (esu^2).

exp(x) = Exponential function (natural base) of quantity x .

erf(x) = Error function of quantity x ; $\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x (\exp - x^2)\, dx$.

$\vec{e}_{\alpha s}$ = Unit vector along component vibration $s (s = 1, 2, 3, \ldots)$ of normal vibration $\alpha (\alpha = 1, 2, 3, \ldots)$.

$\vec{e}_{\alpha}$ = Unit vector along net vibrational displacement direction of normal vibration α .

$\vec{e}_a, \vec{e}_b, \vec{e}_c$ = Unit vectors along rotational axes of the molecular principal moments of inertia I_A , I_B , and I_C respectively of a polyatomic molecule.

$\vec{e}_d$ = Unit vector along permanent dipole moment direction of a molecule.

E = Special constant used in the calculation of vibrational parameters of a pyramidal molecule, defined by Eq. (B.171).

E = Energy of some internal molecular state or level, ergs or eV.

$E_{v_m}, E_{v_n}, E_{v_k}$ = Energy of molecular vibrational upper energy level m, lower level n, or general level k, with vibrational quantum number v_m, v_n, or v_k, in ergs or eV.

E = Group-theoretical symbol to indicate a doubly-degenerate symmetry species ($d_E = 2$).

E.D. = Used as subscript, meaning: electric dipole.

E.Q. = Used as subscript, meaning: electric quadrupole.

E_m, E_n, E_k = Internal excitation energy of upper level m, lower level n, and general level k of a molecule or atom, erg or eV.

E', E'' = Internal excitation energy of first level (′) and second level (″) of a molecule or atom, erg or eV.

E_{ion} = Ionization energy of a molecule or atom, eV or ergs.

E_o = Special parameter defined by Eq. (4.65) used in Stark-broadening calculations, Volts/m.

E_o = Fundamental energy of harmonic oscillator approximation of electron motion about the atom or molecule, ergs or eV.

E_{mn} = Energy difference between molecular (or atomic) levels m and n, in ergs or eV.

E = Electron kinetic energy, eV.

E_J, E_{J_m}, E_{J_n} = Energy of rotational level with quantum number J, J_m, or J_n of diatomic linear, or spherical-top molecule, in ergs or eV.

$E_{J,K}$ = Energy of rotational level with rotational quantum numbers J and K of symmetric-top molecule, in ergs or eV.

$E_{J,W}$ = Energy of rotational level with rotational quantum numbers J and W of an asymmetric-top molecule, in ergs or eV.

ΔE_e = Energy difference between two electronic levels of a molecule or atom, ergs or eV .

ΔE_v = Energy difference between two vibrational levels of a molecule, ergs or eV .

ΔE_r = Energy difference between two rotational levels of a molecule, ergs or eV .

ΔE_D = Shift in emission or absorption photon energy due to Doppler broadening, ergs or eV .

f = Special factor defined by Eq. (4.89c).

$f(\nu)$ = General function dependent on photon frequency ν .

f_d = Special factor defined by (4.111) and (4.112) to weight P-, Q-, and R-Branch transitions.

f_β = Special factor defined by Eq. (B.166)

f_I = Nuclear statistics weighting factor for rotational transitions of a polyatomic molecule.

$\bar{f}_I$ = Averaged nuclear statistics weighting factor defined by Eq. (4.134) for a linear molecule.

$f_I(J_m, s_m)$ = Nuclear-statistics weighting factor for rotational transitions defined by Eq. (4.118) for a linear molecule which depends on rotational quantum number J_m and parity factor s_m .

f_I^{PR}, f_I^Q = Nuclear-statistics weighting factors for rotational transitions in the P- and R-Branch, and the Q-Branch respectively of a linear molecule, defined by Eqs. (4.131) and (4.132).

f_i = Special photon fraction factor defined by Eq. (5.60).

f_e = Special factor defined by Eq. (B.8).

f_v, f_{v_m} = Fraction of molecules in vibrational level v or $v_m (v_{(m)} = v_{\alpha(m)}, v_{\beta(m)}, \ldots)$ given by Eq. (4.80) (= vibrational Boltzmann factor).

f_J, f_{J_m} = Fraction of molecules in rotational level J or J_m given by Eq. (4.81) (= rotational Boltzmann factor).

f_{v_m, J_m} = $f_{v_m} f_{J_m}$ = Eq. (1.22).

f_Λ, f_{Λ_m} = Fraction of molecules in electronic level Λ or Λ_m given by Eq. (4.282) (= electronic Boltzmann factor).

f_{nm} = Absorption oscillator strength (dimensionless) for transitions from lower level n to upper level m, defined by Eq. (3.14).

f_{mn} = Emission oscillator strength (dimensionless) for transitions from upper level m to lower level n , defined by Eq. (3.16).

$f_{\substack{nm\\elc}}$ = Oscillator strength for absorptive electronic transitions from lower level n to upper level m .

F = Special constant used in the calculation of vibrational parameters of a tetrahedral molecule, defined by Eq. (B.190) or (B.202).

$F_{mn}^{vib/rot}$ = Dimensionless factor defined by Eq. (1.20).

F_{mn}^{rot} = Dimensionless factor defined by Eq. (1.27).

F, F_u, F_g = Group-theoretical symbol to indicate a triply-degenerate symmetry species ($d_F = 3$).

F = Fluence (omnidirectional flux), particles (or quanta) $\cdot$ cm^{-2} $\cdot$ sec^{-1} .

F_m = Molecular fluence, molecules $\cdot$ cm^{-2} $\cdot$ sec^{-1} .

F_e = Electron fluence, electrons $\cdot$ cm^{-2} $\cdot$ sec^{-1} .

F_φ = Photon fluence (omnidirectional photon flux), photons $\cdot$ cm^{-2} $\cdot$ sec^{-1} .

$F_\varphi(\nu)$ = Photon fluence of photons with frequency ν , photons $\cdot$ cm^{-2} $\cdot$ sec^{-1} .

$F(a;b;c;z)$ = Hypergeometric function (with four arguments a , b , c , and z) defined by Eq. (3.20).

$g(v_m)$ = Fractional population of vibrationally excited molecules possessing vibrational quantum number v_m per unit frequency range, Hz^{-1} or Hb^{-1} .

$g_{mn} = g_{mn}(\nu) = g(\nu, \nu_{mn}, \Delta\nu_{mn})$ = General line, band, or bandsystem contour function for $m \leftrightarrow n$ transitions, Hz^{-1} or Hb^{-1}.

$g_e = g_e(\nu) = g_e(\nu, \nu_{mn}, \Delta\nu_{mn})$ = Bandsystem contour function for electronic transitions from electronic level m to n , Hz^{-1} or Hb^{-1} .

$g_v = g_v(\nu) = g_v(\nu, \nu_{mn}, \Delta\nu_{mn})$ = Band contour function for vibrational transitions from electronic level m to n , Hz^{-1} or Hb^{-1} .

$g_r = g_r(\nu) = g_r(\nu,\nu_{mn},\Delta\nu_{mn})$ = Rotational line contour function for rotational transitions from rotational level m to n , Hz^{-1} or Hb^{-1} .

$g_o = g_o(\nu) = g_o(\nu,\nu_{mn},\Delta\nu_{mn})$ = Line, band, or bandsystem contour function of electronic (o = e), vibrational (o = v), or rotational (o = r) transition from level m to n, Hz^{-1} or Hb^{-1} .

$g_G(\nu,\nu_{mn},\Delta\nu_{mn})$ = Gaussian line, band, or bandsystem contour function defined by Eq. (4.20) or (4.22), Hb^{-1} or Hz^{-1} .

$g_L(\nu,\nu_{mn},\Delta\nu_{mn})$ = Lorentzian line, band, or bandsystem contour function defined by Eq. (4.21) or (4.23), Hb^{-1} or Hz^{-1} .

$g_N = g_N(\nu) = g_N(\nu,\nu_{mn},\Delta\nu_{mn})$ = Line contour function for naturally broadened spectral line, Hz^{-1} or Hb^{-1} .

$g_D = g_D(\nu) = g_D(\nu,\nu_{mn},\Delta\nu_{mn})$ = Line contour function for Doppler- (or temperature-) broadened spectral line, Hz^{-1} or Hb^{-1} .

$g_C = g_C(\nu) = g_C(\nu,\nu_{mn},\Delta\nu_{mn})$ = Line contour function for collisional- (or pressure-) broadened spectral line, Hz^{-1} or Hb^{-1} .

$g_S = g_S(\nu) = g_S(\nu,\nu_{mn},\Delta\nu_{mn})$ = Line contour function for stark-broadened spectral line, Hz^{-1} or Hb^{-1} .

g = General designation of either one of the principal moment-of-inertia axes a, b, or c of an asymmetric rotor, if used as a pre-superscript.

g_I^s, g_I^a = Special weighting factors defined by Eqs. (4.123) and (4.124) used in the calculation of the nuclear-spin-statistics effect on rotational transitions.

$g_J(\nu,\nu_J,\Delta\nu_J)$ = Contour function for a rotational transition line of a diatomic, linear, or spherical-top molecule with quantum number J, in Hz^{-1} or Hb^{-1}.

$g_{JK}(\nu,J,K,\Delta\nu_J)$ = Contour function for a rotational transition line of a symmetric-top molecule with quantum numbers J, K, in Hz^{-1} or Hb^{-1} .

$g_{JW}(\nu,J,W,\Delta\nu_J)$ = Contour function for a rotational transition line of an asymmetric-top molecule with quantum numbers J, W, in Hz^{-1} or Hb^{-1} .

$g_v^Q = g_v^Q(\nu) = g_v^Q(\nu,\nu_{mn},\Delta\nu_{mn})$ = Continuous contour function for the Q-Branch of a rotationally broadened vibrational band, in Hz^{-1} or Hb^{-1} .

$g_v^{PR} = g_v^{PR}(\nu) = g_v^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Continuous $(0 < \nu < \infty)$ contour function for the P- and R-Branches of a rotationally broadened vibrational band, in Hz^{-1} or Hb^{-1} .

$g_v^P(J), g_v^R(J), g_v^Q(J)$ = Discrete $(J = 0,1,2,\ldots)$ contour function for P-, R-, and Q-Branches of a rotationally broadened vibrational band, in Hz^{-1} or Hb^{-1} .

$g_{rov}^{PR} = g_{rov}^{PR}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Detailed rovibrational line contour function for a band with only a P- and R-Branch, in Hz^{-1} or Hb^{-1} .

$g_{rov}^{PQR} = g_{rov}^{PQR}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Detailed rovibrational line contour function for a band with P-, Q-, and R-Branches, in Hz^{-1} or Hb^{-1} .

$g_{vnc}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Contour function of vibronic bands in vibronic bandsystem, in Hz^{-1} or Hb^{-1} .

$g_{rvc}(\nu,\nu_{mn},\Delta\nu_{mn})$ = Detailed rovibronic line contour function in vibronic bandsystem, in Hz^{-1} or Hb^{-1} .

g_α , $g_{\alpha\beta}$ = Third-order anharmonic coefficients (see Eqs. (C.4) and (C.5)).

gam(p,x) = Normalized incomplete gamma function of order p and argument x ; $\mathrm{gam}(p,x) = \left[\int_{x=0}^{x} x^{p-1}(\exp -x)\,dx\right] \cdot \left[\int_{x=0}^{x} x^{p-1}(\exp -x)\,dx\right]^{-1}$

G = Special constant used in the calculations of vibrational parameters of an octahedral molecule, defined by Eq. (B.209).

G^{elc}_{mn} = Distribution function of sublevels in electronic transitions m → n , defined by Eq. (1.24).

G^{vib}_{mn} = Distribution function of sublevels in vibrational transitions m → n , defined by Eq. (1.26).

G_{mn} = Distribution function of sublevels in general transition m → n .

$G(\nu_\alpha, \nu_\beta, \ldots)$ = Total internal vibrational energy (see Eq. (C.6)) of a polyatomic molecule with normal vibrations α , β , ... , in ergs, eV, or Hb .

G_o = Zero-point of internal vibrational energy, in ergs, eV, or Hb (see Eq. (C.6)).

h = Planck's constant = 6.6252×10^{-27} erg · Hz^{-1} .

$\hbar = h/2\pi$ = (Planck's constant)/2π = 1.0544×10^{-27} erg · Hz^{-1} .

$h_v^{PQR}(J,\nu_{mn},\Delta\nu_{mn})$ = Discrete (J) shape function for the detailed lines in a rovibrational band of a linear or spherical-top molecule, defined by Eq. (4.181) or Eq. (4.246).

$h_v^{PQR}(J,K,\nu_{mn},\Delta\nu_{mn})$ = Discrete (J,K) shape function for the detailed lines in a rovibrational band of a symmetric-top molecule, defined by Eq. (4.223).

$h_v^{PQR}(J,W,\nu_{mn},\Delta\nu_{mn})$ = Discrete (J,W) shape function for the detailed lines in a rovibrational band of an asymmetric-top molecule, defined by Eq. (4.280a).

$\tilde{h}_v^{PR}, \tilde{h}_v^{PQR}$ = Modified vibrational band shape functions defined in Table 5-3.

$\tilde{h}_e$ = Modified vibronic bandsystem shape function defined in Table 5-3.

$H_\varphi = H_\varphi(\nu)$ = Omnidirectional energy flux or intensity, in Watts · cm^{-2} or erg · cm^{-2} · sec^{-1} .

$H(x)$ = Heaviside unit step function of parameter x ; $H(x) = 0$ for $x < 0$, and $H(x) = 1$ for $x \geq 0$.

$H_v(\xi)$ = Hermite polynomial function of ξ given by Eq. (A.5).

i = Used as a subscript indicates a general electronic excited level ($i = 1,2,3,\ldots$).

$i,(i')$ = Used as a sub-subscript indicates a state (or a reference state i') of a particular internal energy level ($i = 1,2,\ldots$).

i = Used as a subscript indicates a molecular or atomic species ($i = 1,2,\ldots$).

I, I_X = Nuclear spin quantum number of an atom X.

$I, I_\varphi = I_\varphi(\nu)$ = Unidirectional intensity of stream or beam of photons, in Watts $\cdot$ cm^{-2} . Intensity I_φ is related to stream Γ_φ by $I_\varphi = (h\nu)\,\Gamma_\varphi$.

$I(x)$ = Photon intensity at position x, Watts $\cdot$ cm^{-2} .

I_e = Average rotational moment of inertia of a diatomic molecule, in gm $\cdot$ cm^2 = erg $\cdot$ sec^2 .

I_A, I_B, I_C = Rotational moment of inertia about the principal axes ($\vec{e}_a, \vec{e}_b, \vec{e}_c$) of a polyatomic molecule, in gm $\cdot$ cm^2 = erg $\cdot$ sec^2 .

I_x, I_y, I_z = Rotational moments of inertia of a polyatomic molecule about three cartesian coordinates x, y, and z, in gm $\cdot$ cm^2 = erg $\cdot$ sec^2.

$I(a,\xi)$ = Function used in combined doppler and collisional broadening equations defined by Eq. (4.61).

I_s = Laser internal saturation intensity, Watts/cm^2 .

I_L, I_{out} = Laser output intensity, Watts/cm^2 .

j = Used as a subscript indicates a molecular or atomic species ($j = 1,2,\ldots$).

J = Rotational level quantum number of a molecule, or total electronic angular momentum quantum number of an atom.

J' = Rotational quantum number of first molecular state (′).

J'' = Rotational quantum number of second molecular state (″).

J_m = Rotational molecular quantum number (or total electronic angular momentum quantum number of an atom) of upper state m .

J_n = Rotational molecular quantum number (or total electronic angular momentum number of an atom) of lower state n .

J_k = Rotational molecular quantum number (or total electronic angular momentum quantum number of an atom) of state k .

$J_n(J_m)$ = Functional dependence of quantum number J_n of state n on quantum number J_m of state m .

ΔJ = $J_m - J_n$ = Change in rotational molecular quantum number or change in electronic total angular momentum quantum number of an atom after transition $m \longleftrightarrow n$.

$\vec{J}, (\vec{J}_k)$ = Total electronic angular moment quantum vector of an atom or rotational quantum vector of a molecule (in state k).

k = Used as a subscript indicates a general internal molecular excited level.

$k, (k')$ = Used as a sub-subscript indicates a state (or reference state k') of an internal energy level.

k = General designation of some molecular (atomic) internal energy state (used as subscript usually).

k = When associated with temperature T in kT this parameter is Boltzmann's constant = 1.3804×10^{-16} erg $\cdot$ $(^{\circ}K)^{-1}$.

k_n = Special quantum number parameter used in Eq. (3.19a), defined by Eqs. (3.20b) and (3.20c).

k' = Special factor for anharmonic vibrational transitions defined by Eq. (3.79).

k_o = Force constant of electronic harmonic oscillator model, dyne/cm.

$k_{\alpha s}$ = Force constant for component vibration s $(s = 1,2,\ldots)$ of normal vibration α $(\alpha = 1,2,\ldots)$ of a polyatomic molecule in dynes/cm. Thus $k_{\alpha s} = k_{11}, k_{12}, \ldots; k_{21}, k_{22}, \ldots; k_{31}, k_{32}, \ldots;$ etc.

k_{ij} = Force constant between partners i and j of a vibrating bond, in dynes/cm.

k_{α}, k_{β} = Effective overall force constant for normal vibration α , β , in dynes/cm.

k_y = Special constant defined by Eq. (5.125).

K = Second rotational quantum number of a symmetric-top molecule; $K = J , J - 1 , \ldots , 0, \ldots , -J+1 , -J$.

K_m, K_n, K_k = Second rotational quantum number of upper state m, lower state n, and general state k of a symmetric-top molecule.

$\Delta K = |K_m - K_n|$ = Change in second rotational quantum number of symmetric-top molecule for transition $m \leftrightarrow n$.

K^{o}_{nm} = Total absorption or excitation rate for molecular transitions from level n to m , $\sec^{-1}$.

K_+ , K_- = Supplementary rotational quantum numbers (dependent on W) for an asymmetric-top molecule.

$K_{X_i Y_j}$ = General miscroscopic process rate constant defined by Eq. (5.29), $\sec^{-1}$.

ℓ_m, ℓ_n, ℓ_k = Orbital angular momentum quantum number of an electron in an atom at upper electronic energy level m, and lower electronic level n, or general eletronic level k, respectively.

ℓ = Orbital angular momentum quantum number of an electron in an atom.

ℓ = Special quantum number needed to treat Coriolis effect of doubly-degenerate bending vibrations on rotational transitions in linear molecules, defined by Eq. (3.117).

$\vec{\ell}_{k_i}$ = Orbital momentum quantum vector of an electron i of an atom in excited state k .

ℓ_{XY}, ℓ_{YZ} = Interatomic spacing in a molecule between atoms X and Y , and Y and Z respectively, in cm or Å .

ℓ_{β_i} = Discrete set ($i = 1,2,3,\ldots$) of special quantum numbers needed in the treatment of the Coriolis effect of degenerate normal vibrations β on the rotational levels of a symmetric-top or spherical-top molecule (see Eq. (3.141)).

$\ell n(x)$ = Natural logarithm function of quantity x .

L_m, L_n, L_k = Total orbital electronic angular momentum quantum number of an atom in upper excited level m , lower excited level n , or general excited level k, respectively.

$\vec{L}_m, \vec{L}_n, \vec{L}_k$ = Total orbital electronic angular momentum quantum vector of an atom in upper excited level m , lower excited level n , or general excited level k , respectively.

$\Delta L = L_m - L_n$ = Change in total orbital electronic angular momentum quantum number after a transition $m \leftrightarrow n$.

m = General designation for upper molecular (atomic) internal energy state (used as subscript).

m_i = Component state i of upper molecular level m (subscript).

$m_{i'}$ = Special reference component state i' of upper molecular level m (used as subscript).

m_e = Mass of an electron, in amu or gm .

M = General symbol for mass of a molecule or atom, gm or amu .

$\bar{M}_{AB}$ = Reduced mass of atoms or groups of atoms A and B in a molecule, gm or amu ; $\bar{M}_{AB} = M_A M_B/(M_A+M_B)$.

M_A, M_B = Mass of atom A, atom B respectively, gm or amu .

M_1, M_2 = Mass of molecules 1 and 2 respectively, gm or amu .

M_{1-2} = Reduced mass for colliding molecules 1 and 2 with masses M_1 and M_2 , gm or amu ; $M_{12} = M_1 M_2/(M_1+M_2)$.

M_α = Effective mass of normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule, in gm or amu .

M_{mn} = Effective mass of composite vibration of a polyatomic molecule for transition $m \longleftrightarrow n$, in gm or amu .

$M_{\alpha s}$ = Effective mass of component s ($s = 1,2,3,\ldots$) of normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule, in gm or amu .

M.D. = Used as subscript, meaning Magnetic Dipole.

M_X, M_Y, M_Z = Mass of atom X, atom Y, atom Z respectively, gm or amu.

n = Molecular gas density in units of molecules/cm^3 .

n = General designation of lower molecular (atomic) internal energy state (used as subscript).

n = Electronic principal quantum number of atom or molecule.

n_m, n_n, n_k = Electronic principal quantum number of upper state m , lower state n , or general state k of an atom or molecule.

n_k = Component state k of lower molecular level n (used as subscript).

$n_{k'}$ = Special reference component state k' of lower molecular level n (used as subscript).

n_i = Density of ions used in stark-broadening calculations, ions $\cdot$ cm^{-3} .

n_i = Density of molecules i , molecules $\cdot$ cm^{-3} .

$n_\varphi(\nu)$ = Density of photons of frequency ν , photons $\cdot$ cm^{-3} .

n_v = Principal quantum number of a valence electron of an atom.

n_e = Electron number density, electrons $\cdot$ cm^{-3} .

n_U, n_L = Number density of molecules in upper (U) and lower (L) lasable excited state, molecules $\cdot$ cm^{-3} .

$N_{m_{tot}}$ = Total number of molecules in upper excited state m .

N_m = Number of molecules in an upper excited state m .

$N(v_m)$ = Number of molecules in excited state m , possessing vibrational quantum number v_m .

$N_{tot}=N_o$ = Total number of molecules.

N^* = Number of excited molecules.

N_v = Number of molecules in some vibrational excited state.

$N_{v,J}$ = Number of molecules in some vibrational and rotational excited state.

$N_{(v_m, J_m)}$ = Number of molecules possessing excited vibrational level v_m and rotational excited level J_m of upper excited combined state m .

N_{Λ_m} = Number of molecules in excited electronic state Λ_m .

$N(\Lambda_m, v_m, J_m)$ = Number of molecules possessing excited electronic levels Λ_m , vibrational level v_m , and rotational level J_m of upper excited combined state m .

N_φ = Number of photons in a certain volume of space.

o = Used as a subscript on $g(\nu, \nu_{mn}, \Delta\nu_{mn})$ functions means o = elc (= electronic), o = vib (= vibrational), o = rot (= rotational), o = vbn (= vibronic), o = rov (= rovibrational), o = rvc (= rovibronc) .

o = Used as a subscript means some reference value or constant value.

p = Gas pressure, in units of atm or Torr .

p, p_d = Special parameter used in dipole charge calculations defined by Eqs. (B.46) and (B.47).

$p_{mn}(\nu)$ = Probability of emitted photon having a frequency ν (ν is in the vicinity of ν_{mn}) for a molecular transition between levels m and n .

p_m, p_n, p_k = Special quantum numbers used in Eq. (3.19a), defined by (3.19b).

P_P, P_R, P_Q = Probability that a molecule at a particular excited rotational level makes a transition such that the emitted or absorbed photon appears in the P-Branch, R-Branch, or Q-Branch of a band.

$p(r)\,dr = p(\beta)\,d\beta$ = Probability of finding an ion within a radius r from a molecule causing a dimensionless electric field $\beta = E/E_o$ at the molecule (E, E_o are in Volts/m), used in the calculation of stark-broadening (sec. 4.6).

P = Used as subscript or superscript refers to the P-Branch of a vibrational band.

P = Total rotational angular momentum of a molecule, in units of erg · sec .

P_x, P_y, P_z = Rotational angular momentum of a molecule along cartesian coordinates x, y, and z, in units of erg · sec .

${}^{g}P(J,W) = {}^{g}P(J;K_-, K_+)$ = P-Branch connection factor function (dependent on rotational quantum numbers J and W) for asymmetric-top rotor given in Refs. 16 and 29 (Appendix IV).

q = $\cos\theta$

q_{ℓ} = Energy shift in the rotational energy levels due to the Coriolis effect of the doubly-degenerate bending vibration of a linear polyatomic molecule on the molecule's rotations, in units of Hb (cm^{-1}).

q_{mn}, q_{nm}, q_{ij} = Special quantum numbers used in Eq. (3.19a), defined by Eq. (3.19c).

Q = Used as subscript or superscript refers to the Q-Branch of a vibrational band.

${}^{g}Q(J,W) = {}^{g}Q(J;K_{+},K_{-})$ = Q-Branch connection factor function (dependent on rotational quantum numbers J and W) of an asymmetric-top molecule given in Ref. 16 (Appendix IV) and Ref. 19.

r = Used as subscript, meaning: rotational.

$\vec{r}$ = General quantum mechanical position vector operator, cm .

$\vec{r}_{elc}$ = Electronic quantum mechanical position vector operator, cm .

$\vec{r}_{vib}$ = Vibrational quantum mechanical position vector operator, cm .

$\vec{r}_{rot}$ = Rotational quantum mechanical position vector operator, cm .

rot = Used as subscript or superscript, meaning: rotational.

r = Distance from the center of an atom or molecule, in cm or Å .

$\vec{r}\,\vec{r}$ = Dyadic quantum mechanical vector operator used in electric quadrupole transition calculations, cm^2 .

$|\vec{r}_{mn}|^2$ = Squared absolute value of quantum-mechanical position vector matrix element of molecular transition m→n, cm^2 .

$|\vec{r}_{nm}|^2$ = Squared absolute value of quantum-mechanical position vector matrix element of molecular transition n→m, cm^2 .

r_o = Special parameter defined by Eq. (4.66) used in the calculation of stark-broadening, cm or Å .

r_e = Average equilibrium separation between two atoms of a molecule in the ground electronic state, in cm or Å .

$r_{e_i}, r_{e_m}, r_{e_n}$ = Average equilibrium separation between two atoms of a molecule in electronic state i, upper state m, or lower state n, in cm or Å .

$r_{\alpha_m}, r_{\alpha_n}$ = Equilibrium separation between two atoms or groups of atoms for normal vibration α of a molecule in electronic state m, n, in cm or Å .

$\Delta r_{\alpha_{mn}}$ = $r_{\alpha_m} - r_{\alpha_n}$ = Difference between equilibrium separations in electronic states m and n, in cm or Å .

$R^2_{mn} = R^2_{nm}$ = General designation of the squared reference matrix element for transitions between states m and n of a molecule or atom, cm^2 .

$R^2_{\substack{mn\\elc}}, R^2_{\substack{mn\\vib}}, R^2_{\substack{mn\\rot}}$ = Squared reference matrix element for respectively electronic, vibrational, and rotational transitions between states m and n of a molecule or atom, defined by Eqs. (1.9), (1.14), and (1.17), cm^2 .

$(R^2_{mn})_o$ = Squared reference matrix element for general transition (o = elc, or o = vib, or o = rot) between states m and n of a molecule or atom, cm^2 .

Ry = Rydberg constant = Ionization energy of atomic hydrogen = 13.605 eV .

${}^gR(J,W) = {}^gR(J;K_+,K_-)$ = R-Branch connection factor function (dependent on rotational quantum numbers J and W) of an asymmetric-top molecule given in Ref. 16 (Appendix IV) and 29.

R_1, R_2 = Deexcitation and excitation rates due to electron pumping of lasable levels, defined by Eqs. (5.71) and (5.72) for the CO_2 laser.

s = Used as subscript indicates component s (s = 1,2,3,...) of a normal vibration.

s = Inter-atomic separation of two atoms or groups of atoms of a molecule, in units of cm or Å .

$\vec{s}_{k_i}$ = Spin quantum vector of an electron i of an atom in excited state k .

s_m = Overall parity factor defined by Eq. (4.119).

s_I = Parity of nuclear-spin wave function given by Eq. (4.120) or (4.125).

s_e = Parity of electronic wave function (usually $s_e = +1$).

s_v = Parity of overall vibrational wave-function (see Eq. (4.121)).

s_{v_β} = Parity of vibrational wave-function of the normal vibration β .

$\sinh(x)$ = Hyperbolic sine function of x .

$\sup(x,y)$ = Function of two parameters x and y; $\sup(x,y) = x$, if $x > y$; $\sup(x,y) = y$, if $y > x$; $\sup(x,y) = x = y$, if $x = y$.

$S_{mn} = S_{nm}$ = Transition strength of $m \longleftrightarrow n$ transitions, in units of cm^2 .

$S_{m_i n_k} = S_{n_k m_i}$ = Component transition strength for transitions between states i and k of levels m and n, in units of cm^2 .

S_m, S_n, S_k = Total spin quantum number of the electrons of an atom in upper excited state m, lower excited state n, or general excited state k .

$\vec{S}_k$ = Total spin quantum vector of the electrons of an atom in excited state k .

ΔS = $S_m - S_n$ = Change in total spin quantum number after a transition $m \longleftrightarrow n$.

$\mathcal{S}'_{mn} = \mathcal{S}'_{nm}$ = $a_o^{-2} S_{mn} = a_o^{-2} S_{nm}$ = Transition strength (for electric dipole transitions) for transitions $m \longleftrightarrow n$ in units of a_o^2 (Bohr radius squared).

$\mathcal{S}_{mn} = \mathcal{S}_{nm}$ = $e^2 S_{mn} = e^2 S_{nm}$ = Transition strength of $m \leftrightarrow n$ transitions, in units of erg - cm^3 = esu - cm^2 .

t = Time, sec.

T = Gas temperature, in units of °K .

T_r = Photon transmission.

T_{r_a} = Photon transmission due to photon absorption.

T_{r_s} = Photon transmission due to photon scattering.

$u^{PR}(J,W)$ = Special factor for the P- and R-Branches of a band of an asymmetric-top molecule defined by Eq. (4.268a) or (4.275).

$u^{Q}(J,W)$ = Special factor for the Q-Branch of a band of an asymmetric-top molecule defined by Eq. (4.268b) or (4.276).

U_I = Molecular vibrational potential energy, in ergs, eV, or Mb.

U = Laser gas flow velocity, cm/sec.

U = Special laser parameter defined by Eq. (5.139).

v = Used as subscript, meaning: vibrational.

v', v'' = Vibrational quantum number of first (′) and second (″) molecular state, respectively.

v_b = Quantum level of bending vibration ν_b .

v_m, v_n, v_k = Vibrational quantum number of upper molecular state m, lower state n, or general state k, respectively.

vib = Used as subscript or superscript, meaning: vibration.

$v_n(v_m)$ = Functional dependence of vibrational quantum number v_n of lower state n on vibrational quantum number v_m of upper state m .

v_α = Vibrational quantum number of the normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule.

$v_{\alpha_m}, v_{\alpha_n}, v_{\alpha_k}$; $(v_{\beta_m}, v_{\beta_n}, v_{\beta_k})$ = Vibrational quantum number of the normal vibration α (normal vibration β) of a polyatomic molecule in upper excited state m, lower excited state n, or general excited state k.

$\Delta v_\alpha = v_{\alpha_m} - v_{\alpha_n}$ = Change in vibrational quantum number for normal vibration α in transition $m \longleftrightarrow n$.

v_x, v_y, v_z = Kinetic (thermal) velocity of a molecule along cartesian directions x, y, and z, in cm/sec.

v_n^-, v_n^+ $(v_{\alpha_n}^-, v_{\alpha_n}^+)$ = Two possible vibrational levels (of normal vibration α) in lower electronic state n, occurring in electronic transitions $m \leftrightarrow n$, defined by Eqs. (4.308) and (4.309).

$\bar{v}_{12}, \bar{v}_{ij}$ = Average relative kinetic velocity between molecules 1 and 2, or i and j, cm/sec.

$\bar{v}_e$ = Average electron kinetic velocity, cm/sec.

V = Vibrational potential, ergs or eV .

$V, (V_1)$ = General internal molecular excitation energy (of molecule 1), ergs or eV .

w_m, w_n, w_k = Statistical weight of upper level m, lower level n, or general level k, respectively.

$w_{e_m}, w_{e_n}, w_{e_k}$ = Statistical weight of the electronic level in upper state m, lower state n, and general state k, respectively.

$w_{v_m}, w_{v_n}, w_{v_k}$ = Statistical weight of the vibrational level in upper state m, lower state n, and general state k, respectively.

$w_{r_m}, w_{r_n}, w_{r_k}$ = Statistical weight of rotational level in upper state m, lower state n, and general state k, respectively.

$W = W(J)$ = Non-integer second quantum number to describe rotational levels and transitions of an asymmetric-top molecule, defined by Eq. (3.193).

$W(E)$ = Probability per unit energy range of finding an energy state at energy E (see Eq. (4.30)).

x = General position coordinate or distance of travel along the x-direction of a cartesian frame, in cm or Å .

x_{mn} = Matrix element of quantum-mechanical x-direction position operator for molecular transition $m \longleftrightarrow n$, cm .

x_{mn} = Anharmonic constant for molecular vibrational transition $m \longleftrightarrow n$.

x_e = Equilibrium anharmonic constant for diatomic molecular vibrations in the ground electronic state.

x_α, x_β = Anharmonic vibrational constant for the normal vibration α , β of a polyatomic molecule ($\alpha = 1,2,3,\ldots$) in the ground electronic state.

$x_{e_i}, x_{e_m}, x_{e_n}$ = Equilibrium anharmonic constant for diatomic molecular vibrations in electronic state i, upper state m, and lower state n.

$x_{\alpha_i}, x_{\alpha_m}, x_{\alpha_n}$ = Equilibrium anharmonic constant for the normal vibration α of a polyatomic molecule in electronic state i, upper state m, and lower state n.

x_A, x_B, x_X = Pauling's electronegativity parameter for atom A, B, or X.

X = General symbol for the first atom in a molecule.

$X_\alpha, (X_k)$ = General designation of the symmetry species of a normal vibration α (in state k) of a polyatomic molecule; $X_\alpha = A$, $X_\alpha = B$, $X_\alpha = E$, $X_\alpha = F$; $X_\alpha = \Sigma$, $X_\alpha = \Pi$, $X_\alpha = \Delta$, $X_\alpha = \Phi$.

y_{mn} = Matrix element of quantum-mechanical y-direction position operator for molecular transition $m \leftrightarrow n$, cm.

y = Special parameter defined by Eq. (4.55).

y = Special parameter used in vibronic transition calculations defined by (4.317).

y = $s - r_e$ (or $s - r_\alpha$) = Deviation from equilibrium separation in molecular vibrations, cm or Å .

y_X = Mole fraction of molecules X in a gas mixture.

Y = General symbol of a second atom in a molecule.

z = Special quantum number parameter used in Eq. (3.19a), defined by (3.19e).

z_{mn} = Matrix element of quantum-mechanical z-direction position operator for molecular transition $m \leftrightarrow n$, cm.

z_{mn} = Equivalent charge number of the first-order-derivative or -moment of the molecular dipole moment for $m \leftrightarrow n$ transitions.

$z = z_1$ = Equivalent charge number of the first-order-derivative or -moment of the molecular dipole moment.

z_e = Effective dipole charge due to electron cloud only.

z_o = Equivalent charge number of the molecular permanent dipole moment.

$z = \mu/(se)$ = Equivalent charge of the dipole moment of a molecule.

$z_N = Z_A^{eff} - Z_B^{eff}$ = Nuclear effective dipole charge.

$z_\alpha = (z_1)_\alpha$ = Equivalent charge number of the first-order-derivative or -moment of the dipole moment for normal vibration α ($\alpha = 1,2,3,4,\ldots$) of a polyatomic molecule.

$(z_o)_\alpha$ = Equivalent charge number of the permanent dipole moment for normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule.

$z_{\alpha s}$ = Equivalent charge number of the first-order-derivative of the dipole moment for the s component ($s = 1,2,3,\ldots$) of the normal vibration α ($\alpha = 1,2,3,\ldots$) of a polyatomic molecule.

$z_{XY} = (z_1)_{XY}$ = Equivalent charge number for the first-order-derivative or -moment of the dipole moment of diatomic molecule or radical XY consisting of atoms X and Y.

z_i = Degree of ionization of ions (usually $z_i = 1$). This parameter is used in stark-broadening calculations (see Eq. (4.65)).

zip(p) = Special function used in dipole charge calculations defined by Eq. (B.50).

Z = General symbol for a third atom in a molecule.

Z_Λ = Electronic "partition function" or "normalizing constant" for a discrete distribution of allowed electronic energy levels.

Z_v = Vibrational "partition function" or "normalizing constant" for a discrete distribution of allowed vibrational energy levels.

Z_r = Rotational "partition function" or "normalizing constant" for a discrete distribution of allowed rotational energy levels.

Z'_v = Vibrational "partition function" or "normalizing constant" for an equivalently smeared vibrational energy level distribution.

Z'_r = Rotational "partition function" or "normalizing constant" for an equivalently smeared rotational energy level distribution.

Z'_{v_m}, Z'_{v_n} = Vibrational partition function for a molecule in excited electronic state m, n, for the equivalently smeared vibrational levels model.

$Z'_{\alpha_m}, Z'_{\alpha_n}$ = Partial vibrational partition function for normal vibration α of a molecule in excited electronic state m, n, for the equivalently smeared vibrational levels model.

Z_X, Z_A, Z_B = Charge number of nucleus of atom X, A, or B.

$Z_{eff}, (Z_A^{eff}, Z_B^{eff})$ = Effective charge number of an atom (A, B) whose nuclear charge is partially shielded by inner-shell electrons.

$Z_e = Z_A^{eff} + Z_B^{eff}$ = Combined effective (shielded) nuclear charge of atoms A and B.

$Z_d = Z_A^{eff} - Z_B^{eff}$ = Difference of effective (shielded) nuclear charges of atoms A and B.

α = Special parameter defined by Eq. (4.54) used in combined collision and doppler line-broadening calculations.

α = Used as a subscript to designate the assigned normal vibration number of a polyatomic molecule with several normal vibrations ($\alpha = 1,2,3,\ldots$).

α_e = Vibration-rotation interaction constant (change in average rotational moment of inertia I_e due to vibrations), in units of Hb (cm^{-1}).

α_β = Vibration-rotation interaction constant due to normal vibration β ($\beta = 1,2,3,\ldots$) of a polyatomic molecule (change in average rotational moment of inertia I_e due to normal vibration β), in units of Hb (cm^{-1}).

$\alpha_\beta^A, \alpha_\beta^B, \alpha_\beta^C$ = Vibration-rotation interaction constants of three rotations A, B, and C along three rotational axes $\vec{e}_a$, $\vec{e}_b$, $\vec{e}_c$ due to normal vibration β ($\beta = 1,2,3,\ldots$) of a polyatomic molecule, in units of Hb (cm^{-1}).

${}^1\alpha, {}^2\alpha, {}^3\alpha$ = Used as subscript meaning a normal vibration α of a polyatomic molecule with single (1), double (2), or triple (3) degeneracy.

α_{abs} = Macroscopic absorption (attenuation) coefficient, cm^{-1} .

α_G = Laser gain coefficient, cm^{-1} .

α_o = Zero-power laser gain coefficient, cm^{-1} .

$\beta_i, \beta_m, \beta_n$ = Parameter of vibrational Morse potential (see Eq. (4.304)) for vibrations in electronic state i, upper electronic state m, and lower electronic state n, in Hb or Hz.

$\gamma_{\alpha s}$ = Relative phase sign of component vibration s $(s = 1,2,3,\ldots)$ of normal vibration α $(\alpha = 1,2,3,\ldots)$.

γ_m, γ_n = Ratio of Morse-potential parameters defined by Eq. (4.312); $\gamma_m = \beta_m/\beta_n$; $\gamma_n = \beta_n/\beta_m$.

γ_m, γ_n = Uncertainty due to natural fluctuations (broadening) in frequency ν_m, ν_n of energy levels m, n respectively, Hb or Hz.

γ_{mn} = Uncertainty in transition frequency ν_{mn} due to natural broadening, Hb or Hz.

$\gamma_{\alpha\beta}$ = Special interaction coefficients occurring in molecular vibrational potentials (see Eq. (C-6)).

$\Gamma(x)$ = Gamma function (complete) of parameter x.

$\Gamma_\varphi = \Gamma_\varphi(\nu)$ = Unidirectional stream of photons of frequency ν, photons · cm^{-2} · sec^{-1} .

$\Gamma_L = \Gamma_L(\nu_L)$ = Stream or beam of laser photons of frequency ν_L, photons · cm^{-2} · sec^{-1} .

Γ_{tot} = Total photon stream, photons · cm^{-2} · sec^{-1} .

δ = Fractional loss of internal laser beam photons producing useful lasing output per roundtrip pass in laser cavity.

$\delta(x)$ = Delta function for parameter x ; $\delta(x) = 1$ for $x = o$, $\delta(x) = o$, for $x \neq o$; $\delta(x) = dH(x)/dx$.

δ_α = Parameter used in m ⟷ n vibrational transition matrix element calculations (see Eqs. (3.84) and (3.89)) for normal vibration α ; $\delta_\alpha = 1$ if $v_{\alpha_m} > v_{\alpha_n}$; $\delta_\alpha = -1$ if $v_{\alpha_m} < v_{\alpha_n}$.

$\delta_q = \left(\overline{\frac{dy}{dq}}\right)$ = Special parameter used in dipole charge calculations, defined by Eq. (B.76).

Δ_h = Hot-band frequency shift of vibrational bands, defined by Eq. (4.249) for spherical-top molecules.

$\Delta'(A\text{-}B)$ = Pauling electronegativity energy, defined by Eq. (B.[illegible]), in units of kcal/mole.

ϵ = Kinetic energy of a quantum (photon) or particle (atom, molecule) ; $\epsilon = h\nu$ ergs or eV for a photon.

ζ_β = Coriolis constant giving the magnitude of the effect of a degenerate normal vibration β on the rotational energy levels of a polyatomic molecule which behaves as a symmetric-top or spherical-top rotor.

ζ, ζ_m = Coriolis constant giving the total magnitude of the effect of all degenerate vibrations of a spherical-top molecule in state m on the rotational line frequencies of a rovibrational band.

η = Special factor used in the simple exponential for the Thomas-Fermi self-screening factor.

$\eta = \eta(\nu)$ = Refractive index of gas (dimensionless) for photons of frequency ν .

θ = Angle between molecular axis and position vector $\vec{r}$ of some point in the molecular electric field.

θ_I = Special factor defined by Eq. (4.133) used in the calculation of nuclear-statistics weighting factors for rotational transitions.

κ = Special constant used in asymmetric-top rotor equations, defined by Eq. (3.207).

λ_{abs_i} = Mean free path for absorption of a photon by molecules i, cm.

$\lambda_{mn} = c/\nu_{mn}$ = Transition wavelength between molecular (or atomic) levels m and n, in cm or Å .

λ = c/ν = Photon wavelength, in cm or Å .

Λ = Electronic orbital quantum number of molecule; or general designation of molecular electronic level specified by three quantum numbers (n, Λ, Ω).

Λ' = Electronic orbital quantum number of first molecular state ($'$) ; or general designation of first molecular electronic state specified by three quantum numbers (n', Λ', Ω').

Λ'' = Electronic orbital quantum number of second molecular state ($''$) ; or general designation of second molecular electronic state specified by three quantum numbers $(n'', \Lambda'', \Omega'')$.

Λ_m = Electronic orbital quantum number of upper state m of molecule; or general designation of molecular electronic upper state n specified by three quantum numbers $(n_m, \Lambda_m, \Omega_m)$.

Λ_n = Electronic orbital quantum number of lower state n of molecule; or general designation of molecular electronic lower state n specified by three quantum numbers $(n_n, \Lambda_n, \Omega_n)$.

Λ_k = Electronic orbital quantum number of state k of molecule; or general designation of molecular electronic state k specified by three quantum numbers $(n_k, \Lambda_k, \Omega_k)$.

$\mu = \mu(s)$ = ezs = Dipole moment of a molecule, in units of $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{3/2}$ or debyes (= 10^{-18} $\mathrm{erg}^{1/2}$ $\mathrm{cm}^{3/2}$).

$\mu_o = \mu(r_e)$ = $ez_o r_e$ = Permanent dipole moment of a molecule, in units of $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{3/2}$ or debyes (= 10^{-18} $\mathrm{erg}^{1/2}$ $\mathrm{cm}^{3/2}$).

μ_1 = $(\partial\mu/\partial s)_{s=r_e} = ez_1$ = First-order-derivative or -moment of molecular dipole moment, in units of $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{1/2}$ or debyes (= 10^{-18} $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{3/2}$).

ν = Photon frequency, in units of Hz (= $\sec^{-1}$) or Hb (= cm^{-1}).

ν_m = E_m/h = Frequency of upper molecular energy level m, Hz or Hb.

ν_n = E_n/h = Frequency of lower molecular energy level n, Hz or Hb.

ν_e = Fundamental vibrational frequency of a diatomic molecule at average equilibrium separation, in Hz or Hb.

$\nu_{e_i}, \nu_{e_m}, \nu_{e_n}$ = Fundamental vibrational frequency of a diatomic molecule in electronic state i, upper state m, or lower state n, in Hb or Hz.

$\nu_\alpha, \nu_\beta, \ldots\ldots$ = Fundamental vibrational frequency of normal vibration ν, β, ... of a polyatomic molecule in the ground electronic state, in Hb or Hz.

$\nu_{\alpha_i}, \nu_{\alpha_m}, \nu_{\alpha_n}$ = Fundamental vibrational frequency of normal vibration α of a polyatomic molecule in electronic state i, upper state m, or lower state n, in Hb or Hz.

ν_{o_i} = Effective vibrational zero-point frequency (Eq. (4.298)), in Hz or Hb.

ν_o = Band center frequency, in Hz or Hb.

ν_o = Fundamental frequency of equivalent electron harmonic oscillator, Hz or Hb.

ν_L = Frequency of laser photons, in Hz or Hb.

ν_{mn} = E_{mn}/h = Transition frequency between molecular (or atomic) levels m and n, Hz or Hb.

$(\nu_{mn})_e$ = Frequency of an electronic transition $m \longleftrightarrow n$, in units of Hz or Hb.

$(\nu_{mn})_v$ = Frequency of a vibrational transition $m \leftrightarrow n$, in units of Hb or Hz.

$(\nu_{mn})_r$ = Frequency of a rotational transition $m \leftrightarrow n$, in units of Hz or Hb.

ν_{v_i} = Frequency of vibrational level in electronic state i, in Hz or Hb.

ν_{v_m} = E_{v_m}/h = Frequency of upper vibrational energy level m with vibrational quantum number v_m, Hz or Hb.

ν_{v_n} = E_{v_n}/h = Frequency of lower vibrational energy level n with vibrational quantum number v_n, Hz or Hb.

$\nu_{v_n}(v_m)$ = Functional dependence of frequency of lower vibrational level with vibrational quantum number v_n on upper level vibrational quantum number v_m, Hz or Hb.

$\Delta\nu_v$ = $\nu_{v_m} - \nu_{v_n}$ = Frequency difference between upper and lower vibrational levels m and n, Hz or Hb.

$\Delta\nu_v(v_m)$ = Functional dependence of frequency difference between vibrational levels m and n on upper level vibrational quantum number v_m, Hz or Hb.

ν_b = Fundamental frequency of the bending vibration in a linear polyatomic molecule (for a triatomic linear molecule $\nu_b = \nu_2$), Hz or Hb.

ν_{J_m}, ν_{J_n} = Frequency of rotational level J_m, J_n respectively, in excited molecular states m and n, in units of Hz or Hb.

ν_J = Discrete allowed rotational transition frequency for quantum number J in P- and R-Branches of a linear or spherical-top molecule, in Hz or Hb.

ν_{JK} = Discrete allowed rotational line frequency with quantum numbers J and K in the P- and R-Branches of a symmetric-top molecule, in Hz or Hb.

ν_{JW} = Discrete allowed rotational line frequency with quantum numbers J and W in the P- and R-Branches of an asymmetric-top molecule, in Hz or Hb.

ν_J^Q = Discrete allowed rotational transition frequency for quantum number J in Q-Branch of a linear of spherical-top molecule, in Hz or Hb.

ν_{JK}^Q = Discrete allowed rotational frequency for quantum numbers J and K in the Q-Branch of a symmetric-top molecule, in Hz or Hb.

ν_{JW}^Q = Discrete allowed rotational line frequency with quantum numbers J and W in the Q-Branch of an asymmetric-top molecule, in Hz or Hb.

$\nu_{B\zeta}$ = $\nu_B(1-\zeta_m)$ = Coriolis-modified rotational constant of spherical-top molecules, in Hz or Hb.

ν_A, ν_B, ν_C = Rotational constants for rotations about the three principal moment-of-inertia axes $\vec{e}_a$, $\vec{e}_b$, and $\vec{e}_c$ of a molecule, in Hz or Hb.

ν_B^Q = Q-Branch center shift defined by Eq. (4.92), in Hz or Hb.

ν_{BC} = $(\nu_B+\nu_C)/2$ = Main rotational constant for an asymmetric-top molecule, in Hz or Hb.

ν_{ABC} = $\nu_A - \nu_{BC}$ = Second rotational constant for an asymmetric-top molecule, in Hz or Hb.

ν_s = Band-center frequencies of vibrational bands in a vibronic bandsystem, in Hb or Hz.

$\nu_{d_i}, \nu_{d_m}, \nu_{d_n}$ = Dissociation frequency for molecular vibration in electronic state i, upper state m, and lower state n, in Hz or Hb.

$\nu^{-}_{v_n}, \nu^{+}_{v_n}$, $(\nu^{-}_{v\alpha_n}, \nu^{+}_{v\alpha_n})$ = Two possible vibrational frequency levels (for normal vibration α) in lower electronic state n occurring in electronic transitions m → n, defined by Eqs. (4.310) and (4.311), in Hb or Hz.

ν_p, ν_q = Frequency parameters used in vibronic transition calculations, defined by Eqs. (4.325) and (4.326), in Hz or Hb.

$\Delta\nu_J$ = Line spread of a rotational transition emission/absorption line with quantum number J, Hz or Hb.

$\Delta\nu_A, \Delta\nu_B, \Delta\nu_C$ = Difference between rotational constants for upper excited state m and lower excited state n, that is $\Delta\nu_A = \nu_{A_n} - \nu_{A_m}$, $\Delta\nu_B = \nu_{D_n} - \nu_{B_m}$; $\Delta\nu_C = \nu_{C_n} - \nu_{C_m}$, in Hz or Hb.

$\Delta\nu_{BC}$ = $\frac{1}{2}(\nu_{B_m} - \nu_{B_n} + \nu_{C_m} - \nu_{C_n})$ = Difference between combined rotational constants ν_B and ν_C in state m, and in state n, in Hz or Hb.

$\Delta\nu_o$ = Shift of the band center frequency of a symmetric-top molecule, defined by Eq. (4.186) or (4.188), in Hz or Hb.

$\Delta\nu_{A\zeta}$ = Coriolis-effect constant for rotational transition lines of symmetric-top molecules defined by Eq. (4.187) and Eq. (4.189), in Hz or Hb.

$\Delta\nu_{mn}$ = Spread of frequency about the center transition frequency ν_{mn} of the line-, band-, or bandsystem-broadened contour function in transitions m ⟷ n, Hz or Hb.

$\bar{\Delta}\nu_{mn}$ = Width at half-height of the line-, band-, or bandsystem-broadened contour function in transitions m ⟷ n, Hz or Hb.

$(\Delta\nu_{mn})_N, (\bar{\Delta}\nu_{mn})_N$ = Natural-broadened line spread and width-at-half-height respectively (Eqs. (4.36) and (4.37)), in Hz or Hb.

$(\Delta\nu_{mn})_D, (\bar{\Delta}\nu_{mn})_D$ = Doppler-broadened line spread and width-at-half-height respectively (Eqs. (4.42) and (4.44)), in Hz or Hb.

$(\Delta\nu_{mn})_C, (\bar{\Delta}\nu_{mn})_C$ = Collision-broadened line spread and width-at-half-height respectively (Eqs. (4.47) and (4.49)), in Hz or Hb.

$(\Delta\nu_{mn})_S$ = Stark-broadened line spread (Eq. (4.72)), in Hz or Hb.

$(\Delta\nu_{mn})_{N,C,D}$ = Combined collision-, Doppler-, natural-broadened line spread (Eq. (4.57)), in Hz or Hb.

$\Delta\nu_{mn}, \Delta\nu^{v}_{mn}$ = Vibrational band spread, in Hz or Hb.

$\Delta\nu_{mn}, \Delta\nu^{e}_{mn}$ = Electronic bandsystem spread, in Hz or Hb.

$\Delta\nu_{s}$ = Band-center spacing parameter used in vibronic transition calculations, defined by Eq. (4.345b), in Hb or Hz.

$\Delta\nu_{sp}$ = Frequency distribution parameter for vibrationally broadened electronic bandsystems, defined by Eq. (4.293), in Hz or Hb.

$\Delta\nu_{sp\alpha_m}$ = Frequency distribution parameter for normal vibration α used in vibronic transition calculations, defined by Eq. (4.349), in Hz or Hb.

$\Delta\nu^{+}_{sp}, \Delta\nu^{-}_{sp}$ = Frequency distribution parameters occurring in vibronic transition calculations, defined by Eqs. (4.329) and (4.330).

$\Delta\nu_{\alpha s}$ = Band-center spacing parameter for normal vibrations α used in vibronic transition calculations, defined by Eq. (4.368b), in Hb or Hz.

$\delta\nu_{J}$ = Frequency distribution factor for rotational lines in P- and R-Branches of a linear of spherical-top molecule, defined by Eq. (4.155d), Hz or Hb.

$\delta\nu'_J$ = Frequency spacing of the center frequencies of adjacent rotational lines in P- and R-Branches of a linear or spherical-top molecule, defined by Eq. (4.155c), Hz or Hb.

$\delta\nu^Q_J$ = Frequency distribution factor for rotational lines in Q-Branch of a linear or spherical-top molecule, defined by Eq. (4.180b).

$\delta\nu_K$ = Frequency distribution factor for rotational lines of a symmetric-top molecule, defined by Eq. (4.185b), Hz or Hb.

$\delta\nu'_K$ = Frequency spacing of the center frequencies of adjacent rotational lines in the P- and R-Branches of a symmetric-top molecule, defined by Eq. (4.185a), in Hz or Hb.

$\delta\nu_W$ = Frequency distribution factor for rotational lines in the P- and R-Branches of an asymmetric-top molecule, defined by Eq. (4.280b), in Hz or Hb.

$\delta\nu^Q_W$ = Frequency distribution factor for rotational lines in the Q-Branch of an asymmetric-top molecule, defined by Eq. (4.280c), in Hz or Hb.

$\delta\nu_s$ = Spacing between band-centers of a vibronic bandsystem defined by Eq. (4.345a), in Hb or Hz.

$\delta\nu_{\alpha s}$ = Spacing between band-centers with different v_α of normal vibration α in a vibronic bandsystem, defined by Eq. (4.368a), in Hb or Hz.

$\xi, (\xi_\alpha)$ = Special parameter defined by Eq. (A.6), (for normal vibration α).

ξ = Special parameter defined by Eq. (4.60) used in combined collision, doppler, and natural line-broadening calculations.

ξ = r/a = Non-dimensionalized distance from the center of a molecule or atom.

ξ_B = $\Delta\nu_B/\nu_B$ = Non-dimensional parameter defined by Eq. (4.170).

ξ_{BC} = $\Delta\nu_{BC}/\nu_{BC}$ = Non-dimensional parameter for asymmetric-top molecules defined by Eq. (4.269).

ξ_n, ξ_m = Ratio parameter used in vibronic transition calculations, defined by (4.327); $\xi_n = \nu_{e_n}/\nu_{e_m}$ (or $\nu_{\alpha_n}/\nu_{\alpha_m}$) ; $\xi_m = \nu_{e_m}/\nu_{e_n}$ (or $\nu_{\alpha_m}/\nu_{\alpha_n}$) .

π = Constant = 3.14159 .

ρ_n = Special parameter used in vibronic transition calculations, defined by Eq. (4.324).

ρ_e = Electron charge density in an atomic or molecular field, $\text{esu} \cdot \text{cm}^{-3}$.

σ = General designation for an interaction cross-section between two particles or quanta, cm^2 .

σ_{mn}, σ_{nm} = General designation of a photon emission ($mn = m \rightarrow n$) or absorption ($nm = n \rightarrow m$) cross-section, cm^2 .

$\sigma_{abs} = \sigma_{\substack{nm \\ abs}} = \sigma_{\substack{nm \\ abs}}(\nu)$ = Photon absorption cross-section per molecule (at photon frequency ν), cm^2 .

$\sigma_{s.e.} = \sigma_{\substack{mn \\ s.e.}} = \sigma_{\substack{mn \\ s.e.}}(\nu)$ = Photon-stimulated emission cross-section per molecule (at photon frequency ν), cm^2 .

$\sigma_{o.s.}$ = Oscillation-perturbing collision cross-section between dissimilar or like molecules causing a collision broadening of the photon emission or absorption resonant frequency , cm^2 .

σ_{1-2} = Collision cross-section for momentum (kinetic energy) transfer between two molecules (or particles) labeled 1 and 2 , cm^2 .

$\sigma_{T_1 V_2}$ = Collisional deexcitation cross-section by molecule 1 on excited molecule 2 , cm^2 .

$\sigma_{V_1 V_2}$ = Excitation energy transfer cross-section between molecules 1 and 2 , cm^2 .

Σ = Electronic spin quantum number of a molecule.

Σ_k = Electronic spin quantum number of electronic state k of a molecule.

$\vec{\Sigma}_k$ = Electronic spin quantum vector of electronic state k of a molecule.

τ_e = Electronic level mean life for emission (radiative decay time), sec.

τ_r = Rotational level mean life for emission (radiative decay time), sec.

τ_v = Vibrational level mean life for emission (radiative decay time), sec.

$\tau_{mn} = \tau_m(\nu)$ = Decay time constant for the spontaneous emission of a photon frequency ν causing a molecular transition from state m to n , sec.

τ^o_{mn} = Total decay time constant for the spontaneous emission of a photon (of any frequency) causing a molecular transition from state m to n , sec.

$d\tau$ = Elemental volume in the integration over the quantum-mechanical wave-function space of a molecule or atom, cm^3 (or volume units of phase space).

$d\tau_v, d\tau_J$ = Elemental volume in the integration over the quantum-mechanical vibrational (v) and rotational (J) wave-function space (or phase space) of a molecule, cm^3 (or volume units of phase space).

τ_1, τ_2 = Collisional deexcitation lifetimes of the lower and upper lasing levels, defined by (5.73) and (5.74) for the CO_2 laser, sec.

τ_{VT}, τ_{TV} = Excited-state lifetime of a molecule due to vibrational-translational (VT) energy exchange (collisional deexcitation) collisions, sec.

τ_{VE}, τ_{EV} = Excited-state lifetime of a molecule due to vibrational-electron-impact (VE) energy exchange collisions, sec.

$\tau_{V_1 V_2}, \tau_{V_2 V_1}$ = Excited-state lifetime of a molecule due to vibrational-vibrational (VV) energy exchange between molecules 1 and 2 , sec.

$\varphi(r)$ = Thomas-Fermi potential for an atom, in Volts/cm.

$\Phi(\xi)$ = Special Thomas-Fermi potential function for an atom.

$\Phi, \Phi^{\dagger}$ = Designation of quantum-mechanical wave function, conjugate wave-function (†) .

χ_1, χ_3 = Special parameters defined by Eqs. (B.97) and (B.98).

χ_{AB} = Parameter used in symmetric-top molecule calculations defined by Eq. (4.210).

χ_n = Special parameter used in vibronic transition calculations defined by Eq. (4.339).

$\Psi_{\Lambda_m}, \Psi_{v_m}, \Psi_{J_m}$ = Electronic (Λ), vibrational (v), and rotational (J) wavefunctions of internal molecular level Λ_m, v_m, of J_m respectively, of upper state m.

$\Psi^{\dagger}_{\Lambda_n}, \Psi^{\dagger}_{v_n}, \Psi^{\dagger}_{J_n}$ = Electronic (Λ), vibrational (v), and rotational (J) conjugate wavefunctions of internal molecular level Λ_n, v_n, or J_n respectively, of lower state n.

$\Psi_{\Lambda_{m_i}}, \Psi_{v_{m_i}}, \Psi_{J_{m_i}}$ = Electronic (Λ), vibrational (v), and rotational(J) wavefunctions of state i of level Λ_m, state i of level v_m, and state i of level J_m respectively, of combined upper state m.

$\Psi^{\dagger}_{\Lambda_{n_k}}, \Psi^{\dagger}_{v_{n_k}}, \Psi^{\dagger}_{J_{n_k}}$ = Electronic (Λ), vibrational (v), and rotational (J) conjugate wavefunctions of state k of level Λ_n, state k of level v_n, and state k of level J_n respectively, of combined lower state n.

$\Psi_{J_m}, \Psi_{J_n}; \Psi^{\dagger}_{J_m}, \Psi^{\dagger}_{J_n}$ = Rotational wavefunctions (conjugate wavefunction $\dagger$) for rotational levels J_m and J_n, respectively.

$\Psi_{v_{\alpha_m}}, \Psi_{v_{\alpha_n}}; \Psi^{\dagger}_{v_{\alpha_m}}, \Psi^{\dagger}_{v_{\alpha_n}}$ = Vibrational wavefunctions (conjugate wavefunctions) for vibrational levels v_{α_m} and v_{α_n} of normal vibration α ($\alpha = 1, 2, 3, \ldots$) .

$\Psi^{\dagger}_{e}, \Psi_{e}$ = Electronic wavefunction.

ω = Angular frequency = $\nu/2\pi$ = radians/sec.

ω_e = Symbol used by Herzberg in his molecular tables for the equilibrium fundamental vibrational frequency of a diatomic molecule in units of Hb (cm^{-1}) ; $\omega_e = \nu_e$ (Hb) = $c\nu_e$ (Hz).

ω = Symbol used by Herzberg for the photon frequency in units of Hb (cm^{-1}) ; $\omega = \nu$ (Hb) = $c\nu$ (Hz).

Ω = Total electronic angular momentum quantum number of molecule.

Ω_k = Total electronic angular momentum quantum number of electronic state k of molecule.

Ω_m = Total electronic angular momentum quantum number of upper electronic state m of molecule.

Ω_n = Total electronic angular momentum quantum number of lower electronic state n of molecule.

Ω_C = Special weighting factor used in mixed doppler and collisional broadening, defined by Eq. (5.126a).

Ω_D = Special weighting factor used in mixed doppler and collisional broadening, defined by Eq. (5.126b).

APPENDIX A

HARMONIC AND ANHARMONIC OSCILLATOR TRANSITIONS

The normalized eigenfunctions Ψ_v of the Schrodinger equation for the harmonic oscillator,

$$\frac{d^2\Psi}{dy^2} + \frac{8\pi^2\bar{M}}{h^2}\left(E - \frac{1}{2}ky^2\right)\Psi = 0 \quad , \qquad (A.1)$$

are (Ref. 2):

$$\Psi_v = N_v\left[\exp-\left(\frac{\alpha y^2}{2}\right)\right] H_v(\sqrt{\alpha}\,y) =$$

$$\Psi_v = \left[\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^v v!}\right]^{1/2}\left[\exp-\frac{\alpha y^2}{2}\right] H_v(\sqrt{\alpha}\,y) \quad , \qquad (A.2)$$

where the normalization factor N_v is:

$$N_v = \left[\left(\frac{\alpha}{\pi}\right)^{1/2}\frac{1}{2^v v!}\right]^{1/2} \qquad (A.3)$$

and where v are the vibrational quantum numbers v = 0 , 1 , 2 , 3 , ... The parameter k in (A.1) is the "force constant" (dyne/cm) and y is the displacement (cm) from equilibrium of the oscillator. E is the total energy. The parameter α is for a diatomic molecule given by:

$$\alpha = 4\pi^2\bar{M}\left(\frac{\nu_e}{h}\right) = \frac{2\pi}{h}\sqrt{\bar{M}k}\ , \quad \text{cm}^{-2}\ , \qquad (A.4)$$

and $H_v(\xi)$ are the Hermite polynomials, the first five of which are given by:

$$H_o(\xi) = 1 \qquad (A.5a)$$

$$H_1(\xi) = 2\xi \qquad (A.5b)$$

$$H_2(\xi) = 4\xi^2 - 2 \qquad (A.5c)$$

$$H_3(\xi) = 8\xi^3 - 12\xi \qquad (A.5d)$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \qquad (A.5e)$$

$$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi \qquad (A.5f)$$

Here

$$\xi = \sqrt{\alpha}\ y \qquad (A.6)$$

The dipole transition matrix element for a transition from vibrational level v_m to v_n is given by (Ref. 7):

$$R^2_{\substack{mn \\ v_m \to v_n}} = \left| \int_{-\infty}^{\infty} \Psi^{\dagger}_{v_m} \, z_1 y \, \Psi_{v_n} \, dy \right|^2 =$$

$$= \left(\frac{z_1^2}{\alpha\pi}\right)\left(\frac{1}{2^{v_m} \, v_m!}\right)\left(\frac{1}{2^{v_n} \, v_n!}\right)\left[\int_{-\infty}^{\infty} \exp(-\xi^2) \, H_{v_m}(\xi) \, \xi \, H_{v_n}(\xi) \, d\xi\right]^2 =$$

$$= \frac{z_1^2}{2\alpha}\left(\frac{v_m + v_n + 1}{2}\right) \delta\left(\left|v_m - v_n\right| - 1\right) \quad , \quad \text{cm}^2 \qquad \text{(A.7)}$$

The eigenfunctions $\Psi_v = N_v \exp\text{-}\left(\frac{1}{2}\xi^2\right) \cdot H_v(\xi)$ are orthogonal, that is:

$$\int_{-\infty}^{+\infty} \Psi^{\dagger}_{v_m} \Psi_{v_n} \, d\xi = \delta(v_m - v_n) \qquad \text{(A.8)}$$

and the nonzero result (A.7) is due to the fact that for the Hermite polynomials we have the recursion relation:

$$\xi H_v(\xi) = vH_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi) \qquad \text{(A.9)}$$

With the aid of (A.4) the result (A.7) can be written for a diatomic molecule:

$$\boxed{R^2_{\substack{mn\\ |v_m - v_n| = 1\\ \text{diatomic}}} = \frac{z_1^2 h}{16\pi^2}\left(\frac{v_m + v_n + 1}{\bar{M}\nu_e}\right) , \ \text{cm}^2} \tag{A.10}$$

In Eq. (A.10), $\bar{M}$ is the effective mass of the harmonic oscillator which for two vibrating atoms in a diatomic molecule with masses M_A and M_B is equal to the reduced mass (Ref. 2, pp 74 and 75):

$$\bar{M} = \frac{M_A M_B}{M_A + M_B} , \quad \text{grams} \tag{A.11}$$

Note that we could also have written (A.10) in terms of the force constant k instead of the fundamental frequency ν_e :

$$R^2_{\substack{mn\\ |v_m - v_n| = 1}} = \frac{z_1^2 h}{4\pi} \ \frac{v_m + v_n + 1}{\sqrt{\bar{M}k}} , \quad \text{cm}^2 , \tag{A.12}$$

since:

$$2\pi\nu_e = \sqrt{\frac{k}{\bar{M}}} , \quad \text{sec}^{-1} \tag{A.13}$$

Usually the expression (A.10) which is in terms of ν_e is preferred since we can measure the frequency ν_e directly but not the force constant k.

Now for the harmonic vibration of two atoms in a diatomic molecule, the determination of the effective mass $\bar{M}$ is no problem since we have Eq. (A.11). However for a polyatomic molecule, the situation is more complicated. For a polyatomic molecule, the potential energy has, instead of the simple form:

$$V_{diatomic} = \frac{1}{2} ky^2 \tag{A.14}$$

as used in Eq. (A.1), the form:

$$V_{polyatomic} = \frac{1}{2} \sum_{ij} k_{ij}\, y_i y_j \tag{A.15}$$

where the summations over i and j are over all pairs of atoms in the molecule (including i = j). Instead of finding the simple relation (A.13), one usually obtains an expression of the form (Ref. 10):

$$4\pi^2 \nu_\beta^2 = \sum_s \frac{k_{\beta s}}{M_{\beta s}} \quad , \tag{A.16}$$

where $\nu_\beta = \nu_1, \nu_2, \nu_3, \ldots$ are the fundamental frequencies of the "normal vibrations" of the molecule (Ref. 10) and s is a summation over "internal or structural symmetry coordinates" along which model component vibrations with model values for $\frac{k}{M}$ can be calculated. Because of (A.16), we have no one-to-one relation between one ν_β and one M_β say, from which we can calculate one parameter α_β according to Eq. (A.4) and thence the transition element $(R^2_{mn})_\beta$ for the β vibration. Instead of (A.7), the non-vanishing matrix element for a transition in the β vibration of a polyatomic molecule may be expressed by:

$$\left(R^2_{mn}\right)_{\substack{\beta \\ |v_{\beta_m} - v_{\beta_n}| = 1}} = \left| \int_{-\infty}^{\infty} \Psi^\dagger_{\beta_n} \left(\sum_s z_{\beta s}\, \vec{y}_{\beta s} \right) \Psi_{\beta_m}\, dy_\beta \right|^2 =$$

$$= \frac{h}{8\pi^2 M_\beta \nu_\beta} \left| \int_{-\infty}^{\infty} \Psi^\dagger_{\beta_n} \left(\sum_s z_{\beta s} \frac{\xi_{\beta s}\, \vec{e}_{\beta s}}{M^{1/4}_{\beta s}\, k^{1/4}_{\beta s}} \right) \Psi_{\beta_m}\, d\xi_\beta \right|^2 =$$

$$\boxed{\left(R^2_{mn}\right)_{\substack{\beta \\ |v_{\beta_m} - v_{\beta_n}| = 1 \\ \text{polyatomic}}} = \frac{h\left(v_{\beta_m} + v_{\beta_n} + 1\right)}{16\pi^2} \, \frac{z^2_\beta}{M_\beta \nu_\beta} \;, \quad \text{cm}^2} \qquad \text{(A.17)}$$

Here $\vec{e}_{\beta s}$ are unit vectors along the internal symmetry coordinates directed from the negative to the positive charge of the electric dipole along coordinate s, and $z_{\beta s}$ is the effective dipole charge along internal coordinate s.* The factor $(M_{\beta s}\, k_{\beta s})^{-1/4}$ in (A.17) makes the coordinate $y_{\beta s}$ dimensionless and such that $\vec{y}_\beta = \sum_s \vec{y}_{\beta s}$. That is we have:

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*We shall assume here that $z_{\beta s}$ can be positive or negative depending on whether the βs bond is stretching or contracting compared to the others. That is $z_{\beta s} = |z_{\beta s}|\, \gamma_{\beta s}$ includes the vibration sign $\gamma_{\beta s}$ here (see Appendix B).

$$z_\beta \vec{y}_\beta = \sum_s z_{\beta s} \vec{y}_{\beta s} = \sum_s \frac{z_{\beta s} \xi_{\beta s} \vec{e}_{\beta s}}{M_{\beta s}^{1/4} k_{\beta s}^{1/4}} \tag{A.18}$$

Thus since ν_β is given by (A.16), we have:

$$\frac{z_\beta^2}{M_\beta} = \left[\sum_s \left(\frac{k_{\beta s}}{M_{\beta s}}\right)\right]^{\frac{1}{2}} \left|\sum_s \left(\frac{z_{\beta s} \vec{e}_{\beta s}}{M_{\beta s}^{1/2}}\right)\left(\frac{k_{\beta s}}{M_{\beta s}}\right)^{-\frac{1}{4}}\right|^2 , \tag{A.19}$$

where the absolute signs $|\ |$ are to be taken as the absolute value of the vector product $|\vec{V}|^2 = \vec{V} \cdot \vec{V}$.

If we define:

$$M_\beta \equiv \left[\sum_s M_{\beta s}^{-1/2}\right]^{-2} , \tag{A.20}$$

then clearly:

$$z_\beta \equiv \left[\sum_s \frac{k_{\beta s}}{M_{\beta s}}\right]^{1/4} \left|\sum_s \left(\frac{M_{\beta s}}{k_{\beta s}}\right)^{1/4} \left(\frac{z_{\beta s} \vec{e}_{\beta s}}{M_{\beta s}^{1/2}}\right)\right| \left[\sum_s M_{\beta s}^{-1/2}\right]^{-1} \tag{A.21}$$

Also we can then define k_β from:

$$\frac{k_\beta}{M_\beta} = \sum_s \frac{k_{\beta s}}{M_{\beta s}} = 4\pi^2 \nu_\beta^2 \tag{A.22}$$

yielding:

$$k_\beta = \frac{\sum_s k_{\beta s} M_{\beta s}^{-1}}{\left(\sum M_{\beta s}^{-1/2}\right)^2} \tag{A.23}$$

Thus if we have values for $M_{\beta s}$, $k_{\beta s}$, and $z_{\beta s}$, we can calculate k_β , M_β , and z_β . By means of mechanical molecular models, values for the mechanical parameters $M_{\beta s}$ and $k_{\beta s}$ have been calculated for a number of commonly occuring molecules (Ref. 10). However few calculated values for $z_{\beta s}$ have been reported due to the much more difficult problem of determining charge distributions in a molecule. In Appendix B, we give a semi-experimental method for obtaining values of $z_{\beta s}$ for polyatomic molecules based on experimentally-measured diatomic dipoles. In many of the mechanical models, the $\vec{e}_{\beta s}$ are perpendicular to each other in which case we can omit the $\vec{e}_{\beta s}$ and absolute signs in Eqs. (A.17) through (A.21).

The above relations for the transition element R^2_{mn} were derived assuming harmonic oscillations which only allow transitions with $\Delta v = |v_m - v_n| = 1$. If an anharmonic term $-g_e y^3$ is added to the potential energy $\frac{1}{2} ky^2$ in (A.1), that is:

$$V = \frac{1}{2} ky^2 - g_e y^3 , \tag{A.24}$$

overtone transitions with $\Delta v = |v_m - v_n| = 2 , 3 , 4 , \ldots$ are allowed as well. From the work by Heaps and Herzberg (Ref. 17), we find that the matrix elements (A.10) and (A.17) for a diatomic molecule become in this case:

$$\boxed{\begin{aligned}\left(R^2_{mn}\right)_{\substack{(v_m > v_n)\\ \text{diatomic}}} &= \frac{z_1^2 h}{8\pi^2 \bar{M}\nu_e}\;\frac{v_m!}{v_n!}\;\frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)^2} = \\ &= \frac{z_1^2 h}{8\pi^2 \bar{M}\nu_{mn}}\;\frac{v_m!}{v_n!}\;\frac{x_e^{(v_m - v_n - 1)}}{(v_m - v_n)}\text{ , cm}^2\text{ ,}\end{aligned}} \qquad \text{(A.25)}$$

if $(v_m + v_n)\, x_e \ll 1$ (Ref. 7), which is almost always true in cases of practical interest. Similarly for polyatomic molecules then:

$$\boxed{\begin{aligned}\left(R^2_{mn}\right)_{\substack{\left(v_{\beta_m} > v_{\beta_n}\right)\\ \text{polyatomic}}} &= \frac{z_\beta^2 h}{8\pi^2 M_\beta \nu_\beta}\;\frac{v_{\beta_m}!}{v_{\beta_n}!}\;\frac{x_\beta^{\left(v_{\beta_m} - v_{\beta_n} - 1\right)}}{\left(v_{\beta_m} - v_{\beta_n}\right)^2} = \\ &= \frac{z_\beta^2 h}{8\pi^2 M_\beta \nu_{mn}}\;\frac{v_{\beta_m}!}{v_{\beta_n}!}\;\frac{x_\beta^{\left(v_{\beta_m} - v_{\beta_n} - 1\right)}}{\left(v_{\beta_m} - v_{\beta_n}\right)}\text{ , cm}^2\end{aligned}} \qquad \text{(A.26)}$$

Here we choose v_m and v_{β_m} to be the larger of v_m , v_n and v_{β_m} , v_{β_n} respectively, and for the diatomic case:

$$\nu_{mn} = (v_m - v_n)\,\nu_e - \left\{ v_m(v_m + 1) - v_n(v_n + 1) \right\} x_e\nu_e \approx (v_m - v_n)\,\nu_e \qquad \text{(A.27)}$$

while for the polyatomic case:

$$\nu_{mn} = \left(v_{\beta_m} - v_{\beta_n}\right) \nu_\beta - \left\{v_{\beta_m}\left(v_{\beta_m} + 1\right) - v_{\beta_n}\left(v_{\beta_n} + 1\right)\right\} x_\beta \nu_\beta \approx \left(v_{\beta_m} - v_{\beta_n}\right) \nu_\beta \ , \qquad \text{(A.28)}$$

The dimensionless anharmonic constant x_e or x_β is related to the anharmonic constant g_e or g_β (dynes/cm^2) of Eq. (A.24) by (Ref. 2, p. 93):*

$$x_\beta = \frac{15\, h\, \nu_\beta}{4k_\beta^3}\, g_\beta^2 \ , \qquad \text{(A.29)}$$

If instead of (A.24), a Morse potential (see Appendix C) is assumed, it may be related to the dissociation energy D_β of the β vibration by (Ref. 16):

$$x_\beta = \frac{h\, \nu_\beta}{4\, D_\beta} = 3.099 \times 10^{-5}\ \frac{\nu_\beta(\mathrm{cm}^{-1})}{D_\beta(\mathrm{eV})} \qquad \text{(A.30)}$$

Here ν_β is the fundamental frequency of the β vibration. Herzberg (Refs. 2 and 11) has tabulated values of anharmonic constants x_e and x_β and dissociation energies D_β for many diatomic and polyatomic molecules.

It should be noted that (A.25) and (A.26) reduce to Eqs. (A.10) and (A.17) respectively if $\Delta v = 1$, as they must of course. The factor $(v_m!/v_n!) \cdot \cdot \left(x_e^{(v_m - v_n - 1)}/(v_m - v_n)^2\right) = 1$ in this case.

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*Subscript e refers to the equilibrium value of a diatomic molecule and subscript β to the equilibrium value of a β vibration of a polyatomic molecule.

For "combination-band" transitions in polyatomic molecules, in which transitions of several normal vibrations $\beta = 1, 2, 3 \ldots$ can take place simultaneously, the transition element R^2_{mn} may be written:

$$\left(R^2_{mn}\right)_{\substack{\text{vibration}\\ \text{polyatomic}}} =$$

$$= \left| \int_{-\infty}^{\infty} \left\{ \prod_{\beta} \left(\Psi^{\dagger}_{\beta}\right)_n \right\} \left\{ \left(z_\beta \vec{y}_\beta + z_{\beta-1} \vec{y}_{\beta-1} + \ldots z_1 \vec{y}_1 \right) dy_\beta dy_{\beta-1} \ldots dy_1 \right\} \left\{ \prod_{\beta} \left(\Psi_\beta\right)_m \right\} \right|^2 =$$

$$= \frac{h}{8\pi^2} \left| \sum_{\beta} \frac{z_\beta \ \vec{e}_\beta}{M_\beta^{1/2} \ \nu_\beta^{1/2} \ x_\beta^{1/2}} \left(\frac{|v_{\beta_m} - v_{\beta_n}| + 1}{|v_{\beta_m} - v_{\beta_n}|} \right) \right|^2 \left[\prod_{\beta} \left(\frac{v_{\beta_m}!}{v_{\beta_n}!} \right)^{\delta_\beta} \frac{x_\beta^{|v_{\beta_m} - v_{\beta_n}|}}{\left(|v_{\beta_m} - v_{\beta_n}| + 1 \right)^2} \right] =$$

$$\boxed{\left(R^2_{mn}\right)_{\substack{\text{vibration}\\ \text{polyatomic}}} = \frac{h}{8\pi^2} \frac{z^2_{mn}}{M_{mn} \ \nu_{mn} \ x_{mn}} \cdot \prod_{\beta} \left(\left(\frac{v_{\beta_m}!}{v_{\beta_n}!} \right)^{\delta_\beta} \frac{x_\beta^{|v_{\beta_m} - v_{\beta_n}|}}{\left(|v_{\beta_m} - v_{\beta_n}| + 1 \right)^2} \right), \ \text{cm}^2} \tag{A.31}$$

Here:

$$\nu_{mn} = \sum_{\beta} \left(v_{\beta_m} - v_{\beta_n} \right) \nu_\beta , \tag{A.32}$$

where ν_β is the fundamental frequency of the β vibration, while:

$$\delta_\beta = 1 \ , \quad \text{if } \nu_{\beta_m} > \nu_{\beta_n} \tag{A.33a}$$

$$\delta_\beta = -1 \ , \quad \text{if } \nu_{\beta_m} < \nu_{\beta_n} \ , \tag{A.33b}$$

and:

$$\boxed{\frac{z^2_{mn}}{M_{mn}\ x_{mn}} \equiv \left(\frac{z^2_1}{\bar{M}\ x_e}\right)_{mn} = \left|\sum_\beta \frac{z_\beta\ \vec{e}_\beta}{M_\beta^{1/2}\nu_\beta^{1/2}x_\beta^{1/2}}\ \frac{|\nu_{\beta_m}-\nu_{\beta_n}|+1}{|\nu_{\beta_m}-\nu_{\beta_n}|}\right|^2 \cdot \left(\sum_\beta \left(\nu_{\beta_m}-\nu_{\beta_n}\right)\nu_\beta\right)} \tag{A.34}$$

The unit vectors $\vec{e}_\beta$ in Eqs. (A.31) through (A.34) are along the "normal coordinates" of the normal β vibrations of the polyatomic molecule.

If we define:

$$M_{mn} = \left[\sum M_\beta^{-1/2}\left(\nu_{\beta_m} - \nu_{\beta_n}\right)\right]^{-2} \tag{A.35}$$

and:

$$x_{mn} = \left[\sum x_\beta^{-1/2}\left(\nu_{\beta_m} - \nu_{\beta_n}\right)\right]^{-2} \tag{A.36}$$

then:

$$z_{mn} = \left(\nu_{mn}\ M_{mn}\ x_{mn}\right)^{1/2}\left|\sum_\beta \left(\frac{|\nu_{\beta_m}-\nu_{\beta_n}|+1}{|\nu_{\beta_m}-\nu_{\beta_n}|}\right)\frac{z_\beta\ \vec{e}_\beta}{M_\beta^{1/2}\nu_\beta^{1/2}x_\beta^{1/2}}\right| \tag{A.37}$$

The absolute sign $| \; |$ in (A.37) is again to be taken with respect to a vector, that is $|\vec{V}| = (\vec{V} \cdot \vec{V})^{1/2}$. If the normal vibrations β are perpendicular with respect to each other in three-dimensional (x,y,z) space, we can omit the absolute notation and the unit vectors $\vec{e}_\beta$ in the above relations since only $\vec{e}_\beta \cdot \vec{e}_\beta = 1$, and all $\vec{e}_\beta \cdot \vec{e}_\alpha = 0$ $(\alpha \neq \beta)$.

How to obtain values of z_β for polyatomic molecules is discussed in Appendix B, while the M_β can be calculated via Eq. (A.20). Once the z_β and M_β are known, z_{mn} and M_{mn} can be directly calculated from Eqs. (A.35) and (A.37). Values for x_β (and thence x_{mn}) can be obtained either via Eq. (A.30) or from Herzberg's tables (Refs. 2 and 11).

It should be noted from an inspection of Eq. (A.31), that in general, a double combination-band ($\beta = j \; , \; k$) transition is proportional to the first power of an averaged anharmonic constant, a triple combination-band ($\beta = i \; , \; j \; , \; k$) transition is proportional to the second power of an averaged anharmonic constant, etc., while for a single band transition the anharmonic constants in expression (A.31) drop out. Since anharmonic constants x_β are usually on the order of $\sim 10^{-2}$, this shows that a two-combination-band or first overtone (see Eq. (A.26)) transition ($n = 2$) is about 10^{-2} weaker than a single-band transition with $\Delta v_\beta = 1$, while a triple combination-band or double overtone ($n = 3$) transition is 10^{-4} times weaker, etc. The proportionality of the combination-band and/or overtone transitions to the factor $\bar{x}_\beta^{(n-1)}$ is somewhat mitigated due to the fact that the ratio of factorial factors $(v_{\beta_m}!/v_{\beta_n}!)^{\delta_\beta}$ in Eqs. (A.26) or (A.31) works in the opposite direction, that is it becomes larger, the higher the degree of the overtone or combination-band. However this factor grows much slower with increasing n than $\bar{x}_\beta^{(n-1)}$ decreases with respect to it. These qualitative results agree well with actual observations of the radiative absorption coefficients for single-band, overtone and combination-band transitions of gaseous molecules.

The results shown for the indicated integrations over the eigenfunctions Ψ_{β_k} in (A.31), depend on the following considerations. For the pure harmonic oscillator eigenfunctions, we have:

$$\int_{-\infty}^{\infty} \Psi^{\dagger}_{v_{\beta_n}}(\xi_\beta) \quad \Psi_{v_{\beta_m}}(\xi_\beta) \quad d\xi_\beta = \delta\left(v_{\beta_m} - v_{\beta_n}\right), \qquad \text{(A.38)}$$

where $\delta(x=o) = 1$; $\delta(x \neq o) = 0$ is the Dirac delta function. Also for the pure harmonic oscillator eigenfunctions one has:

$$\underset{\left(v_{\beta_m} > v_{\beta_n}\right)}{\int_{-\infty}^{+\infty}} \Psi^{\dagger}_{v_{\beta_n}}(\xi_\beta) \quad \xi_\beta \, \Psi_{v_{\beta_m}}(\xi_\beta) \quad d\xi_\beta = \left(\frac{v_{\beta_m} + v_{\beta_n} + 1}{4}\right)^{\frac{1}{2}} \delta\left(v_{\beta_m} - v_{\beta_n} - 1\right) \qquad \text{(A.39)}$$

which can be proven with the aid of Eqs. (A.2) and (A.9).

For the anharmonic oscillator (to first order), we have according to Eq. (A.26) (see also Ref. 17) instead of (A.39):

$$\underset{\left(v_{\beta_m} > v_{\beta_n}\right)}{\int_{-\infty}^{\infty}} \Psi^{\dagger}_{v_{\beta_n}}(\xi_\beta) \quad \xi_\beta \, \Psi_{v_{\beta_m}}(\xi_\beta) \quad d\xi_\beta = \left[\frac{1}{2}\left(\frac{v_{\beta_m}!}{v_{\beta_n}!}\right) \frac{x_\beta^{\left(v_{\beta_m} - v_{\beta_n} - 1\right)}}{\left(v_{\beta_m} - v_{\beta_n}\right)^2}\right]^{\frac{1}{2}} \qquad \text{(A.40)}$$

This expression reduces to (A.39) if $v_{\beta_m} - v_{\beta_n} = 1$ as it should if it is to be general. Then by application of (A.9) we must have also for the anharmonic oscillator (to first order):

$$\int_{-\infty \atop (v_{\beta_m} > v_{\beta_n})}^{\infty} \Psi^{\dagger}_{v_{\beta_n}} \Psi_{v_{\beta_m}} \, d\xi_\beta = N_{v_{\beta_m}} N_{v_{\beta_n}} \int_{-\infty}^{+\infty} \left[2\xi_\beta \, \phi^{\dagger}_{v_{\beta_n}-1} - 2\left(v_{\beta_n}-1\right) \phi^{\dagger}_{v_{\beta_n}-2} \right] \cdot$$

$$\cdot \, \phi_{v_{\beta_m}} \, d\xi_\beta = \left(\frac{2 N_{v_{\beta_n}}}{N_{v_{\beta_n}-1}} \right) \int_{-\infty}^{+\infty} \Psi^{\dagger}_{v_{\beta_n}-1} \, \xi_\beta \, \Psi_{v_{\beta_m}} \, d\xi_\beta =$$

$$= \left(\frac{2}{v_{\beta_n}} \right)^{1/2} \left[\frac{1}{2} \, \frac{v_{\beta_m}!}{\left(v_{\beta_n}-1\right)!} \, \frac{x_\beta^{\left(v_{\beta_m}-v_{\beta_n}\right)}}{\left(v_{\beta_m}-v_{\beta_n}+1\right)^2} \right]^{1/2} = \left[\frac{v_{\beta_m}!}{v_{\beta_n}!} \, \frac{x_\beta^{\left(v_{\beta_m}-v_{\beta_n}\right)}}{\left(v_{\beta_m}-v_{\beta_n}+1\right)^2} \right]^{1/2} \qquad \text{(A.41)}$$

where we used (A.40). Here:

$$\phi_{v_{\beta_k}} = \frac{1}{N_{v_\beta}} \Psi_{v_\beta} \,, \qquad \text{(A.42)}$$

and N_{v_β} is the normalization constant defined by:

$$N_{v_\beta} = \left[\left(\frac{2\sqrt{M_\beta \; k_\beta}}{h} \right)^{1/2} \left(\frac{1}{2^{v_\beta} \; v_\beta!} \right) \right]^{1/2} \qquad \text{(A.43)}$$

The second term in (A.41) involving integration over the product $\left(\phi^{\dagger}_{v_{\beta_n}-2}\ \phi_{v_{\beta_m}}\right)$ is zero if the pure harmonic oscillator eigenfunctions are used and nonzero but negligibly small compared to the first term involving $\left(\phi^{\dagger}_{v_{\beta_n}-1}\ \xi_\beta\ \phi_{v_{\beta_m}}\right)$ if the anharmonic (first-order) eigenfunctions are employed. It may therefore be dropped.

In Eq. (A.31) we used Eq. (A.41) for the products $\int \Psi^{\dagger}_{v_{\beta_n}}\ \Psi_{v_{\beta_m}}\ d\xi_\beta$, and Eq. (A.40) for products involving $\int \Psi^{\dagger}_{v_{\beta_n}}\ \xi_\beta\ \Psi_{v_{\beta_m}}\ d\xi_\beta$, which appear in this expression as follows:

$$
\begin{aligned}
R^2_{mn} = \frac{h}{8\pi^2} \Bigg| \int \Psi^{\dagger}_{v_{\beta_n}}\ \Psi^{\dagger}_{v_{\beta-1_n}} \cdots \Psi^{\dagger}_{v_{1_n}} \left(\frac{z_\beta}{\sqrt{M_\beta\ k_\beta}}\ \xi_\beta\ \vec{e}_\beta + \frac{z_{\beta-1}}{\sqrt{M_{\beta-1}\ k_{\beta-1}}}\ \xi_{\beta-1}\ \vec{e}_{\beta-1} + \cdots \right.& \\
\left. + \cdots \frac{z_1}{\sqrt{M_1\ k_1}}\ \xi_1\ \vec{e}_1 \right) \Psi_{v_{\beta_m}}\ \Psi_{v_{\beta-1_m}} \cdots \Psi_{v_{1_m}}\ d\xi_\beta\ d\xi_{\beta-1} \cdots d\xi_1 \Bigg|^2 &= \\
= \frac{h}{8\pi^2} \Bigg| \left[\frac{z_\beta}{\sqrt{M_\beta\ k_\beta}} \int \Psi^{\dagger}_{v_{\beta_n}}\ \xi_\beta\ \Psi_{v_{\beta_m}}\ d\xi_\beta \right] \cdot \left[\int \Psi^{\dagger}_{v_{\beta-1_n}}\ \Psi_{v_{\beta-1_m}}\ d\xi_{\beta-1} \right] \cdots& \\
\cdots\cdots \left[\int \Psi^{\dagger}_{v_{1_n}}\ \Psi_{v_{1_m}}\ d\xi_1 \right] + \left[\int \Psi^{\dagger}_{v_{\beta_n}}\ \Psi_{v_{\beta_m}}\ d\xi_\beta \right] \cdot& \\
\cdot \left[\frac{z_{\beta-1}}{\sqrt{M_{\beta-1}\ k_{\beta-1}}} \int \Psi^{\dagger}_{v_{\beta-1_n}}\ \xi_{\beta-1}\ \Psi_{v_{\beta-1_m}}\ d\xi_{\beta-1} \right] \cdots\cdots \left[\int \Psi^{\dagger}_{v_{1_n}}\ \Psi_{v_{1_m}}\ d\xi_1 \right] +& \\
+ \cdots\cdots\cdots + \left[\int \Psi^{\dagger}_{v_{\beta_n}}\ \Psi_{v_{\beta_m}}\ d\xi_\beta \right] \left[\int \Psi^{\dagger}_{v_{\beta-1_n}}\ d\xi_{\beta-1} \right] \cdots\cdots& \\
\cdots\cdots \left[\frac{z_1}{\sqrt{M_1\ k_1}} \int \Psi^{\dagger}_{v_{1_n}}\ \xi_1\ \Psi_{v_{1_m}}\ d\xi_1 \right] \Bigg|^2 &
\end{aligned}
\qquad \text{(A.44)}
$$

Note that the formalism we developed so far calculates only second-order or higher-order transitions which are mechanically second-order or anharmonic but first-order in the electric dipole. That is at least one dipole charge z_β must be non-vanishing in the summation in Eq. (A.37). If all z_β's are zero in the combination transition, the transition will become second-order in the dipole (assuming it does not vanish also).

Looking first at a Δv = 1 transition involving only one single normal vibration β , we have for a second-order dipole transition:

$$\underset{\left(v_{\beta_m} - v_{\beta_n} = 1\right)}{\left(R^2_{mn}\right)_\beta} = \left| \int_{-\infty}^{\infty} \Psi^\dagger_{\beta_n} \left\{ \sum_s \left(\frac{\partial z_{\beta s}}{\partial y_{\beta s}}\right) \vec{e}_{\beta s}\, y^2_{\beta s} \right\} \Psi_{\beta_m}\, dy_\beta \right|^2 =$$

$$= \frac{h^2}{16\pi^3 M_\beta \nu_\beta} \left| \int_{-\infty}^{\infty} \Psi^\dagger_{\beta_n} \left\{ \sum \frac{(\partial z_{\beta s}/\partial \xi_{\beta s})}{(M_{\beta s}\, k_{\beta s})^{1/4}}\, \vec{e}_{\beta s}\, \xi^2_{\beta s} \right\} \Psi_{\beta_m}\, d\xi_\beta \right|^2 =$$

$$= \left(\frac{h^2}{16\pi^3 M_\beta \nu_\beta}\right) \left(\frac{2v_{\beta_m} + 1}{2}\right)^2 \left(\frac{v_{\beta_m}!}{v_{\beta_n}!}\right) \left(\frac{x_\beta^{(v_{\beta_m} - v_{\beta_n})}}{(v_{\beta_m} - v_{\beta_n} + 1)^2}\right) \left| \sum_s \frac{(\partial z_{\beta s}/\partial y_{\beta s})}{(M_{\beta s}\, k_{\beta s})^{1/2}}\, \vec{e}_{\beta s} \right|^2 \qquad (A.45)$$

Here we made use of Eq. (A.41) and the recursion relation:

$$\xi^2 H_v(\xi) = v(v - 1)\, H_{v-2}(\xi) + \frac{1}{2}\,(2\, v + 1)\, H_v(\xi) + \frac{1}{4}\, H_{v+2}(\xi) \qquad (A.46)$$

Comparing Eq. (A.45) with (A.17), we see that a second-order-dipole transition is weaker than a first-order-dipole transition by a factor of f on the order of:

$$f \sim \frac{h x_\beta}{2\pi (M_\beta \; k_\beta)^{1/2}} \left(\frac{\partial z_\beta}{\partial y_\beta}\right)^2 \left(\frac{1}{z'_{\beta'}}\right) \qquad \text{(A.47)}$$

where we assume that the summation over s extends over only one component for convenience and where a prime refers to the first-order-dipole transition and unprimed quantities to the second-order-dipole case. Since $x_\beta \sim 10^{-2}$ usually, and:

$$\left(\frac{1}{z'_{\beta'}} \frac{\partial z_\beta}{\partial y_\beta}\right)^2 \sim \frac{1}{r_\beta^2} \sim 10^{16} \text{ cm}^{-2} , \qquad \text{(A.48)}$$

while:

$$\frac{h}{2\pi (M_\beta \; k_\beta)^{1/2}} \sim 10^{-19} \text{ cm}^2 , \qquad \text{(A.49)}$$

we see that $f \approx 10^{-2} \times (10^{-19} \times 10^{16}) \approx 10^{-5}$. In other words, a second-order-dipole transition is about 10^{-5} times weaker than a first-order-dipole transition. On the other hand, as we noted before, a mechanically-anharmonic, but first-order-dipole transition such as an overtone or double combination band transition is only weaker by a factor of $x_\beta \sim 10^{-2}$, and even a second overtone or triple combination band transition (with first-order dipole) is only weaker by a factor of $x_\beta \sim 3 \times 10^{-4}$. Thus second-order-dipole transitions are comparable in strength to third overtone or quadruple combination band transitions.

The generalization of (A.45) to a multi-level transition as was done in going from (A.17) to (A.26) to (A.31) is straightforward but tedious. It must include terms $\partial z_{\beta s}/\partial \xi_{\alpha s}$ and $\partial z_{\alpha s}/\partial \xi_{\beta s}$ besides $\partial z_{\beta s}/\partial \xi_{\beta s}$ and $\partial z_{\alpha s}/\partial \xi_{\alpha s}$. Since data about these terms are virtually non-existent and since transitions that depend on these terms are even weaker yet by a factor of about x_β^n than the $\Delta v = 1$ transition of (A.45), we shall not consider them further.

Note that the factor $F = \left[\sum_\beta (|v_{\beta_m} - v_{\beta_n}| + 1)(|v_{\beta_m} - v_{\beta_n}|)^{-1}\right]^2 \cdot \prod_\beta \left[(|v_{\beta_m} - v_{\beta_n}| + 1)^{-2} \cdot \left\{(v_{\beta_m}!)/(v_{\beta_n}!)\right\}^{\delta_\beta}\right]$ used in Eq. (A.32) has different values for a degenerate overtone vibration, depending on the composition of the overtone. For example for a triply-degenerate $3\nu_3$ vibration, $F = 2/3$ for a $3\nu_{3a}$, $3\nu_{3b}$, or $3\nu_{3c}$ vibration; $F = 49/72$ for a $(2\nu_{3a} + \nu_b)$, $(2\nu_{3b} + \nu_c)$, ..., etc. vibration, and $F = 9/16$ for the $(\nu_{3a} + \nu_{3b} + \nu_{3c})$ vibration, even though all are $3\nu_3$ vibrations. The weights of these compositions are 3, 6, and 1 and thus the average factor $\bar{F}$ for a triply-degenerate $3\nu_3$ vibration is $\bar{F} = (3/10)(2/3) + (6/10)(49/72) + (1/10)(9/16) = 0.664583$, which is not too different from $F = 2/3 = 0.666667$ if a non-degenerate $3\nu_3$ vibration had been assumed. Thus no great error results if one neglects degeneracy considerations of the normal vibrations in calculating R_{mn}^2 from (A.31).

In applying the multi-overtone, multi-band, matrix element relation (A.31) to various molecules, one finds that for the higher overtones and more-than-two combination-band transitions, this equation gives progressively less satisfactory results (the higher the degree of the multiplicity) when calculations are compared with experiment. That is, predicted transition strengths are consistently too low, and the more so, the higher the multiplicity. One could expect such deviations, since the formula is based on first-order anharmonicity only.

An empirically corrected version of Eq. (A.32) which is found to give better agreement with experiment is:

$$\boxed{\left(R^2_{mn}\right)_{\substack{\text{vibration}\\ \text{polyatomic}}} = \frac{h}{8\pi^2}\left|\sum_\beta \frac{z_\beta \vec{e}_\beta}{M_\beta^{1/2}\, \nu_\beta^{1/2}\, (x_\beta^{1/2})^{f}}\left(\frac{|v_{\beta_m} - v_{\beta_n}| + 1}{|v_{\beta_m} - v_{\beta_n}|}\right)\right|^2 \cdot \; \cdot \prod_\beta\left[\frac{x_\beta^{|v_{\beta_m} - v_{\beta_n}| f}}{(|v_{\beta_m} - v_{\beta_n}| + 1)^2}\left(\frac{v_{\beta_m}!}{v_{\beta_n}!}\right)^{\delta_\beta}\right], \ \text{cm}^2} \tag{A.50}$$

where:

$$\boxed{f = 1 - \frac{1}{2}\left[\frac{\left(\sum_\beta |v_{\beta_m} - v_{\beta_n}|\right)! - 1}{\left(\sum_\beta |v_{\beta_m} - v_{\beta_n}|\right)! + 1}\right]} \tag{A.51}$$

APPENDIX B

EFFECTIVE MASSES, FORCE CONSTANTS, AND DIPOLE CHARGES IN POLYATOMIC MOLECULES

B.1 INTRODUCTION

An important parameter in the calculation of the dipole transition element of a vibrational transition in a polyatomic molecule is the effective dipole charge number z_β of a normal vibration β or its components $z_{\beta s}$ along a symmetry coordinate. An exact calculation of the charge distribution in a polyatomic molecule can in principle be carried out if electron wave functions for the molecule are available. In practice few wave functions of molecules are well established, and if available, they are often based on many approximations. This causes a large uncertainty in the accuracy of any calculation of small differences in the electron distribution (such as the dipole moment) which are based on these wave functions (Ref. 18). Instead of attempting to calculate z_β's via the laborious and uncertain method of using molecular wave functions, we give here an approximate scheme based on some simplifying assumptions about molecular bonds and using measured diatomic dipole moments. This method has the advantage that values for $z_{\beta s}$ of polyatomic molecules can be obtained immediately if measurements on diatomic dipoles are available. Although its accuracy may not be better than fifty percent in the worst case, it still makes the calculation of R^2_{mn} parameters for use in preliminary design problems (e.g., lasers) much better than an educated guess.

B.2 DIATOMIC MOLECULES

Before investigating polyatomic molecules, consider first a simple diatomic molecule such as CO. The permanent dipole moment $\mu_o = e\, z_o\, r_e$ of this molecule has been measured to be 0.112×10^{-18} $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{3/2}$, while the equilibrium separation of the centers of the C and O atoms is $r_e = 1.1281 \times 10^{-8}$ cm. Therefore the effective dipole charge z_o must equal 0.0207 electron charges, since $e = 4.80285 \times 10^{-10}$ $\mathrm{erg}^{1/2} \cdot \mathrm{cm}^{1/2}$ (see below). This means that one of the atoms, C or O, has slightly more negative charge residing on it than the other. In the case of CO, it is the oxygen atom around which the two "valence" or "bonding" electrons spent a little bit more time on the average during their orbital motions in the outer shell of the molecule CO than around the carbon atom. To be exact, the two electrons that travel around C and O and bond them, spend 0.0207/2 = 1.035% more of their time moving about the oxygen electron than about the carbon atom.

Now in vibrational transitions, it is not the permanent dipole moment μ_o which enters in the expression of the transition element R^2_{mn}, but rather the first derivative of the dipole moment, namely:

$$\mu_1 = \left(\frac{\partial\mu}{\partial s}\right)_{s=r_e} = \left(\frac{\partial\mu}{\partial y}\right)_{y=o} = e z_1 \qquad \text{(B.1)}$$

where μ_1 is the coefficient of the second member of the series expansion for μ about $y = o$:

$$\mu(y) = \mu_o + \mu_1\, y + \ldots = e\, r_e\, z(y) = e\, z_o\, r_e + e\, z_1 \cdot (s - r_e) + \ldots \qquad \text{(B.2)}$$

The parameter y is the displacement of the atoms from their equilibrium position in the molecule, that is:

$$y = s - r_e \;, \qquad (B.3)$$

The parameter z is an effective dipole charge placed on the two atoms, one having charge -z (oxygen in the case of CO) and the other +z (carbon in the case of CO). The value for z is defined by the second member of Eq. (B.2) and equals z_o when the atoms are separated by distance r_e. Since the electronic charge is actually distributed around the atoms, the precise definition of z_o for a diatomic molecule as we use it, is:

$$z_o \, r_e = (Z_A - Z_B) \, r_e - \int_{-\infty}^{\infty} \Psi_e^{\dagger}(\vec{r}) \, \vec{r} \, \Psi_e(\vec{r}) \, d\tau = \int_{-\infty}^{\infty} z_e(r) \, dr = \mu_o/e \qquad (B.4)$$

Here Z_A and Z_B are the nuclear charges, $\Psi_e(\vec{r})$ is the total electron wave function of molecule AB with bond distance r_e , and $z_e(r)$ is the net charge at r , where r is along the molecular axis, and r = o is midway between atoms. For atomic separations different from r_e , the same formula as Eq. (B.4) applies with r_e replaced by some other value say s , z_o by z , and μ_o by μ.

It is tempting to determine whether z_o could be derived from Pauling's electronegativity concept (Ref. 19). Pauling defines a bond energy Δ' which is due to the electric attraction only:

$$\Delta'(A{-}B) = D(A{-}B) - \left\{ D(A{-}A) \cdot D(B{-}B) \right\}^{1/2} \qquad (B.5)$$

Here D(A–B) is the actual measured bond or dissociation energy of the molecule A–B and D(A–A) and D(B–B) are the measured bond energies for the covalent molecules A–A and B–B. Pauling expresses the Δ' and D's in units of kcal/mole = 0.0433 eV/molecule and further introduces the parameter x_X, called "the electronegativity of atom X" via the relation:

$$x_A - x_B = \sqrt{\Delta' \text{ (kcal/mole)}/30} \qquad \text{(B.6)}$$

In Tables B-1 and B-2, values of Δ' and x_X are given which were taken from Ref. 19.

If Δ' is due to a nonsymmetric distribution of electric charge on and between atoms A and B, we must have:

$$\Delta' = e^2 \int_{-\infty}^{\infty} \frac{-z_e^2(r)}{r^2}\, dr = \frac{e^2\ z_o^2}{r_e\ f_e} \qquad \text{(B.7)}$$

where:

$$f_e = \frac{\left[\int_{-\infty}^{\infty} z_e(r)\ dr\right]^2}{r_e \int_{-\infty}^{\infty} -z_e^2(r) \left(\frac{r_e}{r}\right)^2 dr} \qquad \text{(B.8)}$$

Solving for z_o, we have then:

$$z_o = 0.05484\ (\Delta'\ r_e\ f_e)^{1/2} \qquad \text{(B.9a)}$$
$$\left(\frac{\text{kcal}}{\text{mole}}\right)(\text{A}^\circ)$$

TABLE B-1. EXTRA IONIC ENERGY OF BONDS AND ELECTRONEGATIVITY DIFFERENCES OF THE BONDED ATOMS (Ref. 19)*

BOND	Δ'	$0.18\sqrt{\Delta'}$	$x_A - x_B$
C—H	5.8	0.4	0.4
Si—H	4.0	.4	.3
N—H	30.1	1.0	.9
P—H	3.3	0.3	.0
As—H	0.8	.2	.1
O—H	41.8	1.2	1.4
S—H	8.3	0.5	0.4
Se—H	− 1.6	—	.3
Te—H	− 1.9	—	.0
H—F	72.9	1.5	1.9
H—Cl	25.4	0.9	0.9
H—Br	18.2	0.8	.7
H—I	10.1	.6	.4
C—Si	10.0	.6	.7
C—N	13.2	.7	.5
C—O	31.5	1.0	1.0
C—S	− 2.4	—	0.0
C—F	50.2	1.3	1.5
C—Cl	9.1	0.5	0.5
C—Br	4.0	.4	.3
C—I	2.6	.3	.0
Si—O	50.7	1.3	1.7
Si—S	7.8	0.6	0.7
Si—F	90.0	1.7	2.2
Si—Cl	36.2	1.1	1.2
Si—Br	25.0	0.9	1.0
Si—I	11.8	.6	0.7
Ge—Cl	50.8	1.3	1.2
N—F	27.0	0.9	1.0
N—Cl	0.5	.1	0.0
P—Cl	24.5	.9	.9
P—Br	16.7	.7	.7
P—I	8.3	.5	.4
As—F	77.0	1.6	2.0
As—Cl	25.8	0.9	1.0
As—Br	18.0	.8	0.8
As—I	7.5	.5	.5
O—F	9.3	.5	.5
O—Cl	4.6	.4	.5
S—Cl	5.3	.4	.5
S—Br	2.2	.3	.3
Cl—F	14.5	.7	1.0
Br—Cl	0.6	.1	0.2
I—Cl	4.5	.4	.5
I—Br	1.7	.3	.3

* Δ' is in Kcal/mole

TABLE B-2. ELECTRONEGATIVITY VALUES FOR SOME ELEMENTS BASED ON x_H = 2.1 (Ref. 19)

H 2.1			
C 2.5	N 3.0	O 3.5	F 4.0
Si 1.8	P 2.1	S 2.5	Cl 3.0
Ge 1.8	As 2.0	Se 2.4	Br 2.8
			I 2.5

If we apply Eq. (B.9a) to the covalent molecule CO, using $\Delta' = 31.5$ kcal/mole (see Table B-1) and $r_e = 1.1281$ Angstrom as before, we find:

$$\left(z_o\right)_{CO} = 0.327\ f_e^{1/2} \tag{B.9b}$$

Comparing this result with the measured value of $(z_o)_{CO} = 0.0207$, we see that $(f_e^{1/2})_{CO} = 0.0633$. Making the same comparison for an ionic molecule such as HCℓ, we find that $(z_o)_{HC\ell} = 0.176$, and $(f_e)_{HC\ell}^{1/2} = 0.565$. Thus the more ionic, the larger the value of f_e is. If no measured dipole moment μ_o is available from which we can obtain $z_o = \mu_o/(e\ r_e)$, but values for Δ' and r_e are known one might use as a coarse approximation $f_e^{1/2} \approx 0.25$ and thus from Eq. (B.9a):

$$z_o \approx 0.0137 \sqrt{\Delta'\ (\text{kcal/mole})\ r_e\ (\text{A}^\circ)} \tag{B.10}$$

A better approach is probably to use Eq. (B.9a) and to estimate a value for $f_e^{1/2}$ between 0.02 and 0.7 depending on how covalent or ionic the bond is.

Of course a directly-measured value of z_o is always to be preferred over one obtained from (B.9a) or (B.10). Table B-3 lists measured, calculated, or estimated values of a large number of dipole moments and z_o values of diatomic molecules and radicals taken from Refs. 2, 15, 16, and 20. Note that in the literature the value of the dipole moment μ_o is given usually in units of debyes, which is related to z_o by:*

$$z_o = \frac{\mu_o}{e\ r_e} = 0.2801\ \frac{\mu_o(\text{debyes})}{r_e(\text{Angstroms})} \tag{B.11}$$

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*1 debye = 10^{-18} erg$^{1/2}$ cm$^{3/2}$ (esu); 1 Angstrom = 10^{-8} cm = 10^{-10} m.

TABLE B-3. MEASURED OR CALCULATED DIATOMIC DIPOLE MOMENTS AND CHARGES TAKEN OR DEDUCED FROM DATA IN REFS. 2, 10, 11, 15, 16, 19, AND 20

Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1	Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1
CO	1.12809	0.112	0.0207	-0.630	HBr	1.4128	0.82	0.1208	+0.055
CS	1.5344	1.98	0.2687	-0.102	HI	1.604	0.44	0.0533	+0.035
CH	1.1198	1.46	0.2715	+0.110	HS	1.350	0.861	0.1328	+0.062
CD	1.1173		(0.250)	+0.100	SF	(1.63)		(0.245)	(+0.175)
CN	1.1718	⟨0.384⟩	⟨0.0682⟩	-0.870	SCℓ			(0.121)	
CP	1.5621		(0.085)	-0.510	SBr			(0.075)	
CSe			(0.165)		SO	1.4933	1.55	0.2161	-0.255
CF	1.271	⟨0.668⟩	⟨0.1095⟩	-0.700	PO	1.4478		(0.045)	-0.620
CCℓ	(1.96)	(0.400)	(0.0425)	-0.450	PF			(0.078)	
CBr	(2.11)	(0.302)	(0.0298)	-0.455	PCℓ			(0.038)	
CI	(2.35)	(0.167)	(0.0148)	-0.385	PBr			(0.023)	
CSi			(0.065)		PI			(0.015)	
OH	0.9706	1.66	0.3561	+0.0963	PD	1.429		(0.070)	
OD	0.9699	(1.57)	(0.3370)	+0.085	PH	1.4318	⟨0.5185⟩	⟨0.0754⟩	+0.032
OB	1.2039		(0.066)	-0.890	PN	1.4910	3.241	0.4526	-0.600
OF			(0.030)		SiH	1.520	⟨0.624⟩	⟨0.0855⟩	+0.055
OCℓ			(0.021)		SiD	1.528		(0.0825)	+0.055
OBr			(0.020)		SiN	1.5708		(0.256)	-0.152
NH	1.0380	1.016	0.2038	+0.070	SiO	1.5101	3.397	-0.4684	-1.60
ND	1.0398	(0.98)	(0.1962)	+0.067	SiS	1.9283	⟨1.083⟩	-⟨0.1170⟩	-0.77
NB	1.281		(0.120)	-0.722	SiSe			(0.085)	
NC	1.1508	0.153	0.0277	-0.973	SiTe			(0.065)	
NS	1.565		(0.230)	-0.305	SiF	1.603	⟨2.789⟩	-⟨0.3623⟩	-1.38
NF			(0.080)		SiCℓ			(0.123)	
NCℓ			(0.040)		SiBr			(0.090)	
NBr			(0.027)		SiI			(0.045)	
HD	0.74126		0	0	AsH			(0.120)	
HLi	1.59525	5.88	- 0.7674	-2.25	AsN			(0.250)	
HB	1.2325	1.584	0.2676	+0.105	AsF			(0.112)	
HBe	1.3431	0.282	0.0437	-0.722	AsCℓ			(0.050)	
HF	0.9171	1.82	0.4132	+0.0533	AsBr			(0.025)	
HCℓ	1.27460	1.08	0.1764	+0.0826	AsI			(0.017)	

* Angstrom = 10^{-8} cm = 10^{-10} m; ** 1 Debye = 10^{-18} $\mathrm{erg}^{1/2}$ $\mathrm{cm}^{3/2}$

NOTE: ( ) = Estimated values; ⟨ ⟩ = Values calculated via Pauling's Δ′ parameters.

TABLE B-3. MEASURED OR CALCULATED DIATOMIC DIPOLE MOMENTS AND CHARGES TAKEN OR DEDUCED FROM DATA IN REFS. 2, 10, 11, 15, 16, 19, AND 20 (Cont.)

Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1
AsO				
CℓF	1.62813	0.88	0.1125	-0.433
BrD	1.413	0.79	0.1164	+0.055
BrCℓ	(1.9)	0.57	(0.0625)	-0.440
BrF	1.7555	1.29	0.1530	-0.305
ICℓ	2.32069	0.65	0.0583	-0.325
IBr				
IN				
ID	1.72	0.38	0.0460	+0.026
SeH			(0.125)	
SeF			(0.260)	
SeO			(0.205)	
AgH	1.6174			
AgD	1.6172			
AgF				
AgCℓ	(2.62)	5.73	-(0.4553)	-1.062
AgBr				
AgO				
AℓH	1.6459			
AℓD	1.6456			
AℓF	1.654	1.53	0.1926	-0.255
AℓCℓ	2.138	1.28	0.1247	-0.273
AℓBr	2.295			
AℓI				
AℓO	1.6176			
AuH	1.5237			
AuD	1.5237			
AuCℓ				
BaH	2.2318			
BaF				
BaCℓ				
BaBr				
BaI				
BaO	1.940	7.954	-0.8537	-2.15
BaS				
BD	1.2311			
BF	1.262	0.883	0.1457	-0.625
BCℓ	1.7147		(0.073)	-0.470
BBr	1.887		(0.056)	-0.470
BeD	1.3425			
BeF	1.3614			
BeCℓ	1.7			
BeBr				
BeO	1.3308	7.353	-1.1504	-3.05
BeS	1.746			
BiH	1.809			
BiD	1.805			
BiF			(0.200)	
BiCℓ			(0.130)	
BiBr			(0.050)	
BiI				
BiO				
BiS				
CaH	2.0020			
CaD	1.001			
CaF	2.02			
CaCℓ	1.86			
CaBr				
CaI				
CaO	1.821	10.946	-1.2515	-2.85
CaS				
CdH	1.7607			
CdD	1.748			
CdF				

* 1 Angstrom = 10^{-8} cm = 10^{-10} m; ** 1 Debye = 10^{-18} erg$^{1/2}$ cm$^{3/2}$

TABLE B-3. MEASURED OR CALCULATED DIATOMIC DIPOLE MOMENTS AND CHARGES TAKEN OR DEDUCED FROM DATA IN REFS. 2, 10, 11, 15, 16, 19, AND 20 (Cont.)

Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1	Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1
CdCℓ					GaH				
CdBr					GaF				
CdI					GaCℓ				
CdO					GaBr				
CdS					GaI				
CdSe					GaO				
CℓO					GeH				
CoH	1.5423				GeF				
CoF					GeCℓ			(0.155)	
CoBr					GeBr			(0.105)	
CoCℓ					GeI				
CoO					GeO	1.6497			
CrH					GeS				
CrF					GeSe				
CrCℓ					GeTe				
CrO					HgH	1.7404			
CsH	2.494				HgD	1.7378			
CsF	2.34	7.88	-0.7011	-1.65	HgF				
CsCℓ	3.06	10.42	-0.7090	-1.17	HgCℓ	2.23			
CsBr	3.14	(11.0)	-(0.7290)	-1.14	HgBr				
CsI	3.41	12.1	-0.7388	-0.97	HgI	1.6041			
CuH	1.4631				HgO				
CuD	1.46253				HgS				
CuF	1.743				HgSe				
CuCℓ					InH	1.8376			
CuBr					InF				
CuI					InCℓ	2.318			
CuO					InBr	2.57			
FeH					InI	2.86			
FeF					InO				
FeCℓ					IO				
FeO					KH	2.244			

* 1 Angstrom = 10^{-8} cm = 10^{-10} m; ** 1 Debye = 10^{-18} erg$^{1/2}$ cm$^{3/2}$

TABLE B-3. MEASURED OR CALCULATED DIATOMIC DIPOLE MOMENTS AND CHARGES TAKEN OR DEDUCED FROM DATA IN REFS. 2, 10, 11, 15, 16, 19, AND 20 (Cont.)

Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1	Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1
KD	2.288				NaD	1.8865			
KF	2.553	8.60	-0.7014	-1.52	NaF	1.9198	8.16	-0.8850	-2.22
$\mathrm{KC\ell}$	2.79	10.27	-0.7664	-1.50	$\mathrm{NaC\ell}$	2.3733	8.50	-0.7457	-1.67
KBr	2.94	10.41	-0.7372	-1.28	NaBr	2.5024	8.74	-0.7272	-1.58
KI	3.23	11.05	-0.7123	-1.09	NaI	2.88			
LiNa	2.91				NiH	1.4736			
LiD	1.5949				NiF				
LiB	2.434				$\mathrm{NiC\ell}$				
LiC	2.011				NiBr				
LiN	1.799				NiO				
LiF	1.564	6.33	-0.8427	-2.305	PbH	1.839			
$\mathrm{LiC\ell}$	2.492	7.12	-0.5949	-1.385	PbF				
LiBr	2.151	7.27	-0.7037	-1.755	$\mathrm{PbC\ell}$				
LiI	(2.0)	7.43	-(0.7735)	-1.915	PbBr				
LiO	1.685				PbI				
MgH	1.7306				PbO	2.02			
MgD	1.76				PbS	2.3938			
MgF	1.752				PbSe				
MgBr					PbTe				
$\mathrm{MgC\ell}$					RbH	2.367			
MgI					RbF	2.310	8.55	-0.7706	-1.76
MgO	1.749	8.342	-1.0526	-2.495	$\mathrm{RbC\ell}$	2.89			
MnH	1.73075				RbBr				
MnF					RbI	3.26			
$\mathrm{MnC\ell}$					SbF			(0.175)	
MnBr					$\mathrm{SbC\ell}$			(0.080)	
MnI					SbBr			(0.040)	
MnO					SbI				
MnS					SbN				
MoH					SbO				
MoF	(1.98)		-(0.290)	-1.07	ScF	1.752	4.64	-0.5514	-1.795
NaH	1.8873				ScO	1.614	2.6	-0.3354	-1.325

* 1 Angstrom = 10^{-8} cm = 10^{-10} m; ** 1 Debye = 10^{-18} $\mathrm{erg}^{1/2}$ $\mathrm{cm}^{3/2}$

TABLE B-3. MEASURED OR CALCULATED DIATOMIC DIPOLE MOMENTS AND CHARGES TAKEN OR DEDUCED FROM DATA IN REFS. 2, 10, 11, 15, 16, 19, AND 20 (Cont.)

Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1	Molecule or Radical	Atomic Separation* r_e (Angstrom)	Dipole Moment** μ_o (Debyes)	Dipole Charge z_o	Dipole Charge z_1
SnH	1.785				UH				
SnF					UF	(2.32)		-(0.305)	-0.940
SnCℓ			(0.175)		UCℓ			-(0.210)	
SnBr			(0.120)		UBr			-(0.120)	
SnI					UI			-(0.063)	
SnO	1.8369				UO			-(0.250)	
SnS	2.06				VF				
SnSe					VO	1.540			
SnTe					WH				
SrH	2.1455				WF	(1.98)		-(0.280)	-1.060
SrD	2.1448				WCℓ				
SrF					WBr				
SrCℓ					WI				
SrBr					WO				
SrI					WS				
SrO	1.921	8.90	-0.9646	-2.33	ZnH	1.5945			
SrS					ZnD	1.6048			
TeH			(0.120)		ZnF				
TeF	(1.89)		-(0.240)	-0.983	ZnCℓ				
TeO			(0.215)		ZnBr				
TiH					ZnI				
TiF					ZnO				
TiCℓ			-(0.310)		ZnS				
TiBr					ZnSe				
TiI					ZnTe				
TiO	1.620	4.25	-0.5462	-1.73	ZrH				
TℓH	1.870				ZrD				
TℓF	2.42	4.23	-0.3639	-1.00	ZrF				
TℓCℓ	2.55	4.444	-0.3629	-0.94	ZrCℓ				
TℓBr	2.68				ZrBr				
TℓI	2.87				ZrI				
TℓO					ZrO	1.416			

* 1 Angstrom = 10^{-8} cm = 10^{-10} m; ** 1 Debye = 10^{-18} erg$^{1/2}$ cm$^{3/2}$

Whereas values of μ_o and hence z_o are available for a relatively large number of molecules, measured values of μ_1 or z_1 are rather scarce. In the following we shall therefore derive an approximate expression which allows the calculation of z_1, if z_o and r_e are known.

If s is the separation between the mass centers of atoms or groups of atoms A and B of a normal vibration of a molecule, and if these mass centers have an effective charge Z_A^{eff} and Z_B^{eff} respectively for the valence electrons that bind them, then the dipole moment of the molecule may be written (see Eq. B.4):

$$\mu/e = zs = \left(Z_A^{eff} - Z_B^{eff}\right)\frac{s}{2} - \int \rho_e \, r \cos\theta \, dV = \mu_N/e - \mu_e/e = z_N s - z_e s \qquad (B.12)$$

Here $\rho_e(r,\theta)$ is the density of the valence electrons, and as reference frame we use the spherical coordinate system (r,θ,ϕ), with θ measured from the molecular axis $(0 < \theta < \pi)$, and r measured from the center midway between A and B $(0 < r < \infty)$. Because there is complete symmetry for the coordinate $\phi(0 < \phi < 2\pi)$, the volume element $dV = 2\pi \, r^2 \sin\theta \, d\theta \, dr$. Then setting $q = \cos\theta$, we can write for the electronic contribution in (B.12):

$$\frac{\mu_e}{e} = z_e s = \int_{\theta=o}^{\pi} \int_{r=o}^{\infty} \rho_e \, r \cos\theta \, (2\pi r^2 \sin\theta \, d\theta \, dr) = \int_{q=1}^{-1} \int_{r=o}^{\infty} 2\pi\rho_e \, q dq \, r^3 dr \qquad (B.13)$$

Note that Eq. (5.12) differs from (B.4) in that we make the reasonable assumption that inner-shell electrons on the atoms A and B do not participate in determining the dipole and only valence electrons are involved. Also we shall use a classically-derived electron density ρ_e instead of the quantum-mechanical formulation in Eq. (B.4). We obtain the parameter ρ_e by relating it to the electric potential φ around the molecule as in the Thomas-Fermi model of the atom. In the Thomas-Fermi theory it is shown via the imposition of momentum-space quantization and the virial theorum (see for example pp. 190-197, Ref. 52) that:

$$\rho_e = -\frac{8\pi}{3}\frac{e}{h^3}\left\{2m_e\, e\varphi\right\}^{3/2} \qquad (B.14)$$

For spherically symmetric single atoms of charge Z, Eq. (B.14) together with Poisson's formula

$$\nabla^2\varphi = \frac{1}{r}\frac{d^2}{dr^2}(r\varphi) = -4\pi\rho_e\ , \qquad (B.15)$$

and with appropriate boundary conditions (see pp. 190-197, Ref. 52), leads to the well-known Thomas-Fermi potential:

$$\varphi(r) = \frac{Ze}{r}\Phi(\xi)\ , \qquad (B.16)$$

where $\Phi(\xi)$ is a universal function satisfying the differential equation:

$$\Phi'' = \xi^{-1/2}\,\Phi^{3/2} \qquad (B.17)$$

with:

$$\xi = r/a \qquad (B.18)$$

and:

$$a = \left(\frac{9\pi^2}{128\ Z}\right)^{1/3}\left(\frac{h^2}{4\pi^2 m_e e^2}\right) \tag{B.19}$$

The so-called electron-self-screening function or factor $\Phi(\xi)$ has been approximated by various analytical expressions, the simplest ones of which are (see Ref. 53):

$$\underset{\text{(Exponential Approximation)}}{\Phi(\xi)} = \exp-(0.9\xi) \tag{B.20}$$

$$\underset{\text{(Rosenthal's Approximation)}}{\Phi(\xi)} = 0.7345\left\{\exp-(0.562\xi)\right\} + 0.2655\left\{\exp-(3.392\xi)\right\} \tag{B.21}$$

The Thomas-Fermi solution $\Phi(\xi)$ as solved from (B.17) applies strictly only for an atom with a spherically-symmetric electric potential. In our case of a molecule we have no longer complete spherical symmetry, and the field φ depends now on both r and θ. One could in the same manner as was done by Thomas and Fermi for the atom, solve for a self-consistent φ of a molecule by using the Poisson relation:

$$\nabla^2\varphi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\varphi}{\partial\theta}\right) = -4\pi\rho_e(r,\theta) =$$

$$= \frac{32\pi^2}{3}\frac{e}{h^3}(2m_e e)^{3/2}\left\{\varphi(r,\theta)\right\}^{3/2} \tag{B.22}$$

and imposing appropriate boundary conditions to solve for $\varphi(r,\theta)$.

However instead of following this more exact program, we shall make an approximation and use the Thomas-Fermi result (B.16), assuming that for a molecule:

$$\varphi(r,\theta) \approx \left[\frac{\left(Z_A^{eff} + Z_B^{eff}\right)e}{r} + \left(Z_A^{eff} - Z_B^{eff}\right)\frac{es}{2}\frac{\cos\theta}{r^2}\right]\exp-\left(\eta\frac{r}{a}\right) =$$

$$= \left[\frac{Z_e e}{r} + \frac{Z_d e}{2}\frac{s\cos\theta}{r^2}\right]\exp-\left(\frac{r}{b}\right) , \qquad (B.23)$$

where for convenience we abbreviate:

$$Z_A^{eff} + Z_B^{eff} = Z_e \qquad (B.24)$$

$$Z_A^{eff} - Z_B^{eff} = Z_d \qquad (B.25)$$

and:

$$b = \frac{a}{\eta} = \frac{a_H}{\eta Z_e^{1/3}}\left(\frac{9\pi^2}{128}\right)^{1/3} = 0.8853\frac{a_H}{\eta Z_e^{1/3}} \qquad (B.26)$$

$$a_H = \frac{h^2}{4\pi^2 m_e e^2} = 0.52917 \text{ , Angstrom} \qquad (B.27)$$

In (B.23) we assumed a simple exponential electron self-screening factor for a molecule just like (B.20) for the atom, that is:

$$\Phi\left(\frac{r}{a}\right) = \exp - \eta\left(\frac{r}{a}\right) , \qquad (B.28)$$

except that we leave the coefficient η undetermined for the moment. We shall see that η is a rather sensitive parameter and therefore instead of setting $\eta = 0.9$ or $\eta = 0.562$ (for larger values of $\xi = r/a$ according to (B.21)), we shall compare our ultimate results with experiment to determine the best value of η. It should be kept in mind here also that the Thomas-Fermi differential equations for the atomic field are only valid for intermediate values of $\xi = r/a$ and no longer hold for very small or very large values of ξ.

The two terms in the brackets of (B.23) are the unscreened or bare potentials from a central coulomb field (the first term) and a dipole field (the second term), created by dissimilar charges Z_A^{eff} and Z_B^{eff}. That is:

$$\varphi_{dipole} = \mu_N \frac{\cos\theta}{r^2} = \frac{Z_d e}{2} \frac{s \cos\theta}{r^2} \qquad (B.29)$$

The coulomb and dipole potentials are assumed to be simply additive.

To determine how well the approximation (B.23) satisfies Poisson's equation, we can substitute (B.23) in (B.22) with the result:

$$\frac{Z_e r}{b^2} + \frac{Z_d s \cos\theta}{b^2}\left(\frac{1}{2} + \frac{b}{r}\right) \sim \frac{8\sqrt{2}}{3\pi}\left\{\exp-\left(\frac{r}{2b}\right)\right\}\left\{\frac{Z_e r^{1/3}}{a_H} + \frac{Z_d s \cos\theta}{2a_H r^{2/3}}\right\}^{3/2} \qquad (B.30)$$

Now the approximate solution (B.16) is known to give reasonable results at medium distances r around an atom. That is from the pure coulombic portion of (B.30) we must have that:

$$\frac{Z_e r}{b^2} \sim \frac{8\sqrt{2}}{3\pi} \left\{ \exp-\left(\frac{r}{2b}\right) \right\} \frac{Z_e^{3/2}\ r^{1/2}}{a_H^{3/2}} , \qquad (B.31a)$$

or:

$$\left\{ \exp- \frac{r}{b} \right\}^{1/2} \sim 0.8538 \left(\frac{r}{b}\right)^{1/2} \qquad (B.31b)$$

Obviously the approximation (B.31b) can only hold for values of $r \sim b$. That is for $0.2 \lesssim \frac{r}{b} \leqslant 2$, the difference Δ between the left- and right-hand side varies from 0.523 to -0.840. To the same approximation, that is over the same range of values of r for which (B.31) has an error less than $\Delta \approx \pm 0.8$, the dipole portion of (B.30) should also hold since $s \sim b \sim a_H$. In conclusion, the assumed field (B.23) should not be much less approximate than the Thomas-Fermi solution (B.16) with the approximation $\Phi(r/a) = \exp-(r/b)$.

Using Eqs. (B.13), (B.14), and (B.23), the dipole moment of the electrons of the molecule can now be expressed in terms of the separation s:

$$\mu_e = z_e es = - \frac{16\pi^2}{3} \frac{e}{h^3} \left(2m_e e^2\right)^{3/2} \int_{q=1}^{-1} \int_{r=o}^{\infty} q\ dq\ r^3 dr \cdot \left\{ \frac{Z_e}{r} + \frac{Z_d}{2} \frac{sq}{r^2} \right\}^{3/2} \exp-\left(\frac{3}{2}\frac{r}{b}\right) =$$

$$\mu_e = \frac{16^2\pi^2 e}{15h^3} \Gamma\left(\frac{7}{2}\right) \left(2m_e e^2\right)^{3/2} \left(\frac{2}{3}\ b\right)^{9/2} \left(\frac{Z_e^{7/2}}{Z_d^2 s^2}\right) \cdot \Bigg[\left\{ \cosh\left(\frac{3\ Z_d\ s}{4\ Z_e\ b}\right) \right\} \Bigg\{ \frac{3\ Z_d\ s}{4\ Z_e\ b} +$$

$$+ \frac{9}{7}\ \mathrm{gam}\left(\frac{3\ Z_d\ s}{4\ Z_e\ b}\ ;\ \frac{9}{2}\right) \Bigg\} - \left\{ \sinh\left(\frac{3\ Z_d\ s}{4\ Z_e\ b}\right) \right\} \cdot$$

$$\cdot \left\{ \frac{9}{7} + \left(\frac{3\ Z_d\ s}{4\ Z_e\ b}\right) \mathrm{gam}\left(\frac{3\ Z_d\ s}{4\ Z_e\ b}\ ;\ \frac{7}{2}\right) \right\} \Bigg] \qquad (B.32)$$

Here $\Gamma(x)$ is the gamma function $\left(\Gamma(\frac{7}{2}) = 3.323\right)$ and gam(x;p) is the normalized incomplete gamma function defined by:

$$\text{gam}(x;p) = \frac{\Gamma(x\ ;\ p+1)}{\Gamma(\infty\ ;\ p+1)} = \frac{\Gamma(x\ ;\ p+1)}{\Gamma(p+1)} \qquad (B.33)$$

where:

$$\Gamma(x\ ;\ p+1) = \int_0^x e^{-x}\, x^p\, dx \qquad (B.34)$$

In Ref. 54, values of the incomplete gamma function:

$$I(u;p) \equiv I\left(\frac{x}{\sqrt{p+1}}\ ;\ p\right) \equiv \text{gam}(x;p) \qquad (B.35a)$$

are tabulated. Thus to obtain gam(x,p), where x and p are particular values, we first calculate u from the relation:

$$u = \frac{x}{\sqrt{p+1}}\ , \qquad (B.35b)$$

and then look up the value of I(u,p) from Pearson's tables (Ref. 54).

From Eqs. (B.32) and (B.12), the dipole charge $z = z(s)$ is finally:

$$z = \frac{\mu}{es} = \frac{\mu_N - \mu_e}{es} =$$

$$z(s) = \frac{Z_A^{eff} - Z_B^{eff}}{2} - \frac{C}{s^3} \cdot \left(\frac{Z_A^{eff} + Z_B^{eff}}{Z_A^{eff} - Z_B^{eff}} \right)^2 \cdot \left[\left\{ \cosh\left(\frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} \right) \right\} \cdot \right.$$

$$\cdot \left\{ \frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} + \frac{9}{7} \operatorname{gam}\left(\frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} ; \frac{9}{2} \right) \right\} - \left\{ \sinh\left(\frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} \right) \right\} \cdot$$

$$\left. \cdot \left\{ \frac{9}{7} + \left(\frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} \right) \operatorname{gam}\left(\frac{3s}{4b} \frac{Z_A^{eff} - Z_B^{eff}}{Z_A^{eff} + Z_B^{eff}} ; \frac{7}{2} \right) \right\} \right] \tag{B.36}$$

where the constant:

$$C = \frac{\Gamma\left(\frac{7}{2}\right) \times 16^2 \times \pi^2}{15h^3} \left(2m_e e^2\right)^{3/2} \left\{ \left(\frac{9\pi^2}{128} \right)^{1/3} \frac{2a_H}{3\eta} \right\}^{9/2} =$$

$$= 0.8807 \times 10^{-25}\ \eta^{-9/2}\ ,\ \text{cm}^3 = \frac{0.0881}{\eta^{9/2}}\ \text{Å}^3 \tag{B.37}$$

We shall assume next that the potential field via which we calculated (B.36) only applied to the excess electronic charge which is not evenly distributed about the two atoms. That is we shall assume that all other internal electron charge distributions about the atoms of the molecule are evenly distributed. Then since we can define Z_A^{eff} to be always larger than Z_B^{eff}, we have $Z_B^{eff} = 0$, and thus:

$$\frac{Z_A^{eff} + Z_B^{eff}}{Z_A^{eff} - Z_B^{eff}} = \frac{Z_A^{eff}}{Z_A^{eff}} = 1 \, , \tag{B.38}$$

so that (B.36) becomes:

$$z(s) = \frac{Z_d}{2} - \left(\frac{0.0881\eta^{9/2}}{s^3_{(A)}}\right) \cdot \left[\left\{\cosh\left(\frac{3s}{4b}\right)\right\} \cdot \left\{\frac{3s}{4b} + \frac{9}{7}\,\text{gam}\left(\frac{3s}{4b}\,;\,\frac{9}{2}\right)\right\} + \right.$$

$$\left. - \left\{\sinh\left(\frac{3s}{4b}\right)\right\} \cdot \left\{\frac{9}{7} + \frac{3s}{4b}\,\text{gam}\left(\frac{3s}{4b}\,;\,\frac{7}{2}\right)\right\} \right] \tag{B.39}$$

Note that because of (B.38) we now have also $Z_d = Z_e = Z_A^{eff}$ and thus:

$$b = 0.8853\,\frac{a_H}{\eta Z_d^{1/3}} = \frac{0.4685}{\eta Z_d^{1/3}}\,\text{Å} \tag{B.40}$$

Defining:

$$d = \frac{4}{3}\,\eta Z_d^{1/3}\, b = \frac{4}{3} \times 0.8853\, a_H = 0.6347\,\text{Å} \, , \tag{B.41}$$

we can rewrite Eq. (B.39) finally in the convenient form:

$$\boxed{\begin{aligned} z(s) &= \frac{Z_d}{2} - \left(\frac{C}{s^3}\right) \cdot \left[\left\{\cosh\left(\frac{Z_d^{1/3}\eta s}{d}\right)\right\} \cdot \left\{\frac{Z_d^{1/3}\eta s}{d} + \frac{9}{7}\,\text{gam}\left(\frac{Z_d^{1/3}\eta s}{d}\,;\,\frac{9}{2}\right)\right\} + \right. \\ &\left. - \left\{\sinh\left(\frac{Z_d^{1/3}\eta s}{d}\right)\right\} \cdot \left\{\frac{9}{7} + \frac{Z_d^{1/3}\eta s}{d}\,\text{gam}\left(\frac{Z_d^{1/3}\eta s}{d}\,;\,\frac{7}{2}\right)\right\} \right] \\ &\text{(s is in Angstroms = } 10^{-8} \text{ cm throughout)} \end{aligned}} \tag{B.42}$$

Note that $z = 0$ if $Z_d = 0$ as expected.

The permanent dipole moment $\mu_o = e r_e z_o$ or dipole charge z_o is readily obtained from (B.42) by setting $s = r_e$:

$$z_o = \frac{Z_d}{2} - \frac{0.0881}{\eta^{4.5} r_e^3}\left[\left\{\cosh\left(\frac{Z_d^{1/3} r_e \eta}{0.6247}\right)\right\}\cdot\left\{\frac{Z_d^{1/3} r_e \eta}{0.6247} + \frac{9}{7}\,\mathrm{gam}\left(\frac{Z_d^{1/3} r_e \eta}{0.6247};\frac{9}{2}\right)\right\} + \right.$$

$$\left. - \left\{\sinh\left(\frac{Z_d^{1/3} r_e \eta}{0.62497}\right)\right\}\cdot\left\{\frac{9}{7} + \frac{Z_d^{1/3} r_e \eta}{0.6247}\,\mathrm{gam}\left(\frac{Z_d^{1/3} r_e \eta}{0.6247};\frac{7}{2}\right)\right\}\right]$$

(r_e is in Angstroms = 10^{-8} cm)

(B.43)

Defining for convenience the function:

$$\mathrm{dip}(p) = \left\{\cosh p\right\}\left\{p + \frac{9}{7}\,\mathrm{gam}\left(p\,;\,\frac{9}{2}\right)\right\} - \left\{\sinh p\right\}\left\{\frac{9}{7} + p\,\mathrm{gam}\left(p\,;\,\frac{7}{2}\right)\right\},$$

(B.44)

which is plotted in Figure B-1, we can rewrite (B.43) in the compact form:

$$z_o = \frac{0.3124}{\eta r_e}\,p_d - \frac{0.0881}{\eta^{4.5} r_e^3}\,\mathrm{dip}(p_d) \qquad \text{(B.45)}$$

Here p and p_d are defined by:

$$p = \frac{Z_d\, s\, \eta}{0.6247} \qquad \text{(B.46)}$$

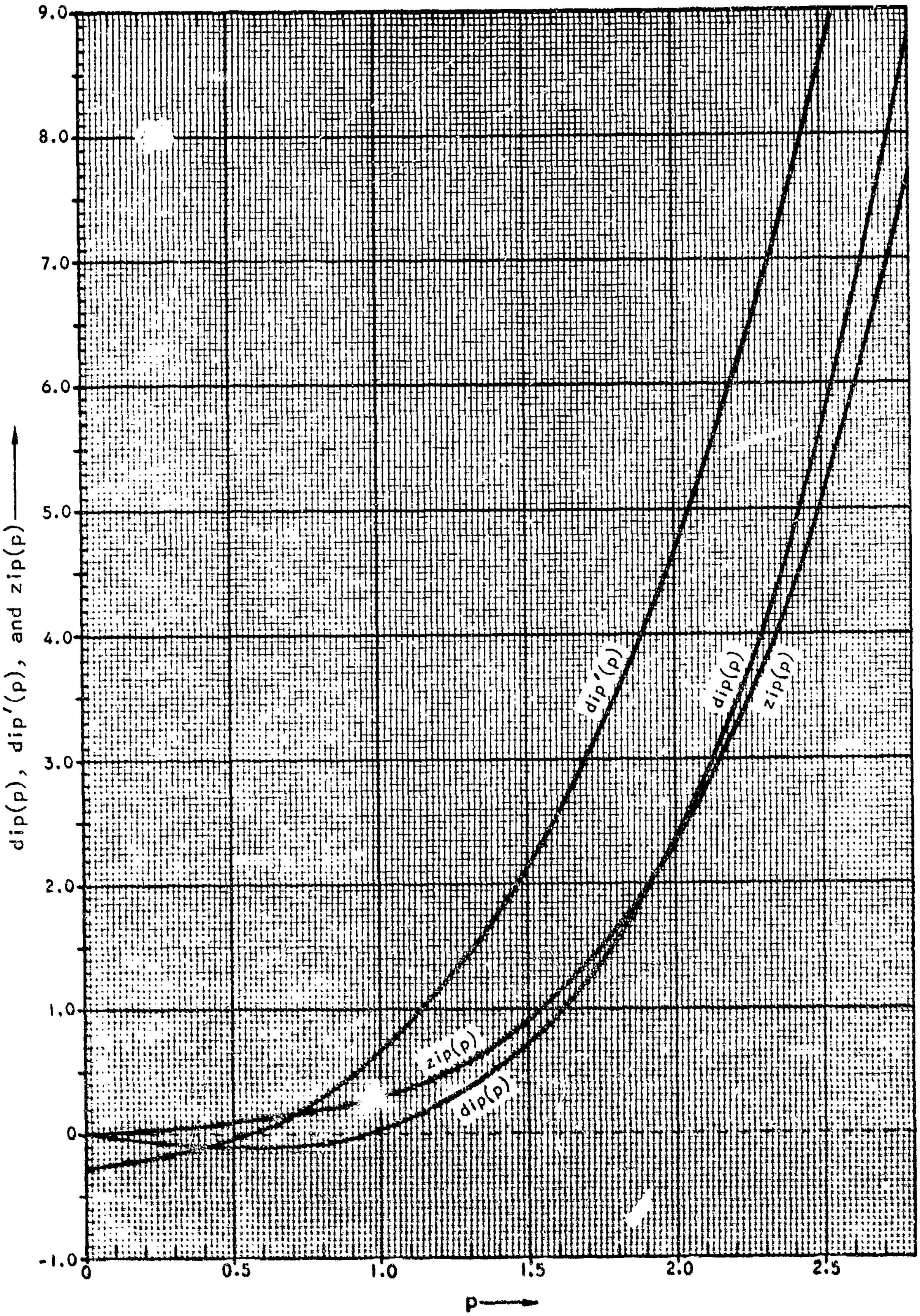

FIGURE B-1. PLOTS OF THE FUNCTIONS dip(p), zip(p), and dip'(p)

$$\boxed{p_d = \frac{Z_d\, r_e\, \eta}{0.6247}} \tag{B.47}$$

The first-order dipole moment derivative $\mu_1 = (\partial\mu/\partial s)_{r=r_e} = ez_1$ may be obtained next from (B.42). The result is:

$$z_1 = \frac{\mu_1}{e} = \left(\frac{\partial(sz)}{\partial s}\right)_{r=r_e} = \frac{Z_d}{2} + 2\left(\frac{0.0881}{\eta^{4.5} r_e^3}\right) \mathrm{dip}(p_d) \; + \; - \left(\frac{0.0881}{\eta^{4.5} r_e^2}\right)\left(\frac{Z_d\, \eta}{0.6247}\right)\left(\frac{d}{dp}\,\mathrm{dip}(p)\right)_{p=p_d} \tag{B.48}$$

Equation (B.48) may be rewritten in the compact form:

$$\boxed{z_1 = \frac{0.3124}{\eta\, r_e}\, p_d - \frac{0.1762}{\eta^{4.5} r_e^3}\, \mathrm{zip}(p_d)} \tag{B.49}$$

where the function zip(p) is defined by:

$$\boxed{\mathrm{zip}(p) \equiv \frac{p}{2}\, \mathrm{dip}'(p) - \mathrm{dip}(p)} \tag{B.50}$$

The derivative of dip(p), that is the function dip′(p) is given by:

$$\boxed{\begin{aligned}\mathrm{dip}'(p) = &\left\{\sinh p\right\}\left\{\left(1 - 0.08597\, p^{3.5} \exp(-p)\right)\, p + \frac{9}{7}\, \mathrm{gam}\left(p\ ;\ \frac{9}{2}\right) + \right.\\ &\left. - \mathrm{gam}\left(p\ ;\ \frac{7}{2}\right)\right\} - \left\{\cosh p\right\}\left\{\frac{2}{7} + p\ \mathrm{gam}\left(p\ ;\ \frac{7}{2}\right) - 0.02456\, p^{4.5} \exp(-p)\right\}\end{aligned}} \quad (B.51)$$

Both zip(p) and dip′(p) are plotted in Figure B-1.

As stated earlier, z_o and r_e are usually known for a molecule, but z_1 is not. From Eqs. (B.45) and (B.49) however we can now obtain z_1 immediately once z_o , r_e , and η are specified. From Eq. (B.45) one obtains p_d and then one substitutes this value of p_d in (B.49) to get z_1 .

We still have to determine the value of η however before we can follow this procedure routinely for various molecules. To get η , we shall apply the above formulas to a molecule for which we know the values of z_o , r_e , and z_1 reasonably well. Such a molecule is CO, for which $z_o = 0.0207$ and $r_e = 1.128$ Angstrom according to the data given in Refs. 2 and 16. The value for $z_1 \approx 0.63$ according to Refs. 7 and 55.* Using these values in Eqs. (B.45) and (B.49), we find that these relations are satisfied if $\eta = 0.576$ which is close to the exponential coefficient 0.562 in the first

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*Actually Ref. 55 (p. 64) shows a dependence of the *f* number (see Eq. (3.14), p. 50) on temperature, yielding a value of z_1 (which is proportional to $f^{1/2}$) of $z_1 = 0.6311$ at T = 287.7 °K, and $z_1 = 0.8925$ at T = 2877 °K. This can obviously not be true since the *f* number (and thus the z_1 value) is a pure intramolecular parameter which is independent of temperature T (and of pressure). The dependence of z_1 on T as reported by Ref. 55 is due to the erroneous inclusion of temperature and pressure broadening effects, and a re-interpretation of the data given by Ref. 55 leads to the conclusion that the true value of $z_1 \approx 0.63$.

member of Rosenthal's equation (B.21) dominating at higher values of $\xi = r/a$, that is in the outer regions of the atomic or molecular field. This is precisely the region in which the valence electrons that determine the dipole moment move about. In fact the values of p_d and $\mathrm{dip}(p_d)$ for the CO molecule which give $\eta = 0.576$, are $p_d = 1.65$ and $\mathrm{dip}(p_d) = 1.08$, which when substituted in Eq. (B.47), give Z_d a value $Z_d = 1.586$. This result agrees resonably with the fact that two valence electrons bind the C and O atoms in the molecule CO.

Assuming then that $\eta = 0.576$, Eq. (B.45) becomes:

$$\boxed{z_o = \left(\frac{0.5424}{r_e}\right) p_d - \left(\frac{1.0546}{r_e^3}\right) \mathrm{dip}(p_d)\ ,} \tag{B.52a}$$

which, for the purpose of obtaining p_d from z_o and r_e, can be rewritten as:

$$\boxed{\mathrm{dip}(p_d) = (0.5143\ r_e^2)\ p_d - (0.9482\ r_e^3)\ z_o} \tag{B.52b}$$

The value of p_d is determined by the intersection of the straight line $L(p_d) = (0.5143\ r_e^2)p_d - (0.9482\ r_e^3)z_o$ with the curve $\mathrm{dip}(p_d)$ which is plotted in Figure B-1. Here r_e and z_o are assumed known of course.

With $\eta = 0.576$, Eq. (B.49) for z_1 becomes similarly:

$$\boxed{z_1 = \left(\frac{0.5424}{r_e}\right) p_d - \left(\frac{2.1092}{r_e^3}\right) \mathrm{zip}(p_d)} \tag{B.53}$$

Thus after obtaining a value of p_d from (B.52b), z_l is obtained from (B.53) by substituting this value of p_d (and the known value of r_e) in this equation. In Figure B-2, z_l is plotted versus z_o by this method. Table B-l list values of z_l for various molecules obtained via Figure B-2.

B.3 POLYATOMIC MOLECULES

Having developed a general method for diatomic molecules to determine z_l if z_o and r_e are known, let us now turn to the problem of obtaining values of z_o and z_l for polyatomic molecules. We shall begin with symmetric linear molecules such as CO_2 whose structure is O-C-O. Here the carbon atom shares four of its outer electrons with the two oxygen atoms, each of whom have two outer electrons that are shared. Thus four outer electrons move about the O, C, and O atom, holding the molecule together.

We shall next make a reasonable approximation and assume that the overall dipole moment of O-C-O is equal to the vector sum of two back-to-back dipoles each of which has the same magnitude and sense as the dipole of CO that is $\mu_o = 0.112$ debyes or charge $z_o = 0.0207$. We shall assume further also that $z_l = z_l(z_o, \ell_{XY})$ for each component XY of a Y-X-Y molecule, where z_l is calculated from z_o and the equilibrium separation ℓ_{XY} in the same manner as $z_l = z_l(z_o, r_e)$ is calculated for a diatomic molecule. We use here the notation ℓ_{XY} rather than r_e to indicate the equilibrium separation between atoms X and Y in a polyatomic molecule.

Now the linear OCO molecule has three normal vibrations as shown in Figure B-3. The three normal vibrations ν_l, ν_2, and ν_3 of a symmetric linear molecule XY_2 such as CO_2 can in general be expressed in terms of two force constants and two atomic masses by the following relations (Ref. 10):

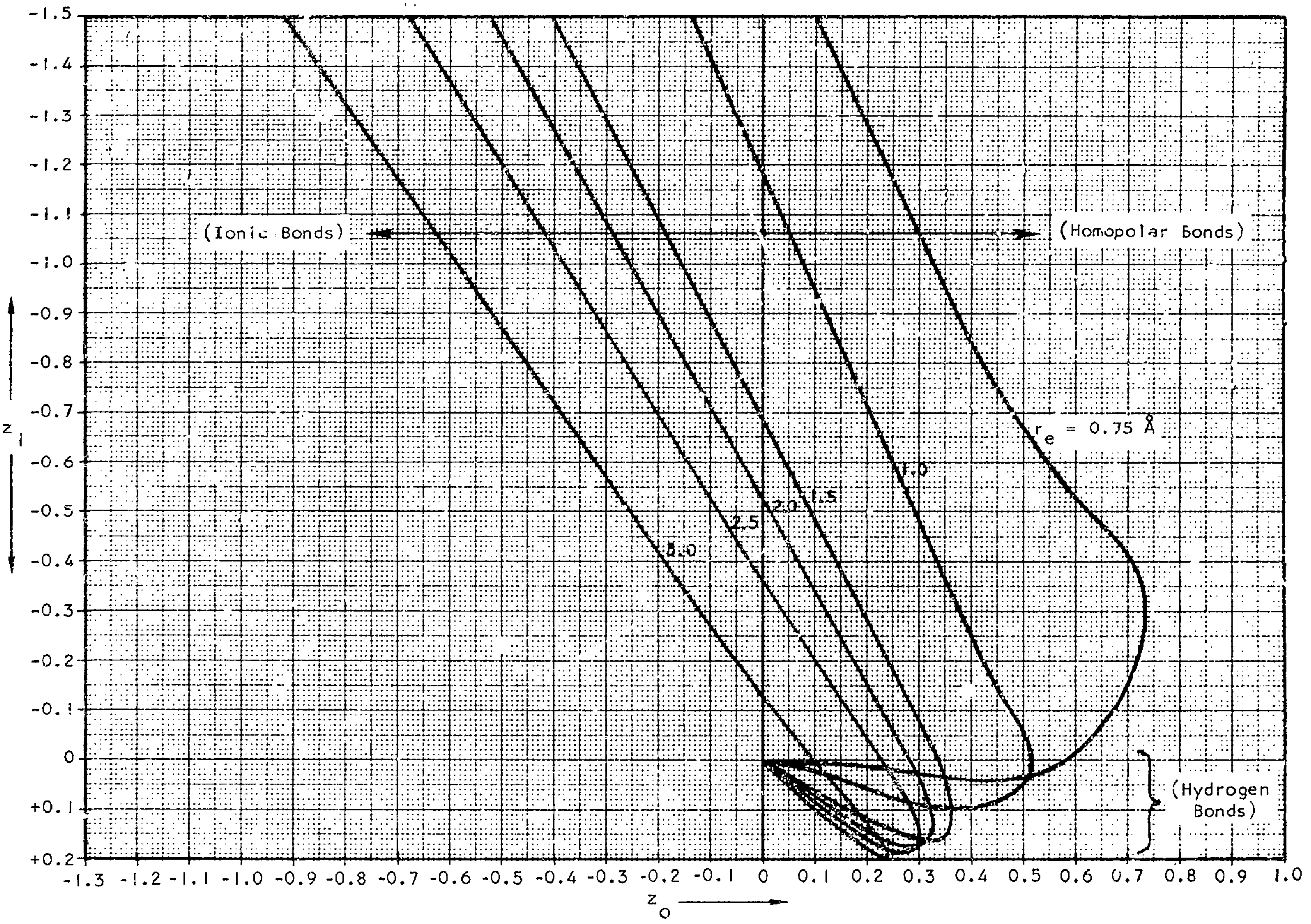

FIGURE B-2. RELATIONS BETWEEN z_0 AND z_1

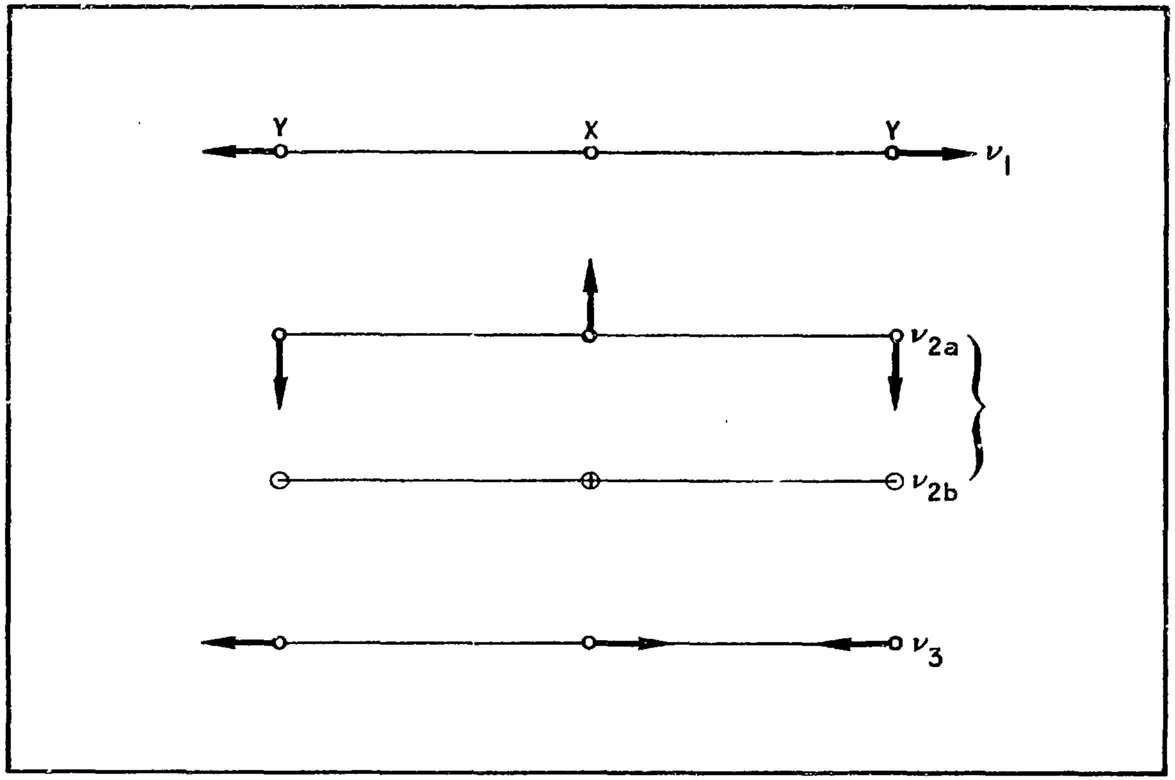

FIGURE B-3. NORMAL VIBRATIONS OF LINEAR XY_2 (Ref. 15)

Linear Symmetric XY_2

$$4\pi^2\nu_1^2 = \frac{k_1}{M_Y} \quad \text{(Symmetric Stretch Vibration)} \tag{B.54}$$

$$4\pi^2\nu_2^2 = \frac{2k_2}{(M_Y M_X)/(M_X + 2M_Y)} \tag{B.55}$$

(Doubly Degenerate Bending Vibration)

$$4\pi^2\nu_3^2 = \frac{k_3}{(M_Y M_X)/(M_X + 2M_Y)} = \frac{k_1}{(M_Y M_X)/(M_X + 2M_Y)} \tag{B.56}$$

(Asymmetric Stretch Vibration)

For symmetric XY_2 molecules we have that the constants $k_3 = k_1$. Herzberg (Ref. 10) uses instead of k_2 the notation $k_\delta/\ell_{XY}^2 = k_2$, where ℓ_{XY} is the equilibrium distance between atoms X and Y. Thus the equivalent masses M_β (β = 1, 2, 3) for the three normal vibrations are:

$$M_1 = M_Y \qquad (\nu_1 \text{ vibration}) \tag{B.57}$$

$$M_2 = \frac{M_Y M_X}{2(M_X + 2M_Y)} \qquad (\nu_2 \text{ vibration}) \tag{B.58}$$

$$M_3 = \frac{M_Y M_X}{M_X + 2M_y} \qquad (\nu_3 \text{ vibration}) \tag{B.59}$$

In Table B-4, values are listed of the force constants $k_1 = k_3$, $k_2 = k_\delta/\ell_{XY}^2$, ℓ_{XY}, and ν_1, ν_2, ν_3 for linear symmetric CO_2 and CS_2 adapted from Ref. 10. The valence-force model on which Eqs. (B.54) through (B.56)

TABLE B-4. SPRING CONSTANTS OF SELECTED TRIATOMIC MOLECULES (After Refs. 10,11)

Molecule XYZ	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	$\ell_{XY} = \ell_1$ (Angstrom)	$\ell_{YZ} = \ell_2$ (Angstrom)	k_1 (Megadynes per cm)	k_3 (Megadynes per cm)	$k_2 = k_\delta/\ell_1\ell_2$ (Megadynes per cm)	Angle Between Two Bonds (2α)	
									Calculated	Observed
<u>Linear</u>										
CO_2 (OCO)	1387	667	2349	1.1621	1.1621	1.68*	1.42**	0.057	180°	180°
CS_2 (SCS)	657	397	1523	1.5545	1.5545	0.81*	0.69**	0.0234	180°	180°
SCO	859	527	2079	1.561	1.161	0.80	1.42	0.037	180°	180°
N_2O (NNO)	1285	589	2224	1.126	1.191	1.46	1.37	0.049	180°	180°
HCN	2089	712	3312	1.068	1.156	0.58	1.79	0.020	180°	180°
$C\ell CN$	729	397	2201	1.629	1.163	0.52	1.67	0.020	180°	180°
BrCN	580	368	2187	1.789	1.160	0.42	1.69	0.017	180°	180°
ICN	470	321	2158	1.995	1.159	0.30	1.67	0.012	180°	180°
OUO	860	220	940	1.58	1.58	0.698	0.698	0.020	180°	180°
<u>Non-Linear</u>										
H_2O (HOH)	3657	1594.7	3755.7	0.956	0.956	0.776	0.776	0.069	120°	105°
D_2O (DOD)	2666	1179	2784	0.955	0.955	0.794	0.794	0.070	113°	105°
H_2S (HSH)	2614.6	1182.7	2627.5	1.328	1.328	0.414	0.414	0.045	156°	92°
D_2S (DSD)	1892	934	1999	1.33	1.33	0.446	0.446	0.044	159°	92°
H_2Se (HSeH)	2344.5	1034.2	2357.8	1.460	1.460	0.324	0.324	0.031	—	90°
D_2Se (DSeD)	1630	745	1696	1.46	1.46	0.333	0.333	0.030	—	90°
CH_2 (HCH)	2968	1444	3000	1.029	1.029	0.477	0.477	0.058	98°	115°
SO_2 (OSO)	1151.3	517.6	1361.7	1.4321	1.4321	0.997	0.997	0.081	120°	120°
NO_2 (ONO)	1320	648	1621	1.1934	1.1934	0.913	0.913	0.152	119°	120°
F_2O (FOF)	830	490	1110	~1.55	~1.55	0.557	0.557	0.055	87°	104°
$C\ell_2O$ ($C\ell OC\ell$)	680	330	973	~1.47	~1.47	0.493	0.493	0.041	81°	111°

*Calculated from ν_1 ; **Calculated from ν_3

are based is not exact since $k_1 = k_3$ as calculated from the observed value of ν_1 does not agree with the $k_3 = k_1$ value calculated from ν_3 as shown in Table B-4. Theoretically they should be equal. The discrepancy is due to the fact that in the valence-force model, it is assumed that all forces may be represented by simple constants acting along or perpendicular to the bond coordinates, whereas in reality the action by the bonding forces is a little more complex than that.

The ν_1 and ν_3 vibrations are clearly along the molecular axis as shown in Figure B-3, while the ν_2 vibrations describe displacements of the atoms that are perpendicular to this axis. Composing the dipole moment μ (to first-order) for an XY_2 molecule then, using the measured dipole moment or charge of the XY molecule or radical, and applying the previously mentioned assumption that the dipole charge of each XY bond in YXY is the same as for XY, we get for the ν_1 "symmetric stretch" vibration along the YXY axis that:

$$(\mu)_1 = \left(\mu_0\right)_1 + \left(\mu_1\right)_1 y_1 = e\left(z_0\right)_1 \ell_1 + e\left(z_1\right)_1 (\ell_1 - s_1) = e\left(z_0\right)_{XY} \ell_{XY} - e\left(z_0\right)_{XY} \ell_{XY} +$$

$$- e\left(z_1\right)_{XY} (s_{XY} - \ell_{XY}) - e(s_{XY} - \ell_{XY}) = 0 , \qquad \text{(B.60)}$$

while for the ν_3 vibration, which is also along the XYX axis:

$$(\mu)_3 = \left(\mu_0\right)_3 + \left(\mu_1\right)_3 y_3 = e\left(z_c\right)_3 \ell_3 + e\left(z_1\right)_3 (s_3 - \ell_3) = e\left(z_0\right)_{XY} \ell_{XY} - e\left(z_0\right)_{XY} \ell_{XY} +$$

$$- e\left(z_1\right)_{XY} (\ell_{XY} - s_{XY}) + e\left(z_1\right)_{XY} (s_{XY} - \ell_{XY}) = 2e\left(z_1\right)_{XY} (s_{XY} - \ell_{XY}) = 2e\left(z_1\right)_{XY} y_3 \qquad \text{(B.61)}$$

Here s_{XY} is the non-equilibrium separation and ℓ_{XY} the equilibrium separation of the X and Y atom, while $y_i = s_i - \ell_i$ is the displacement from equilibrium of the two mass centers of the ν_i vibration. For the ν_1 vibration we have $y_1 = s_1 - \ell_1 = s_{XY} - \ell_{XY}$ for both XY components while for the ν_3 vibration $y_3 = s_3 - \ell_3 = s_{XY} - \ell_{XY}$ for one XY component and $y_3 = -(s_{XY} - \ell_{XY})$ for the other XY component.

The sign (plus or minus) of the first-derivative $(\mu_1)_{XY} = e(z_1)_{XY}$ of a component dipole must be carefully chosen. It is the product of the signs of two parts, one due to the component dipole directional sense and one due to the relative phase of the component vibration. We shall adopt the convention that a plus sign (+) will be given to a component dipole, if the vector drawn from the negative end to the positive end of the dipole is in the positive direction of a reference symmetry axis while the negative sign (-) applies if the dipole's direction from its negative to its positive end is in the opposite (negative) direction. We shall refer to this as the component "dipole direction sign."

The relative phase sign may be determined by whether a component vibration is stretching or shrinking with respect to an adjacent component vibration of the same normal vibration at a particular instant of time. If two adjacent components of a normal vibration are both stretching or shrinking they both have the same sign, if one is stretching while the other is contracting, they have opposite signs. Thus in the ν_3 asymmetric stretch vibration of YXY, one component XY dipole is stretching while the other XY component is contracting, while in the ν_1 symmetric stretch vibration the XY bonds vibrate in phase. Thus for the ν_3 vibration (Eq. (B.61)), if the net sign of one of the XY vibrations is taken as positive the other's sign is (-) · (-) = (+), where the first sign (-) in the product is the dipole direction sign and the second is what we shall call the "component vibration phase sign." In the ν_1 vibration of Eq. (B.60), the net sign of the first XY bond is (+)(+) = (+), while the second XY dipole has a net sign of (-)(+) = (-).

From Eqs. (B.60) and (B.61) it is clear that for the ν_1 and ν_3 vibrations $\mu_o = \mu(y=o) = 0$ and thus:

$$\left(z_o\right)_1 = \left(z_o\right)_3 = 0 \tag{B.62}$$

The first moment $(\mu_1)_1 = (\partial\mu/\partial y)_{y=o} = 0$ for the ν_1 vibration, and $(\mu_1)_3 =$ $= 2e(z_1)_{XY}$ for the ν_3 vibration. Thus:

$$\left(z_1\right)_1 = 0 \tag{B.63}$$

$$\left(z_1\right)_3 = 2\left(z_1\right)_{XY} \tag{B.64}$$

For the doubly-degenerate bending vibration ν_2 of the XY_2 molecule which takes place at right angles to the ν_1 and ν_3 vibrations, the composite dipole moment is:

$$(\mu)_2 = \left(\mu_o\right)_2 + \left(\mu_1\right)_2 y_2 = e\left(z_o\right)_2 + e\left(z_1\right)_2 y_2 = e\left(z_o\right)_{YX} \ell_{YX}\,\bar{\theta}_1 + e\left(z_o\right)_{XY} \ell_{XY}\,\bar{\theta}_2 +$$

$$+ e\left(z_1\right)_{YX} \overline{\left(\frac{ds}{dq}\right)}_{YX} y_2 + e\left(z_1\right)_{XY} \overline{\left(\frac{ds}{dq}\right)}_{XY} y_2 = 2e\left(z_1\right)_{YX} \left(\delta_q\right)_{YX} y_2 \tag{B.65}$$

Here:

$$\delta_q \equiv \left(\overline{\frac{dy}{dq}}\right)_{XY} \tag{B.66}$$

The time-averaged angle $\bar{\theta}_1 = \bar{\theta}_2 = 0$ during a bending vibration so that:

$$\left(z_o\right)_2 = \left(\frac{\left(\overline{\mu_o}\right)_2}{es_2}\right)_{s_2=\bar{s}_2} = 0 \tag{B.67}$$

The first-derivative-dipole charge for the ν_2 bending vibration is:

$$\left(z_1\right)_2 = \frac{2}{e}\left(\overline{\frac{\partial\mu}{\partial q}}\right)_{XY} = \frac{2}{e}\left(\overline{\frac{\partial\mu}{\partial s}}\right)_{XY}\left(\overline{\frac{ds}{dq}}\right)_{XY} = \frac{2}{e}\left(\overline{\frac{\partial\mu}{\partial s}}\right)_{XY}\left(\overline{\frac{dy}{dq}}\right)_{XY} =$$

$$= 2\left(z_1\right)_{XY}\left(\overline{\frac{dy}{dq}}\right)_{XY} = 2\delta_q\left(z_1\right)_{XY} \tag{B.68}$$

Here q is the displacement of the Y atom perpendicular to the molecular axis as shown in Figure B-4, and $y = \ell_{XY} - s$ as before.

The time-averaged value of δ_q may be calculated as follows. Referring to Figure B-4, we can write down the following relations for either one of the two Y atoms which is moving in a bending vibration and which at a certain instant of time is at say position 2 :

$$q/s = q/(\ell_{XY}-y) \approx q/\ell_{XY} = \sin\theta_1 \,, \tag{B.69}$$

where $y \ll \ell_{XY}$, and also in the small-angle approximation:

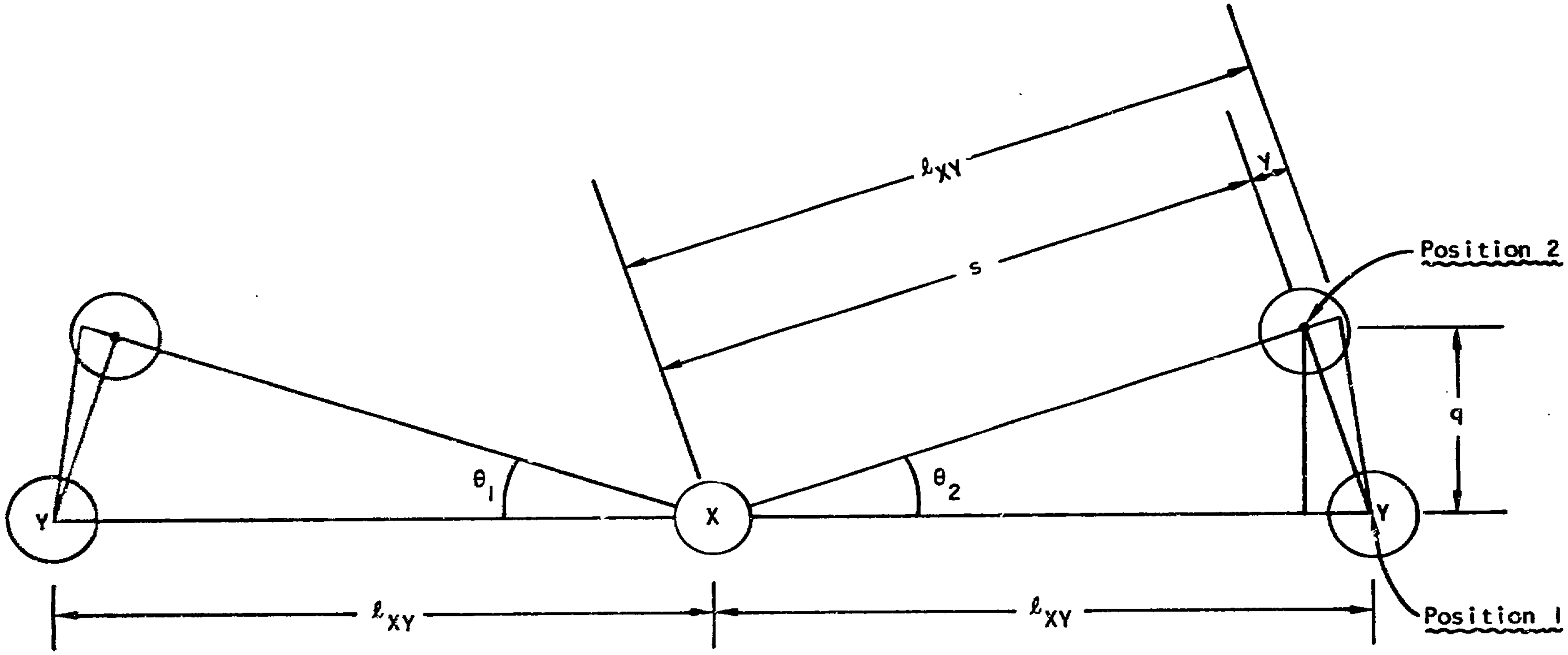

FIGURE B-4. ILLUSTRATION OF GEOMETRICAL RELATIONS OF THE BENDING VIBRATION OF LINEAR XY_2

$$y/q \approx \tan\theta_1 \approx \sin\theta_1 \qquad \text{(B.70)}$$

Therefore:

$$q^2 = y\,\ell_{XY} \qquad \text{(B.71)}$$

From Eq. (B.71) we obtain:

$$\frac{dy}{dq} = 2\sqrt{\frac{\bar{y}}{\ell_{XY}}} \qquad \text{(B.72)}$$

and thus:

$$\delta_q = \left(\overline{\frac{dy}{dq}}\right) = 2\sqrt{\frac{\bar{y}}{\ell_{XY}}} \qquad \text{(B.73)}$$

To find the mean value of $\bar{y}$ during a bending vibration we obtain first the mean value of q^2 by invoking the virial theorem which states that the mean potential energy $V_2 = \frac{1}{2} k_q q^2$ equals half the total energy (sum of kinetic plus potential energy) which equals $(v_2 + \frac{1}{2}) h\nu_2$. Considering further that half the bending vibration occurs above the straight-line axis shown in Figure B-3 and half below this axis, we can write:

$$\overline{q^2} = \frac{2}{k_q}\cdot\frac{1}{4}\left(v_2 + \frac{1}{2}\right) h\nu_2 = \frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{2\,k_2} \qquad \text{(B.74)}$$

Here k_q is the force constant for the ν_2 bending vibration and thus $k_q = k_2$. Then using (B.71) again we get:

$$\bar{y} = \frac{\bar{q}_2}{\ell_{XY}} = \frac{1}{\ell_{XY}}\;\frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{k_2}\,, \qquad \text{(B.75)}$$

and finally:

$$\boxed{\delta_q = \left(\overline{\frac{dy}{dq}}\right) = 2\left(\frac{(v_2 + \frac{1}{2})\, h\nu_2}{2k_2\, \ell_{XY}^2}\right)^{1/2}} \qquad (B.76)$$

Thus, substituting (B.76) into (B.68), we have for the first-derivative moment u_1 or charge z_1 of the ν_2 bending vibration:

$$\boxed{\underset{(\text{Symmetric } XY_2)}{\left(z_1\right)_2} = 4\left(z_1\right)_{XY}\left\{\frac{(v_2 + \frac{1}{2})\, h\nu_2}{2\kappa_2\, \ell_{XY}^2}\right\}^{1/2}} \qquad (B.77)$$

Note from (B.77) that in contrast to the ν_1 and ν_3 stretching vibrations, the value of z_1 for the ν_2 vibrations depends on the level of excitation v_2 .

Applying the above results to linear CO_2 for example, using $(z_1)_{CO} = 0.630$, we obtain for the z_1 values of CO_2:*

$$\left(z_1\right)_{CO_2} = 0 \qquad (B.78a)$$

$$\left(z_2\right)_{CO_2} = 0.286 \quad , \quad \text{for } v_2 = 1 \qquad (B.78b)$$

$$\left(z_3\right)_{CO_2} = 1.260 \quad , \qquad (B.78c)$$

---

*We shall omit the minus sign on $(z_1)_{CO}$ and other molecules in what follows since it is only relative to z_o , and in expressions for R_{mn}^2 the square of z_1 is used.

where we omitted the subscript I on z_I to indicate the first-derivative dipole charge. From here on we shall understand that z stands for z_I if we are dealing with a polyatomic molecule. The subscripts on z will indicate a particular normal vibration. We shall retain the nomenclature z_o for the permanent dipole charge and $(z_o)_\alpha$ to indicate its value for the α vibration.

The results (B.78) for CO_2 which were calculated via the "component dipole method," compare favorably with measured z values for CO_2 which may be obtained from the data of Ref. 55 which are estimated to be good to within 50 percent:

$$\left(z_2\right)_{CO_2} \text{ measured} = 0.216 \quad , \quad \text{for } v_2 = 1 \tag{B.79a}$$

$$\left(z_3\right)_{CO_2} \text{ measured} = 1.698 \tag{B.79b}$$

For CS_2 we get similarly, using $(z_I)_{CS} = 0.102$, that:

$$\left(z_1\right)_{CS_2} = 0 \; ; \; \left(z_2\right)_{CS_2} = 0.0423 \; ; \; \left(z_3\right)_{CS_2} = 0.204 \tag{B.80}$$

For unsymmetric linear XYZ molecules such as OCS, the expressions for the three normal vibrations are not of the simple form:

$$4\pi^2\nu_\beta^2 = \frac{k_\beta}{M_\beta} \tag{B.81}$$

as is the case for the symmetric linear molecules XY_2 , but instead we have in the valence-force model approximation (Ref. 10) that:

Linear XYZ

$$4\pi^2\nu_1^2 = \frac{\left(1 - \sqrt{1 - A}\right) k_{11}}{2\, M_X M_Y/(M_X+M_Y)} + \frac{\left(1 - \sqrt{1 - A}\right) k_{12}}{2\, M_Y M_Z/(M_Y+M_Z)} \,, \tag{B.82}$$

$$4\pi^2\nu_2^2 = \frac{k_{21}}{M_Z} + \frac{k_{22}}{M_X} + \frac{k_{23}}{M_Y} \,, \tag{B.83}$$

$$4\pi^2\nu_3^2 = \frac{\left(1 + \sqrt{1 - A}\right) k_{31}}{2\, M_X M_Y/(M_X+M_Y)} + \frac{\left(1 + \sqrt{1 - A}\right) k_{32}}{2\, M_Y M_Z/(M_Y+M_Z)} \,, \tag{B.84}$$

where:

$$A = \frac{4\, k_{11} k_{12} (M_X+M_Y+M_Z)\, M_X M_Y M_Z}{\left[k_{11}(M_X+M_Y)\, M_Z + k_{12}(M_Y+M_Z)\, M_X\right]^2} = \frac{4\, k_1 k_3 (M_X+M_Y+M_Z)\, M_X M_Y M_Z}{\left[k_1(M_X+M_Y)\, M_Z + k_3(M_Y+M_Z)\, M_X\right]^2} \tag{B.85}$$

Here $k_{11} = k_{31} = k_1$ and $k_{12} = k_{32} = k_3$ are the force constants between atoms X and Y , and Y and Z respectively, while $k_{21} = k_\delta/\ell^2_{YZ}$, $k_{22} = k_\delta/\ell^2_{XY}$ and $k_{23} = k_\delta(\ell_{XY}+\ell_{YZ})^2/\ell^2_{XY}\ell^2_{YZ}$ are bending force constants which restore respectively atoms Z, X, and Y back to the linear XYZ form if they are moved outward normal to the axis.* Figure B-5 illustrates the three normal vibrations of linear XYZ. We hav thus the relations:

$$k_{21} = \frac{\ell^2_{XY}}{\ell^2_{YZ}}\, k_{22} \tag{B.86}$$

---

*The parameters ℓ_{XY} and ℓ_{YZ} are the equilibrium bond separation atoms X and Y, and Y and Z, respectively. We use these symbols for polyatomic molecules instead of the symbol r_e which is traditionally used for diatomic molecules.

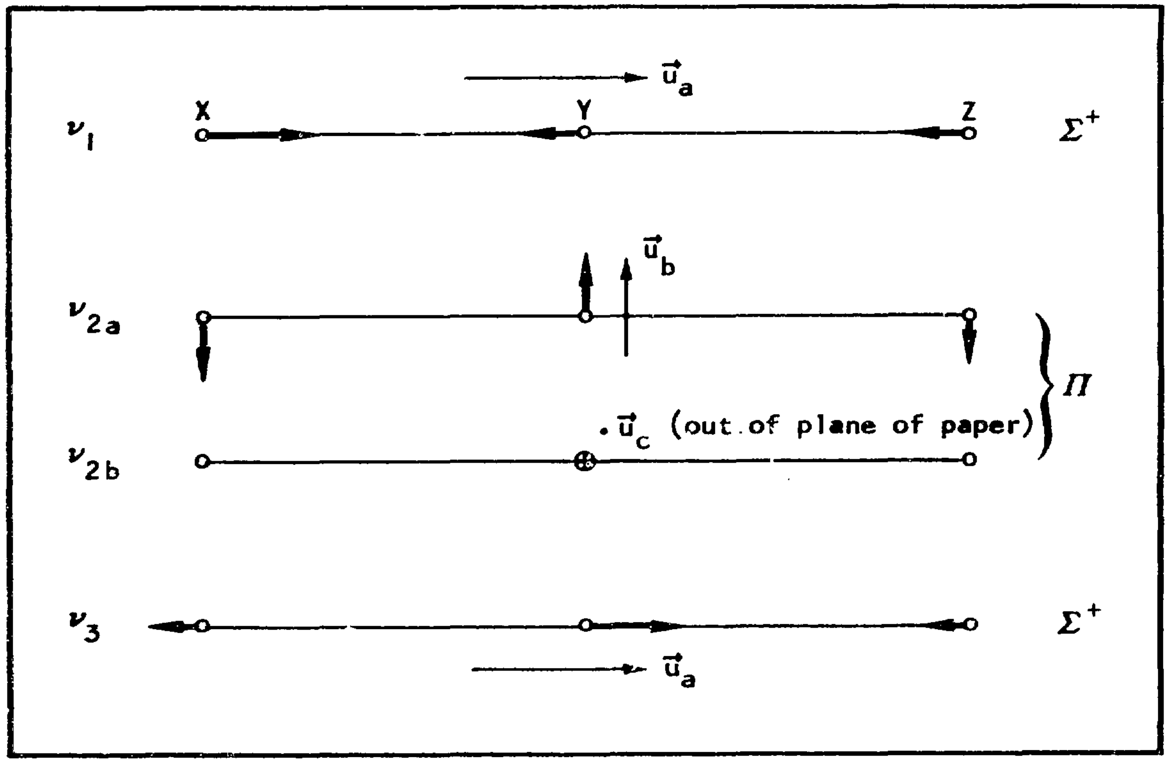

FIGURE B-5. NORMAL VIBRATIONS OF A LINEAR XYZ MOLECULE

$$k_{23} = \frac{(\ell_{YZ} + \ell_{XY})^2}{\ell_{XY}^2}\, k_{21} = \frac{(\ell_{YZ} + \ell_{XY})^2}{\ell_{YZ}^2}\, k_{22} \tag{B.87}$$

Instead of describing the normal vibrations of a linear triatomic molecule by means of the five spring constants $k_{11}\left(= k_{31}\right)$, $k_{12}\left(= k_{32}\right)$, k_{21}, k_{22}, and k_{23}, one can clearly also use the three spring constants $k_1 = k_{11} = k_{31}$; $k_3 = k_{12} = k_{32}$; $k_2 = k_\delta/(\ell_{YZ}\ell_{XY}) = (\ell_{YZ}/\ell_{XY})\, k_{21} = (\ell_{XY}/\ell_{YZ})\, k_{22} = (k_{23}\ell_{XY}\ell_{YZ}) \cdot (\ell_{XY} + \ell_{YZ})^{-2}$, and the two equilibrium atomic separation parameters ℓ_{XY} and ℓ_{YZ}. In Table B-4, the latter five parameters are given for a number of linear XYZ molecules taken from Ref. 10. To obtain k_{11}, k_{12}, k_{21}, k_{22}, k_{23}, k_{31}, and k_{32} from these constants then we need the relations:

$$k_{11} = k_{31} = k_1 \ , \quad \text{dynes/cm} \tag{B.88}$$

$$k_{12} = k_{32} = k_3 \ , \quad \text{dynes/cm} \tag{B.89}$$

$$k_{21} = (\ell_{XY}/\ell_{YZ})\, k_2 \ , \quad \text{dynes/cm} \tag{B.90}$$

$$k_{22} = (\ell_{YZ}/\ell_{XY})\, k_2 \ , \quad \text{dynes/cm} \tag{B.91}$$

$$k_{23} = \left[(\ell_{XY} + \ell_{YZ})^2/(\ell_{XY}\ell_{YZ})\right] k_2 \ , \quad \text{dynes/cm} \tag{B.92}$$

We can define masses M_1, M_2, ... of a molecule (see Appendix A) by:

$$M_\beta = \left[\sum_s M_{\beta s}^{-1/2}\right]^{-2} \tag{B.93}$$

Applying this formula to the linear triatomic molecule XYZ we then get:

$$M_1 = \left[M_{11}^{-1/2} + M_{12}^{-1/2}\right]^{-2} = \left[\left\{\frac{X_1(M_X + M_Y)}{2\,M_X M_Y}\right\}^{1/2} + \left\{\frac{X_1(M_Y + M_Z)}{2\,M_X M_Y}\right\}^{1/2}\right]^{-2} \tag{B.94}$$

$$M_2 = \left[M_{21}^{-1/2} + M_{22}^{-1/2} + M_{23}^{-1/2}\right]^{-2} = \left[M_Z^{-1/2} + M_X^{-1/2} + M_Y^{-1/2}\right]^{-2} \tag{B.95}$$

$$M_3 = \left[M_{31}^{-1/2} + M_{32}^{-1/2}\right]^{-2} = \left[\left\{\frac{X_3(M_X + M_Y)}{2\,M_X M_Y}\right\}^{1/2} + \left\{\frac{X_3(M_Y + M_Z)}{2\,M_X M_Y}\right\}^{1/2}\right]^{-2}, \tag{B.96}$$

where:

$$X_1 = 1 - \sqrt{1 - A} \tag{B.97}$$

$$X_3 = 1 + \sqrt{1 - A} \tag{B.98}$$

The XYZ molecule is the first example for which the simple relation (B.81) does not hold. In fact the normal vibrations of nearly all polyatomic molecules with the exception of linear XY_2, can only be reasonably described by an expression of the type:

$$4\pi^2\nu_\beta^2 = \sum_s \frac{k_{\beta s}}{M_{\beta s}}, \tag{B.99}$$

Here the s components of the normal vibration β are component vibrations along "internal symmetry coordinates" in the molecule (Ref. 10).

Now like we already tacitly assumed for the symmetric linear molecules we discussed so far, we shall assume that for more complicated molecules we can also envision dipole moments $\mu_{\beta s}$ for each symmetry coordinate s along the restoring force $\vec{F}_{\beta s}$ with restoring constant $k_{\beta s}$. To obtain the net dipole moment $(\mu_o)_\beta$ and first-derivative dipole moment $(\mu_1)_\beta$ of the normal vibration β of a polyatomic molecule then, or its charge $(z_o)_\beta$ and first-derivative charge z_β (for use in the expressions of R^2_{mn}), we have to weigh the components $(z_o)_{\beta s}$ or $z_{\beta s}$ with the scales of the non-dimensionalized vector component coordinates $\xi_{\beta s}\vec{e}_{\beta s}$ whose vector sum equals the "normal coordinate" $\xi_\beta\vec{e}_\beta$ (see Appendix A). Thus for the first-derivative charge:

$$z_\beta = \frac{\left[\sum_s \frac{k_{\beta s}}{M_{\beta s}}\right]^{1/4}}{\sum_s M_{\beta s}^{-1/2}} \left| \sum_s \left(\frac{M_{\beta s}}{k_{\beta s}}\right)^{1/4} \left(\frac{\gamma_{\beta s} z_{\beta s} \vec{e}_{\beta s}}{M_{\beta s}^{1/2}}\right) \right| =$$

$$= \frac{(2\pi\nu_\beta)^{1/2}}{\sum_s M_{\beta s}^{-1/2}} \left| \sum_s \left(\frac{M_{\beta s}}{k_{\beta s}}\right)^{1/4} \left(\frac{\gamma_{\beta s} z_{\beta s} \vec{e}_{\beta s}}{M_{\beta s}^{1/2}}\right) \right| =$$

$$\boxed{z_\beta = 0.0155736 \underset{(\text{cm}^{-1})(\text{amu})}{\nu_\beta^{1/2} \; M_\beta^{1/2}} \left| \sum_s \underset{(\text{Megadyne/cm})(\text{amu})}{(k_{\beta s} M_{\beta s})^{-1/4}} \; \gamma_{\beta s} z_{\beta s} \vec{e}_{\beta s} \right| \quad ,} \qquad (B.100)$$

while for the permanent dipole charge $(z_o)_\beta$ we have similarly:

$$\boxed{(z_o)_\beta = 0.0155786\, \underset{(\text{cm}^{-1})(\text{amu})}{\nu_\beta^{1/2}\, M_\beta^{1/2}} \left| \sum_s \underset{(\text{Megadyne/cm})\ (\text{amu})}{(k_{\beta s} M_{\beta s})^{-1/4}} (z_o)_{\beta s}\, \vec{e}_{\beta s} \right|} \qquad (\text{B.101})$$

The absolute signs $| \; |$ in (B.100) and (B.101) designates that the absolute value of the resultant vector must be taken. The vectors $\vec{e}_{\beta s}$ in Eqs. (B.100) and (B.101) are unit vectors along the internal symmetry coordinates and essentially give the dipole direction sign, that is whether the direction from the (-) to the (+) charge side of the component dipole is parallel or antiparallel to the chosen positive direction of a symmetry coordinate. The relative-phase factors $\gamma_{\beta s}$ in (B.100) have the values $+1$ or -1, depending on whether a component bond s along a symmetry coordinate is stretching or contracting when an instantaneous snapshot of the displacements of the atoms from their equilibrium positions is taken. In other words the $\gamma_{\beta s}$ give the signs of the relative directions of motion in a composite vibration. Note that $\gamma_{\beta s}$ is only needed in expression (B.100) for the first-derivative dipole charge, and not in Eq. (B.101) for the permanent dipole charge.

We shall take the values of all $(z_o)_{\beta s}$ to be sign-less (i.e., positive), but the $z_{\beta s}\left(\equiv (z_1)_{\beta s}\right)$ values can be either positive or negative (see Table B-3). In our "component-dipole approximation," the $z_{\beta s}$ are further assumed to be equal to $(z_1)_{XY}$ (abbreviated z_{XY}) of the equivalent isolated diatomic molecule or radical if the component vibration s is a stretching vibration between atoms X and Y. If the vibration is a bending vibration of X about Y or vice versa, we assume $z_{\beta s}$ to be equal to $(z_1)_{XY}\delta_{\beta s} = z_{XY}\delta_{\beta s}$. Similarly value of $(z_o)_{\beta s}$ will be assumed to be equal to $(z_o)_{XY}$ for any type of vibration.

In what follows we shall primarily consider the calculation of $z_\beta = (z_1)_\beta$ from the $z_{\beta s} = (z_1)_{\beta s}$ values. Calculation of $(z_o)_\beta$ is almost identical except for the $\gamma_{\beta s}$ factors and need not be carried out also, if expressions for the calculation of z_β are available. One merely sets the $\gamma_{\beta s}$ factors equal to $\gamma_{\beta s} = +1$ and the $\delta_{\beta s} = 0$ in the equations for z_β .

Usually the dipole directions $\vec{e}_{\beta s}$ and the component phase signs $\gamma_{\beta s}$ of the s components of a normal vibration are apparent upon inspection of the particular form of the relation (B.99) that is under consideration (such as (B.82), (B.83), and (B.84) for the XYZ molecule) and of the underlying mechanical model and force constants on which the relations are based. For the linear XYZ molecule, the mechanical model assumed for relations (B.82) through (B.85) is the "valence-force" model (Ref. 10).

Returning to linear XYZ now, the first component of the ν_1 vibration with the force constant $k_{11} = k_1$ between atoms X and Y, as expressed by the first term of (B.82), must have its unit vector $\vec{e}_{11}$ parallel to the bond direction XY, while the second component vector $\vec{e}_{12}$ associated with force constant $k_{12} = k_3$ is antiparallel to the bond direction YZ. For the ν_3 vibration exactly the same can be said for the unit vectors $\vec{e}_{31}$ and $\vec{e}_{32}$. However whereas γ_{11} and γ_{12} are both +1 (or -1) for the ν_1 vibration, the factors γ_{31} and γ_{32} are +1 and -1 respectively (or -1 and +1) for the ν_3 vibration.

Of the three relative-phase signs γ_{21} , γ_{22} , and γ_{23} of the ν_2 vibration of a linear XYZ molecule, the first (γ_{21}) is associated with the vibration of the Z atom perpendicular to the YZ direction and is positive say, the second (γ_{22}) represents vibrations of the X atom perpendicular to the XY direction and has the same sign as γ_{21} thus making it also positive, while the third parameter (γ_{23}) represents a vibration of the Y atom perpendicular to the XYZ axis which of opposite sign as γ_{21} and γ_{22} and is therefore negative (see Figure B-5). Thus $\gamma_{21} = +1$, $\gamma_{22} = +1$, and $\gamma_{23} = -1$.

The dipole directions $\vec{e}_{21}$, $\vec{e}_{22}$, and $\vec{e}_{23}$ are all perpendicular to the XYZ axis and the dipole signs are all in the same direction. Thus $\vec{e}_{21} = \vec{e}_{22} = \vec{e}_{23}$.

Applying the above considerations to the linear SCO molecule for example with $(z_i)_{CO} = 0.630$, and $(z_i)_{CS} = 0.102$ (see Table B-3), we obtain:

$$\gamma_{11}\, z_{11}\, \vec{e}_{11} = (+)(0.102)(+\vec{u}_a) = +0.102\ \vec{u}_a \tag{B.102a}$$

$$\gamma_{12}\, z_{12}\, \vec{e}_{12} = (+)(0.630)(-\vec{u}_a) = -0.630\ \vec{u}_a \tag{B.102b}$$

$$\gamma_{21}\, z_{21}\, \vec{e}_{21} = (+)\left\{0.630\left(\delta_{21}\right)_{YZ}\right\}(+\vec{u}_b) = +0.1408\ \vec{u}_b \tag{B.102c}$$

$$\gamma_{22}\, z_{22}\, \vec{e}_{22} = (+)\left\{0.102\left(\delta_{22}\right)_{XY}\right\}(+\vec{u}_b) = +0.0228\ \vec{u}_b \tag{B.102d}$$

$$\gamma_{23}\, z_{23}\, \vec{e}_{23} = (+)\left\{0.630\left(\delta_{23}\right)_{YZ} + 0.102\left(\delta_{23}\right)_{YX}\right\}(+\vec{u}_b) = +0.0905\ \vec{u}_b \tag{B.102e}$$

$$\gamma_{31}\, z_{31}\, \vec{e}_{31} = (+)(0.102)(+\vec{u}_a) = +0.102\ \vec{u}_a \tag{B.102f}$$

$$\gamma_{32}\, z_{32}\, \vec{e}_{32} = (-)(0.630)(-\vec{u}_a) = +0.630\ \vec{u}_a \tag{B.102g}$$

Here the bending vibration parameters $(\delta_{\beta s})_{YZ}$ and $(\delta_{\beta s})_{XY}$ for a linear molecule XYZ are similarly to (B.76) given by:

$$\delta_a \equiv \left(\delta_{21}\right)_{YZ} = \left(\frac{\overline{dy}}{dq}\right)_{21_{YZ}} = 2\left(\frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{2k_{21}\, \ell_{YZ}^2}\right)^{1/2} \tag{B.103}$$

$$\delta_b \equiv \left(\delta_{22}\right)_{XY} = \left(\frac{\overline{dy}}{dq}\right)_{22_{XY}} = 2\left(\frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{2k_{22}\, \ell_{XY}^2}\right)^{1/2} \tag{B.104}$$

$$\delta_c \equiv \left(\delta_{23}\right)_{YZ} = \left(\frac{\overline{dy}}{dq}\right)_{23_{YZ}} = 2\left(\frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{2k_{23}\, \ell_{YZ}^2}\right)^{1/2} \tag{B.105}$$

$$\delta_d \equiv \left(\delta_{23}\right)_{XY} = \left(\frac{\overline{dy}}{dq}\right)_{23_{XY}} = 2\left(\frac{\left(v_2 + \frac{1}{2}\right) h\nu_2}{2k_{23}\, \ell_{XY}^2}\right)^{1/2} \tag{B.106}$$

For the SCO molecule these parameters have the values:

$$\delta_a \equiv \left(\delta_{21}\right)_{CO} = 0.2235 \qquad (v_2 = 1)\quad , \tag{B.107a}$$

$$\delta_b \equiv \left(\delta_{22}\right)_{SC} = 0.2235 \qquad (v_2 = 1)\quad , \tag{B.107b}$$

$$\delta_c \equiv \left(\delta_{23}\right)_{CO} = 0.1282 \qquad (v_2 = 1)\quad , \tag{B.107c}$$

$$\delta_d \equiv \left(\delta_{23}\right)_{SC} = 0.0953 \qquad (v_2 = 1)\quad , \tag{B.107d}$$

which were the numbers used in (B.102).

The unit vector $\vec{u}_a$ in (B.102) is along the molecular axis XYZ , while $\vec{u}_b$ is a vector perpendicular to the XYZ axis. Note that the ν_2 vibration is doubly-degenerate and while one of its degenerate vibrations is in the direction of $\vec{u}_b$ the other is in the direction $\vec{u}_c$ perpendicular to both the XYZ axis (i.e., $\vec{u}_a$) and the direction $\vec{u}_b$.

From Eqs. (B.82), (B.83), and (B.84), using (B.100) and (B.102) we find for the z_β's of a linear XYZ molecule that:

$$z_1 = \frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}} \left[\left(\frac{M_{11}}{k_{11}}\right)^{1/4} \left(\frac{z_{YX}}{M_{11}^{1/2}}\right) - \left(\frac{M_{12}}{k_{12}}\right)^{1/4} \left(\frac{z_{YZ}}{M_{12}^{1/2}}\right) \right] \qquad \text{(B.108)}$$

$$\begin{aligned} z_2 = {} & \frac{(2\pi\nu_2)^{1/2}}{M_{21}^{-1/2} + M_{22}^{-1/2} + M_{23}^{-1/2}} \left[\left(\frac{M_{21}}{k_{21}}\right)^{1/4} \left(\frac{z_{YZ}\delta_a}{M_{21}^{1/2}}\right) + \right. \\ & \left. + \left(\frac{M_{22}}{k_{22}}\right)^{1/4} \left(\frac{z_{YX}\delta_b}{M_{22}^{1/2}}\right) + \left(\frac{M_{23}}{k_{23}}\right)^{1/4} \left(\frac{z_{YX}\delta_c + z_{YZ}\delta_d}{M_{23}^{1/2}}\right) \right] \end{aligned} \qquad \text{(B.109)}$$

$$z_3 = \frac{(2\pi\nu_3)^{1/2}}{M_{31}^{-1/2} + M_{32}^{-1/2}} \left[\left(\frac{M_{31}}{k_{31}}\right)^{1/4} \left(\frac{z_{YX}}{M_{31}^{1/2}}\right) + \left(\frac{M_{32}}{k_{32}}\right)^{1/4} \left(\frac{z_{YZ}}{M_{32}^{1/2}}\right) \right] , \qquad \text{(B.110)}$$

where δ_a , δ_b , δ_c , and δ_d are given by (B.103) through (B.106) and we use from here on the abbreviation $(z_1)_{AB} \equiv z_{AB}$. Also we used the relations:

$$z_{11} = z_{31} = z_{YX} \qquad \text{(B.111)}$$

$$z_{12} = z_{32} = z_{YZ} \tag{B.112}$$

$$z_{21} = z_{YZ}(\delta_{21})_{YZ} = z_{YZ}\delta_a \tag{B.113}$$

$$z_{22} = z_{YX}(\delta_{22})_{YX} = z_{YX}\delta_b \tag{B.114}$$

$$z_{23} = z_{YZ}(\delta_{23})_{YZ} + z_{XY}(\delta_{23})_{XY} = z_{YX}\delta_c + z_{XY}\delta_d \tag{B.115}$$

The parameters z_{YX} and z_{YZ} are of course the first-derivative dipole charges of diatomic XY and YZ. From (B.94) through (B.96) we also find readily that:

$$M_{11} = \frac{2M_XM_Y}{(1 - \sqrt{1 - A})(M_X+M_Y)} \tag{B.116}$$

$$M_{12} = \frac{2M_YM_Z}{(1 - \sqrt{1 - A})(M_Y+M_Z)} \tag{B.117}$$

$$M_{21} = M_Z \tag{B.118}$$

$$M_{22} = M_X \tag{B.119}$$

$$M_{23} = M_Y \tag{B.120}$$

$$M_{31} = \frac{2M_XM_Y}{(1 + \sqrt{1 - A})(M_X+M_Y)} \tag{B.121}$$

$$M_{32} = \frac{2M_YM_Z}{(1 + \sqrt{1 - A})(M_Y+M_Z)} \tag{B.122}$$

The parameter A was given by Eq. (B.85) and the $k_{\beta s}$ in (B.108) through (B.100) can be obtained from Herzberg's k_i's (see Table B-4) via Eqs. (B.88) through (B.92).

Applying the above relations to the first normal vibration ν_1 of SCO for example, using values for $k_{11} = k_{31} = k_1 = 0.80 \times 10^6$ dynes/cm, $k_{12} = k_{32} = k_3 = 1.42 \times 10^6$ dynes/cm from Table B-4, and values $z_{11} = (z)_{CS} = 0.102$ and $z_{12} = (z)_{CO} = 0.630$ (see Eqs. (B.111) and (B.112)), we obtain:

$$A = 0.49719$$

$$X_1 \equiv 1 - \sqrt{1 - A} = 0.29091$$

$$M_{11} = 30.00 \text{ amu}$$

$$M_{12} = 23.57 \text{ amu}$$

$$z^1_{11} = \left[\frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}}\right]\left[\left(\frac{M_{11}}{k_{11}}\right)^{1/4}\left(\frac{z_{11}}{M_{11}^{1/2}}\right)\right] = 0.0542 \qquad \text{(B.123a)}$$

$$z^1_{12} = \left[\frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}}\right]\left[\left(\frac{M_{12}}{k_{12}}\right)^{1/4}\left(\frac{z_{12}}{M_{12}^{1/2}}\right)\right] = 0.3080 \qquad \text{(B.123b)}$$

$$z_1 = z^1_{11} - z^1_{12} = 0.0542 - 0.3080 = -0.2538 \qquad \text{(B.123c)}$$

A similar calculation for the permanent dipole charge $(z_o)_1$, using $(z_o)_{CS} = 0.2687$ and $(z_o)_{CO} = 0.0207$ yields the values $(z_o)^1_{11} = 0.1427$ and $(z_o)^1_{12} = 0.0101$ for the ν_1 vibration of SCO. Then the permanent dipole moment $(\mu_o)_1$ for the ν_1 vibration of SCO is:

$$\left(\mu_o\right)_{1 \atop \text{calculated}} = e\ell_{XY} \cdot \left(z_o\right)_{11}^{1} - e\ell_{YZ} \cdot \left(z_o\right)_{12}^{1} =$$

$$= 1.0692 - 0.0563 = 1.0129 \text{ debyes} \quad , \qquad (B.124)$$

where we used ℓ_{SC} = 1.56 Angstrom and ℓ_{CO} = 1.16 Angstrom from Table B-4. The value calculated from more accurate theory is μ_o = 0.985 debyes (Ref. 10), while experiment gives μ_o = 0.712 debyes (Ref. 15). The calculated result (B.124) is thus not too bad and shows that the composite dipole charge model we have employed gives reasonably good results at least for the permament dipole moment.

Next let us consider planar molecules. The simplest type in this class is the nonlinear symmetric triatomic molecule XY_2 such as H_2O (see Figure B-6). For planar or nonlinear XY_2 , the valence-force model gives the following relations for the three normal vibrations (Ref. 10):

<u>Planar (Nonlinear) XY_2</u>

$$4\pi^2\nu_1^2 = \frac{\left(1 + \sqrt{1 - B}\right)k_1}{2\ M_X M_Y/(M_X + 2\ M_Y \cos^2\alpha)} + \frac{\left(1 + \sqrt{1 - B}\right)k_2}{M_X M_Y/(M_X + 2\ M_Y \sin^2\alpha)} \quad , \qquad (B.125)$$

$$4\pi^2\nu_2^2 = \frac{\left(1 - \sqrt{1 - B}\right)k_1}{2\ M_X M_Y/(M_X + 2\ M_Y \cos^2\alpha)} + \frac{\left(1 - \sqrt{1 - B}\right)k_2}{M_X M_Y/(M_X + 2\ M_Y \sin^2\alpha)} \quad , \qquad (B.126)$$

$$4\pi^2\nu_3^2 = \frac{k_1}{M_Y M_X/(M_X + 2\ M_Y \sin^2\alpha)} \quad , \qquad (B.127)$$

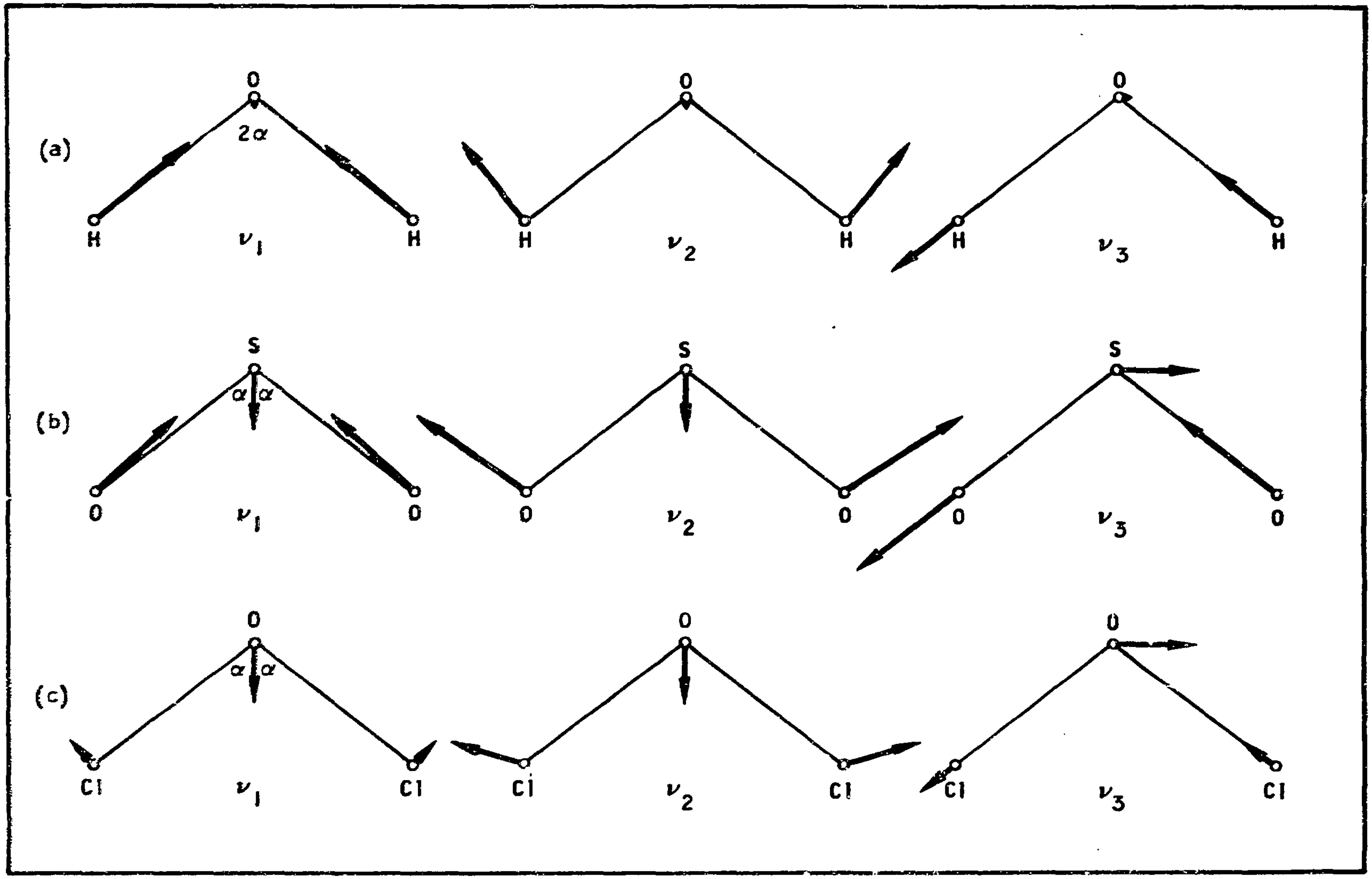

FIGURE B-6. ACTUAL FORM OF THE NORMAL VIBRATIONS OF H_2O, SO_2 AND Cl_2O

where:

$$B = \frac{8\, k_1\, k_2\, M_X\, (M_X + 2\, M_Y)}{\left[k_1(M_X + 2\, M_Y \cos^2\alpha) + 2\, k_2(M_X + 2\, M_Y \sin^2\alpha)\right]^2}\ , \qquad \text{(B.128)}$$

and:

$$k_{11} = k_{21} \equiv k_1 = k_{31} \equiv k_3\ , \ \text{dynes/cm} \qquad \text{(B.129)}$$

$$k_{12} = k_{22} \equiv k_2 \equiv k_\delta/\ell^2_{XY}\ , \ \text{dynes/cm} \qquad \text{(B.130)}$$

The angle α used in the above relations is equal to half the angle 2α between the two XY bonds. Values of k_1 , k_2 , and 2α are given in Table B-4 for some selected nonlinear XY_2 molecules. Note that there are three constants required besides the masses M_X and M_Y to specify ν_1 , ν_2 , and ν_3 , namely: k_1 , k_2 , and α . Since we have three equations and three (measured) values for ν_1 , ν_2 , and ν_3 , while we know the masses M_X and M_Y , there is a unique solution for k_1 , k_2 , and α . The last two columns in Table B-4 show calculated and measured values for 2α , and show that agreement is only fair. Again the disagreement is due to the assumptions inherent in the simple valence-force model.

Since the calculation for α gives only fair results, the force constants k_1 and k_2 are best obtained by using the measured value of α , which is what was done in Table B-4.

To calculate z_1 , z_2 , and z_3 for nonlinear XY_2 from the valence-force model, we use Eq. (B.100) again and Figure B-6 to clarify the signs of $\gamma_{\beta s}$ and $\vec{e}_{\beta s}$. The result is:

$$z_1 = \frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}} \left| \frac{z_{XY}(\vec{e}_{111} + \vec{e}_{112})}{(k_1 M_{11})^{1/4}} + \frac{z_{XY}(\vec{e}_{121} + \vec{e}_{122})}{(k_2 M_{12})^{1/4}} \right| =$$

$$\boxed{z_1 = \frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}} \left[\frac{z_{XY} \cos\alpha}{(k_1 M_{11})^{1/4}} + \frac{z_{XY} \sin\alpha}{(k_2 M_{12})^{1/4}} \right] ,} \quad \text{(B.131)}$$

where:

$$\vec{e}_{111} = \vec{u}_b \cos\alpha - \vec{u}_a \sin\alpha \quad \text{(B.132a)}$$

$$\vec{e}_{112} = \vec{u}_b \cos\alpha + \vec{u}_a \sin\alpha \quad \text{(B.132b)}$$

$\vec{e}_{121} =$ [illegible] $n\,\alpha - \vec{u}_a \cos\alpha$ (B.132c)

$$\vec{e}_{122} = +\vec{u}_b \sin\alpha + \vec{u}_a \cos\alpha \quad \text{(B.132d)}$$

Here the vector $\vec{u}_a$ is a unit vector* along the direction YY of the molecule XY_2 and $\vec{u}_b$ is a unit vector perpendicular to $\vec{u}_a$ in the plane of XY_2, while $\vec{e}_{111}$ is a vector along the left bond coordinate XY (from X to Y) and $\vec{e}_{112}$ is a vector along the right bond coordinate (from X to Y) of the molecule XY_2. The vector $\vec{e}_{121}$ is perpendicular to $\vec{e}_{111}$, and $\vec{e}_{122}$ is a vector perpendicular to $\vec{e}_{112}$. The parameter $z_{XY} \equiv (z_1)_{XY}$ is of course the derivative dipole charge for diatomic XY.

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*Of course $\vec{u}_a \cdot \vec{u}_b = 0$ and $\vec{u}_a \cdot \vec{u}_a = 1$; $\vec{u}_b \cdot \vec{u}_b = 1$.

For z_2 and z_3 we find similarly:

$$\boxed{z_2 = \frac{(2\pi\nu_2)^{1/2}}{M_{21}^{-1/2} + M_{22}^{-1/2}} \left[\frac{z_{XY} \cos\alpha}{(k_1 M_{21})^{1/4}} + \frac{z_{XY} \sin\alpha}{(k_2 M_{22})^{1/4}} \right]} \qquad (B.133)$$

$$\boxed{z_3 = \frac{(2\pi\nu_3)^{1/2}}{M_{31}^{-1/2}} \left[\frac{2 z_{XY} \sin\alpha}{(k_1 M_{31})^{1/4}} \right] = 2 z_{XY} \sin\alpha} \qquad (B.134)$$

The $M_{\beta s}$ in Eqs. (B.131), (B.133), and (B.134) are according to Eqs. (B.125) through (B.128) given by:

$$M_{11} = \frac{2 M_X M_Y}{(1 + \sqrt{1 - B})(M_X + 2 M_Y \cos^2\alpha)} \qquad (B.135)$$

$$M_{12} = \frac{M_X M_Y}{(1 + \sqrt{1 - B})(M_X + 2 M_Y \sin^2\alpha)} \qquad (B.136)$$

$$M_{21} - \frac{2 M_X M_Y}{(1 - \sqrt{1 - B})(M_X + 2 M_Y \cos^2\alpha)} \qquad (B.137)$$

$$M_{22} = \frac{M_X M_Y}{(1 - \sqrt{1 - B})(M_X + 2 M_Y \sin^2\alpha)} \qquad (B.138)$$

$$M_{31} = \frac{M_X M_Y}{M_X + 2 M_Y \sin^2\alpha} \qquad (B.139)$$

Before turning to three-dimensionally-structured molecules, let us consider one other planar molecule with more than three atoms, namely XY_3 represented by BF_3. For planar XY_3 whose four normal vibrations ν_1, ν_2, ν_3, and ν_4 are illustrated in Figure B-7, we find (Ref. 10):

Planar XY_3

$$4\pi^2\nu_1^2 = \frac{k_{11}}{M_Y} \tag{B.140}$$

$$4\pi^2\nu_2^2 = \frac{k_{21}}{M_X M_Y/(M_X + 3\,M_Y)} \tag{B.141}$$

$$4\pi^2\nu_3^2 = \frac{k_{31}\left(1 + \sqrt{1 - C}\right)}{2\,M_X M_Y/(M_X + 3\,M_Y/2)} + \frac{3\,k_{32}\left(1 + \sqrt{1 - C}\right)}{2\,M_X M_Y/(M_X + 3\,M_Y/2)} \tag{B.142}$$

$$4\pi^2\nu_4^2 = \frac{k_{41}\left(1 - \sqrt{1 - C}\right)}{2\,M_X M_Y/(M_X + 3\,M_Y/2)} + \frac{3\,k_{42}\left(1 - \sqrt{1 - C}\right)}{2\,M_X M_Y/(M_X + 3\,M_Y/2)}\,, \tag{B.143}$$

where:

$$C = \frac{12\,k_{31}\,k_{32}\,M_X(M_X + 3\,M_Y)}{\left[\text{[illegible]}_{1} + 3\,k_{32})(M_X + 3\,M_Y/2)\right]^2} = \frac{12\,k_{41}\,k_{42}\,M_X(M_X + 3\,M_Y)}{\left[(k_{41} + 3\,k_{42})(M_X + 3\,M_Y/2)\right]^2} \tag{B.144}$$

Here we have:

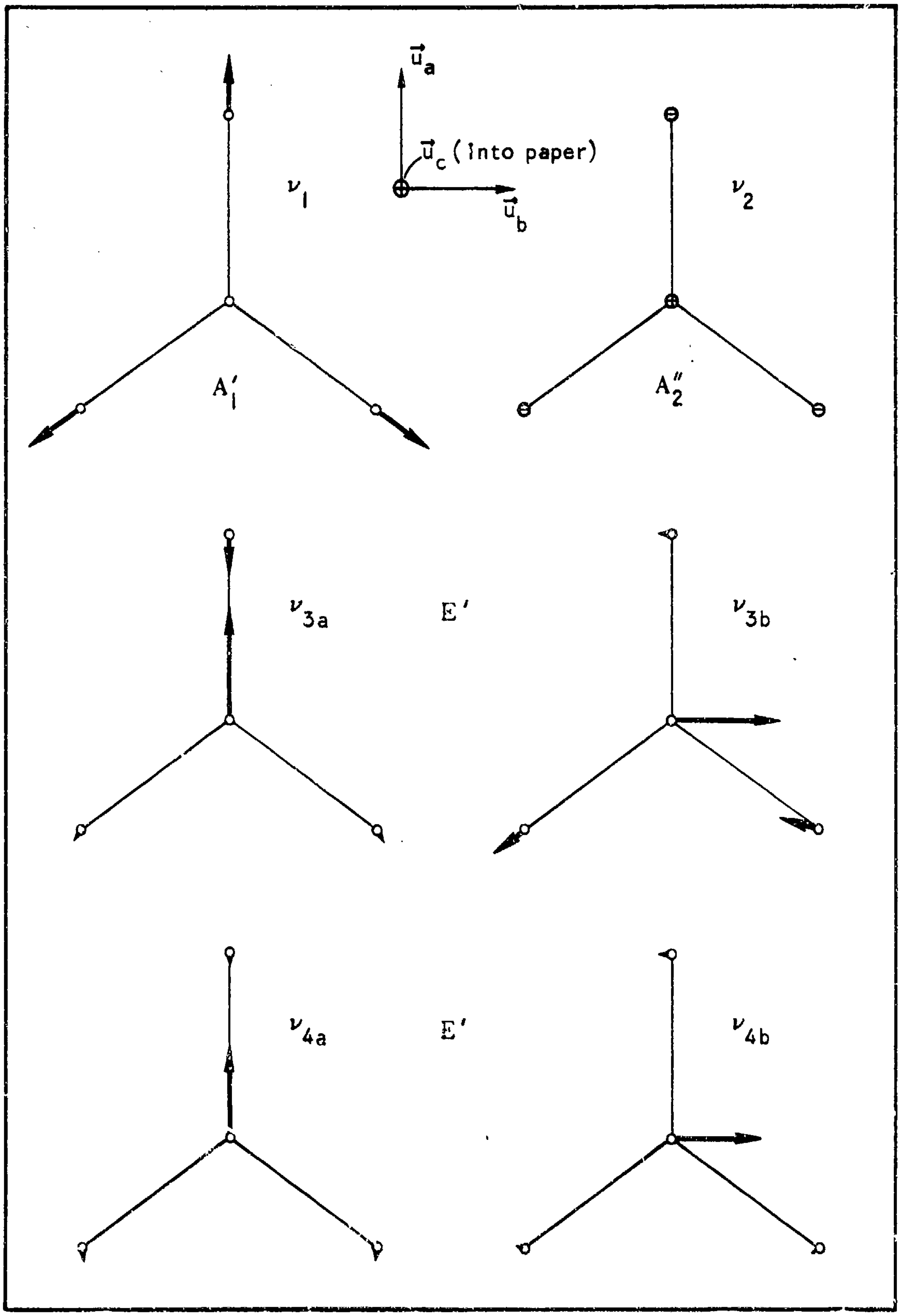

FIGURE B-7. ACTUAL FORM OF THE NORMAL VIBRATIONS OF THE BF_3 MOLECULE (After Ref. 10)

$$k_{11} = k_{31} = k_{41} = k_1 \;, \quad \text{dynes/cm} \qquad (B.145)$$

$$k_{21} = k_\Delta/\ell_{XY}^2 = k_2 \;, \quad \text{dynes/cm} \qquad (B.146)$$

$$k_{32} = k_{42} = k_\delta/\ell_{XY}^2 = k_3 \;, \quad \text{dynes/cm} \qquad (B.147)$$

Values of k_1, k_2, and k_3 of several planar XY_3 molecules taken from Ref. 10 are given in Table B-5. Referring to Figure B-7, and using Eq. (B.100) again, we obtain for z_1, z_2, z_3, and z_4 of planar XY_3 :

$$\boxed{z_1 = \frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2}}\,(0) = 0} \qquad (B.148)$$

$$\boxed{z_2 = \frac{(2\pi\nu_2)^{1/2}}{M_{21}^{-1/2}} \left[\frac{3\,z_{XY}\delta_b}{(M_{21}\,k_2)^{1/4}}\right] = 3\,z_{XY}\delta_b} \qquad (B.149)$$

$$\boxed{z_3 = \left(\frac{(2\pi\nu_3)^{1/2}}{M_{31}^{-1/2} + M_{32}^{-1/2}}\right) \left[\frac{2\,z_{XY}}{(M_{31}\,k_1)^{1/4}} + \frac{z_{XY}}{(M_{32}\,k_3)^{1/4}}\right]} \qquad (B.150)$$

$$\boxed{z_4 = \left(\frac{(2\pi\nu_4)^{1/2}}{M_{41}^{-1/2} + M_{42}^{-1/2}}\right) \left[\frac{2\,z_{XY}}{(M_{41}\,k_1)^{1/4}} + \frac{z_{XY}}{(M_{42}\,k_3)^{1/4}}\right] ,} \qquad (B.151)$$

Here δ_b in Eq. (B.149) is given by Eq. (B.104) with $k_{22} = k_2$.

TABLE B-5. FORCE CONSTANTS OF PLANAR AND PYRAMIDAL XYZ MOLECULES CALCULATED VIA THE VALENCE-FORCE MODEL (After Ref. 10)

Molecule XY_3	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	$\ell_{XY} = \ell$ (Angstrom)	k_1 (Megadynes/cm)	$k_2 = \frac{k_\Delta}{\ell^2}$ (Megadynes/cm)	$k_3 = \frac{k_\delta}{\ell^2}$ (Megadynes/cm)
Planar								
BF_3	888	691	1446	480	1.262	0.883	0.087	0.037
BCl_3	471	462	958	243	1.715	0.463	0.042	0.016
BBr_3	279	372	806	151	1.877	0.366	0.029	0.013
SO_3	1069	652	1330	532	1.493	1.077	0.160	0.046
CO_3^{--}	1063	879	1415	680	1.128	1.065	0.146	0.051
NO_3^{--}	1050	831	1390	720	1.151	1.039	0.147	0.064
Pyramidal								Angle β (Observed)
NH_3	3337	950	3414	1628	1.0124	0.635	0.054	69°
ND_3	2419	749	2555	1191	1.013	0.651	0.056	69°
PH_3	2327	991	2421	1121	1.421	0.324	0.033	62°
PD_3	1694	730	(1780)	806	1.422	(0.329)	(0.035)	62°
PF_3	890	531	840	486	1.535	0.459	0.107	62°
PCl_3	510	257	480	190	(2.10)	0.212	0.032	64°
PBr_3	380	162	400	116	(2.25)	0.163	0.027	65°
AsF_3	707	341	644	274	(2.02)	0.392	0.04[illegible]	60°
$AsCl_3$	410	193	370	159	(2.50)	0.203	0.023	59°
$SbCl_3$	360	165	320	134	(2.71)	0.178	0.018	57°
$BiCl_3$	288	130	242	96	(3.00)	0.119	0.010	57°
UI_3	(157)	(66)	(159)	(57)	(3.05)	(0.12)	(0.01)	(57°)

( ) = Estimated

where according to Eqs. (B.140) through (B.144):

$$M_{11} = M_Y \qquad \text{(B.152)}$$

$$M_{21} = \frac{M_X M_Y}{M_X + 3\ M_Y} \qquad \text{(B.153)}$$

$$M_{31} = \frac{2\ M_X M_Y}{(1 + \sqrt{1 - C})(M_X + 3\ M_Y/2)} \qquad \text{(B.154)}$$

$$M_{32} = \frac{2\ M_X M_Y}{3(1 + \sqrt{1 - C})(M_X + 3\ M_Y/2)} \qquad \text{(B.155)}$$

$$M_{41} = \frac{2\ M_X M_Y}{(1 - \sqrt{1 - C})(M_X + 3\ M_Y/2)} \qquad \text{B.156)}$$

$$M_{42} = \frac{2\ M_X M_Y}{3(1 - \sqrt{1 - C})(M_X + 3\ M_Y/2)} \qquad \text{(B.157)}$$

In arriving at the results (B.148) through (B.151), the following dipole directions $\vec{e}_{3s}$ and vibration signs $\gamma_{\beta s}$ were used which follow from Figure B-7:

$$\begin{aligned}
\gamma_{11}\ z_{11}\ \vec{e}_{11} &= \gamma_{111}\ z_{111}\ \vec{e}_{111} + \gamma_{112}\ z_{112}\ \vec{e}_{112} + \gamma_{113}\ z_{113}\ \vec{e}_{113} = \\
&+ z_{XY}\ \vec{u}_a - z_{XY}(\cos 60^\circ)\ \vec{u}_a - z_{XY}(\cos 60^\circ)\ \vec{u}_a + \\
&+ z_{XY}(\sin 60^\circ)\ \vec{u}_b - z_{XY}(\sin 60^\circ)\ \vec{u}_b = \\
&z_{XY}\ \vec{u}_a - \frac{1}{2}\ z_{XY}\ \vec{u}_a - \frac{1}{2}\ z_{XY}\ \vec{u}_a = 0
\end{aligned} \qquad \text{(B.158)}$$

$$\gamma_{21}\, z_{21} (\delta_q)_{21}\, \vec{e}_{21} = 3\, z_{XY}\, \delta_b\, \vec{u}_c \tag{B.159}$$

$$\gamma_{31}\, z_{31}\, \vec{e}_{31} = (-)\, z_{XY}(+\vec{u}_a) + 2(+)\, z_{XY}(-\vec{u}_a) \cos 60^\circ +$$

$$+ (+)\, z_{XY}(+\vec{u}_b) + (+)\, z_{XY}(-\vec{u}_b) = -2\, z_{XY}\, \vec{u}_a \tag{B.160}$$

$$\gamma_{32}\, z_{32}\, \vec{e}_{32} = (-)\, z_{XY}(\cos 30^\circ)(+\vec{u}_b) + (-)\, z_{XY}(\cos 30^\circ)(-\vec{u}_b)$$

$$+ 2\ (+)\, z_{XY}(\sin 30^\circ)(-\vec{u}_a) = -z_{XY}\, \vec{u}_a \tag{B.161}$$

$$\gamma_{41}\, z_{41}\, \vec{e}_{41} = \gamma_{31}\, z_{31}\, \vec{e}_{31} = -2\, z_{XY}\, \vec{u}_a \tag{B.162}$$

$$\gamma_{42}\, z_{42}\, \vec{e}_{42} = \gamma_{32}\, z_{32}\, \vec{e}_{32} = -z_{XY}\, \vec{u}_a \tag{B.163}$$

In the above we use the convention that a minus sign applies for a contracting vibration and a plus sign for an expanding one. The three mutually perpendicular vectors $\vec{u}_a$, $\vec{u}_b$, and $\vec{u}_c$ are along directions as shown in Figure B-7. Note that the ν_3 and ν_4 vibrations are doubly-degenerate and have components similar to Eqs. (B.160) through (B.163) with $\vec{u}_a$ replaced by $\vec{u}_b$.

Turning next to three-dimensionally-structured molecules, we shall briefly discuss pyramidal XY_3 molecules, tetrahedral XY_4 molecules and octahedral XY_6 molecules, represented by NH_3 , CH_4 , and SF_6 , respectively. For pyramidal XY_3 molecules such as NH_3 or ND_3 , the valence-force model gives the following expressions (Ref. 10) for the normal vibrations which are illustrated in Figure B-8.

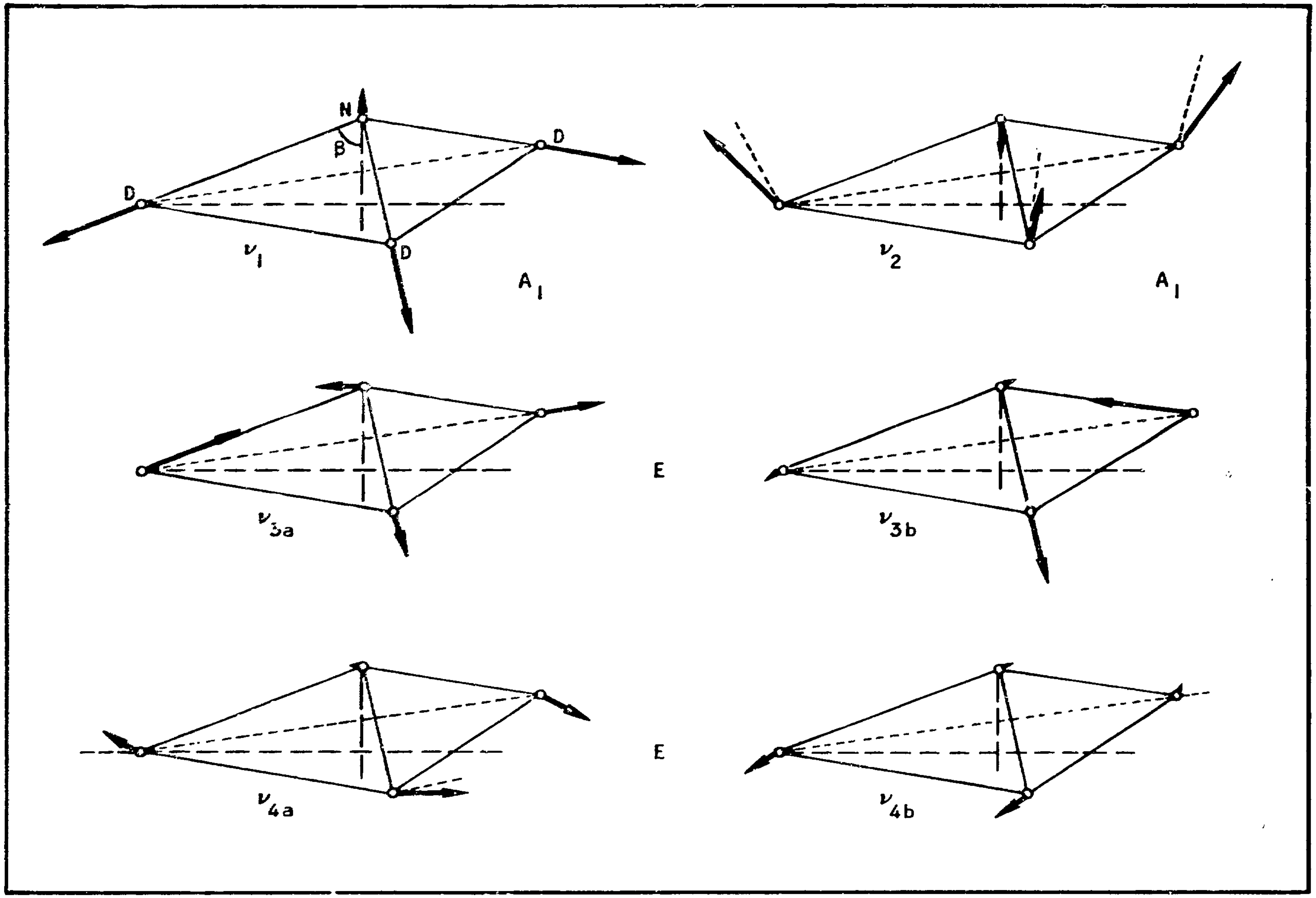

FIGURE B-8. NORMAL VIBRATIONS OF THE ND_3 MOLECULE (Ref. 10)

Pyramidal XY_3

$$4\pi^2\nu_1^2 = \frac{k_{11}\left(1 + \sqrt{1 - D}\right)}{2\,M_XM_Y/\left\{M_X + 3\,M_Y(\cos^2\beta)\right\}} + \frac{k_{12}\left(1 + \sqrt{1 - D}\right)}{2\,f_\beta\,M_XM_Y/\left\{M_X + 3\,M_Y(\sin^2\beta)\right\}} \qquad (B.164)$$

$$4\pi^2\nu_2^2 = \frac{k_{21}\left(1 - \sqrt{1 - D}\right)}{2\,M_XM_Y/\left\{M_X + 3\,M_Y(\cos^2\beta)\right\}} + \frac{k_{22}\left(1 - \sqrt{1 - D}\right)}{2\,f_\beta\,M_XM_Y/\left\{M_X + 3\,M_Y(\sin^2\beta)\right\}} \qquad (B.165)$$

where:

$$f_\beta = \frac{1 + 3\cos^2\beta}{12\cos^2\beta} \qquad (B.166)$$

$$D = \frac{4\,k_{11}\,k_{12}\,f_\beta\,M_X\,(3\,M_Y + M_X)}{\left[k_{11}\,f_\beta\,(M_X + 3\,M_Y\cos^2\beta) + k_{12}\,(M_X + 3\,M_Y\sin^2\beta\right]^2}\,, \qquad (B.167)$$

and:

$$4\pi^2\nu_3^2 = \frac{k_{31}\left(1 + \sqrt{1 - E}\right)}{2\,M_XM_Y/\left\{M_X + 3\,M_Y(\sin^2\beta)/2\right\}} + \frac{k_{32}\left(1 + \sqrt{1 - E}\right)}{2\,M_XM_Yg_\beta/\left\{(1 + \cos^2\beta)\,M_X + 3\,M_Y(\sin^4\beta)/2\right\}} \qquad (B.168)$$

$$4\pi^2\nu_4^2 = \frac{k_{41}\left(1 - \sqrt{1 - E}\right)}{2\,M_XM_Y/\left\{M_X + 3\,M_Y(\sin^2\beta)/2\right\}} + \frac{k_{42}\left(1 - \sqrt{1 - E}\right)}{2\,M_XM_Yg_\beta/\left\{(1 + \cos^2\beta)\,M_X + 3\,M_Y(\sin^4\beta)/2\right\}} \qquad (B.169)$$

where:

$$g_\beta = \frac{1 + 3\cos^2\beta}{3} \tag{B.170}$$

$$E = \frac{4\, k_{31}\, k_{32}\, g_\beta M_X \left\{(1 + \cos^2\beta)\, M_X + 3\, M_Y \sin^2\beta\right\}}{\left[g_\beta k_{31}\left\{M_X + 3\, M_Y(\sin^2\beta)/2\right\} + k_{32}\left\{(1 + \cos^2\beta)\, M_X + 3\, M_Y(\sin^4\beta)/2\right\}\right]^2} \tag{B.171}$$

Here β is the angle that a bond YY makes with the molecular axis (see Figure B-8). The force constants $k_{\beta s}$ are not all independent, but are related via the equations:

$$k_{11} = k_{21} = k_{31} = k_{41} = k_1 \;, \quad \text{dynes/cm} \tag{B.172}$$

$$k_{12} = k_{22} = k_{32} = k_{42} = k_\delta/\ell^2_{XY} = k_2 \;, \quad \text{dynes/cm} \tag{B.173}$$

Table B-5 lists values of k_1 and k_2 for some selected pyramidal molecules.

Referring to Figure B-8, we have according to Eq. (B.100) and with due consideration of the various $\vec{Y}_{\beta s}$ and $\vec{e}_{\beta s}$ factors:

$$\boxed{z_1 = \left(\frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2} + M_{12}^{-1/2}}\right)\left(\frac{3\, z_{XY} \cos\beta}{(k_1\, M_{11})^{1/4}}\right)} \tag{B.174}$$

$$\boxed{z_2 = \left(\frac{(2\pi\nu_2)^{1/2}}{M_{21}^{-1/2} + M_{22}^{-1/2}}\right)\left(\frac{-3\, z_{XY} \cos\beta}{(k_1\, M_{21})^{1/4}}\right)} \tag{B.175}$$

$$\boxed{z_3 = \left(\frac{(2\pi\nu_3)^2}{M_{31}^{-1/2} + M_{32}^{-1/2}}\right)\left(\frac{z_{XY}\ \sin\beta}{(k_1\ M_{31})^{1/4}} + \frac{z_{XY}\ \sin\beta}{(k_2\ M_{32})^{1/4}}\right)} \tag{B.176}$$

$$\boxed{z_4 = \left(\frac{(2\pi\nu_4)^{1/2}}{M_{41}^{-1/2} + M_{42}^{-1/2}}\right)\left(\frac{z_{XY}\ \cos\beta}{(k_1\ M_{41})^{1/4}} + \frac{z_{XY}\ \cos\beta}{(k_2\ M_{42})^{1/4}}\right)} \tag{B.177}$$

Here the $M_{\beta s}$ in Eqs. (B.174) through (B.177) are given by:

$$M_{11} = \frac{2\ M_X M_Y}{(1 + \sqrt{1 - D})\left[M_X + 3\ M_Y(\cos^2\beta)\right]} \tag{B.178}$$

$$M_{12} = \frac{2\ f_\beta M_X M_Y}{(1 + \sqrt{1 - D})\left[M_X + 3\ M_Y(\sin^2\beta)\right]} \tag{B.179}$$

$$M_{21} = \frac{2\ M_X M_Y}{(1 - \sqrt{1 - D})\left[M_X + 3\ M_Y(\cos^2\beta)\right]} \tag{B.180}$$

$$M_{22} = \frac{2\ f_\beta M_X M_Y}{(1 - \sqrt{1 - D})\left[M_X + 3\ M_Y(\sin^2\beta)\right]} \tag{B.181}$$

$$M_{31} = \frac{2\ M_X M_Y}{(1 + \sqrt{1 - E})(M_X + 3\ M_Y(\sin^2\beta)/2)} \tag{B.182}$$

$$M_{32} = \frac{2\, g_\beta M_X M_Y}{(1 + \sqrt{1 - E})\{(1 + \cos^2\beta)\, M_X + 3\, M_Y(\sin^4\beta)/2\}} \tag{B.183}$$

$$M_{41} = \frac{2\, M_X M_Y}{(1 - \sqrt{1 - E})(M_X + 3\, M_Y(\sin^2\beta)/2)} \tag{B.184}$$

$$M_{42} = \frac{2\, g_\beta M_X M_Y}{(1 - \sqrt{1 - E})\{(1 + \cos^2\beta)\, M_X + 3\, M_Y(\sin^4\beta)/2\}} \tag{B.185}$$

Next we consider tetrahedral XY_4 molecules whose three-dimensional structure is shown in Figure B-9. For these molecules the valence-force model gives the following expressions (Ref. 10) for the four normal vibrations ν_1, ν_2 (doubly-degenerate), ν_3 (triply-degenerate), and ν_4 (triply-degenerate):

Tetrahedral XY_4

$$4\pi^2\nu_1^2 = \frac{k_{11}}{M_Y} \tag{B.186}$$

$$4\pi^2\nu_2^2 = \frac{3\, k_{21}}{M_Y} \tag{B.187}$$

$$4\pi^2\nu_3^2 = \frac{k_{31}\left(1 + \sqrt{1 - F}\right)}{2\, M_X M_Y/\{M_X + 4\, M_Y/3\}} + \frac{k_{32}\left(1 + \sqrt{1 - F}\right)}{M_X M_Y/\ M_X + 8\, M_Y/3\}} \tag{B.188}$$

$$4\pi^2\nu_4^2 = \frac{k_{41}\left(1 - \sqrt{1 - F}\right)}{2\, M_X M_Y/\{M_X + 4\, M_Y/3\}} + \frac{k_{42}\left(1 - \sqrt{1 - F}\right)}{M_X M_Y/\{M_X + 8\, M_Y/3\}} \tag{B.189}$$

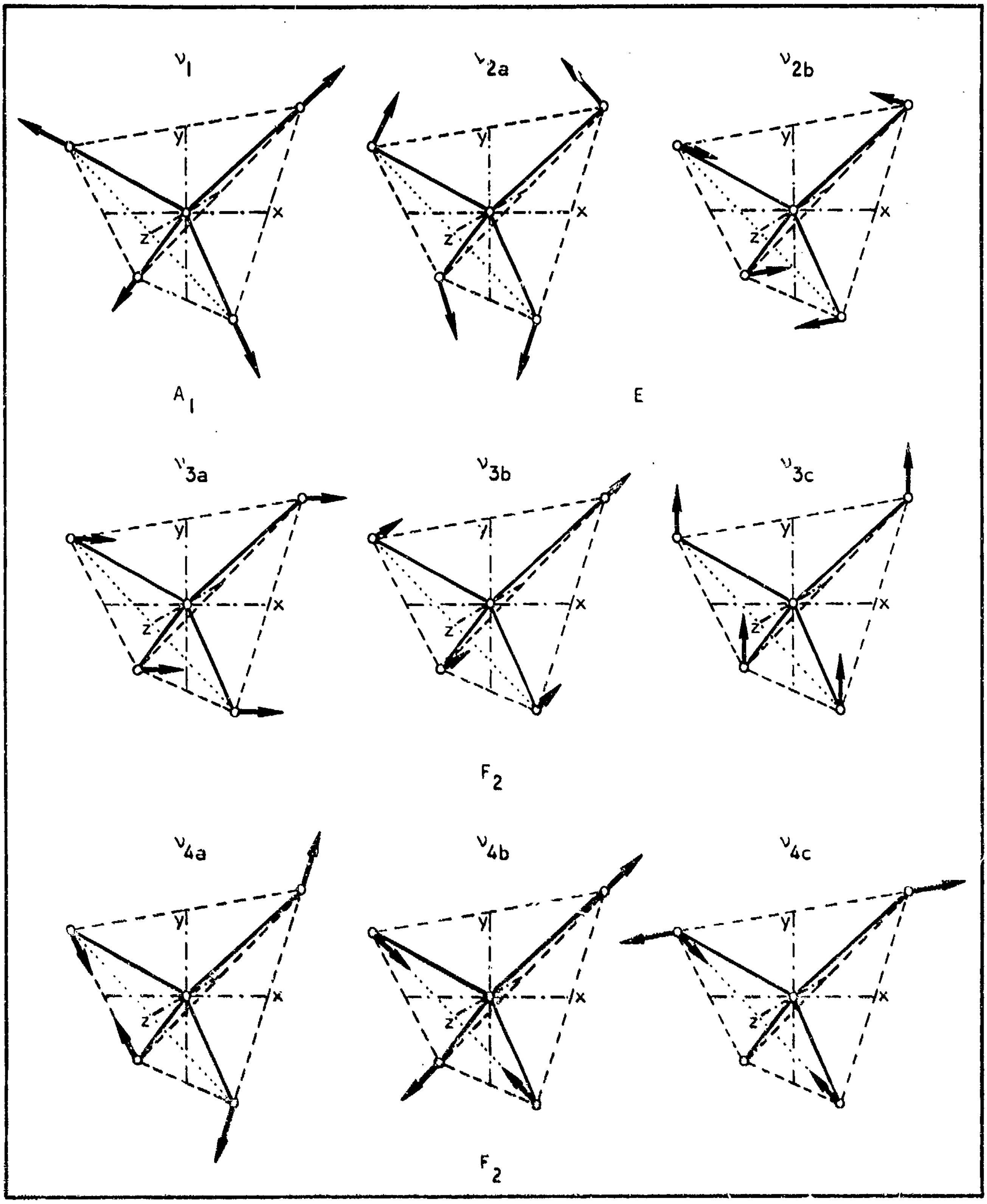

FIGURE B-9. NORMAL VIBRATIONS OF A TETRAHEDRAL XY_4 MOLECULE. – The three two-fold axes (Dot-Dash Lines) are chosen as x, y, and z axes (Ref. 10).

where:

$$F = \frac{8\ k_{31}\ k_{32}\ M_X(M_X + 4\ M_Y)}{\left[k_{31}(M_X + 4\ M_Y/3) + 2\ k_{32}(M_X + 8\ M_Y/3)\right]^2} \qquad (B.190)$$

Again the $k_{\beta s}$ are related in the valence-force model, that is:

$$k_{11} = k_{31} = k_{41} = k_1 \qquad (B.191)$$

$$k_{21} = k_{32} = k_{42} = k_\delta/\ell^2_{XY} = k_2 \qquad (B.192)$$

In Table B-6, values for k_1 and k_2 of some tetrahedral molecules are listed taken from Ref. 10.

The z_β's according to Eq. (B.100) and with the aid of Figure B-9 are then evaluated to be:

$$\boxed{z_1 = \frac{(2\pi\nu_1)^{1/2}}{M_{11}^{-1/2}} \left(\frac{0}{(k_1\ M_{11})^{1/4}}\right) = 0} \qquad (B.193)$$

$$\boxed{z_2 = \frac{(2\pi\nu_2)^{1/2}}{M_{21}^{-1/2}} \left(\frac{0}{(k_1\ M_{21})^{1/4}}\right) = 0} \qquad (B.194)$$

$$\boxed{z_3 = \frac{(2\pi\nu_3)^{1/2}}{M_{31}^{-1/2} + M_{32}^{-1/2}} \left(\frac{(4/\sqrt{3})z_{XY}}{(k_1\ M_{31})^{1/4}} + \frac{(4/\sqrt{3})z_{XY}}{(k_2\ M_{32})^{1/4}}\right)} \qquad (B.195)$$

$$\boxed{z_4 = \frac{(2\pi\nu_4)^{1/2}}{M_{41}^{-1/2} + M_{42}^{-1/2}} \left(\frac{z_{XY}/\sqrt{2}}{(k_1\ M_{41})^{1/4}} + \frac{z_{XY}/\sqrt{2}}{(k_2\ M_{42})^{1/4}}\right)} , \qquad (B.196)$$

TABLE B-6. FORCE CONSTANTS OF SELECTED TETRAHEDRAL XY_4 MOLECULES ACCORDING TO THE VALENCE-FORCE MODEL (Ref. 10)*

Molecule XY_4	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	ℓ_{XY} (Angstroms)	k_1 (Megadynes/cm)	k_2 (Megadynes/cm)
CH_4	2914	1526	3020	1306	1.0940	0.504	0.0461
CD_4	2085	1054	2258	996	1.095	0.516	0.0439
SiH_4	2187	978	2183	910	1.41	[illegible]	0.0139
NH_4^+	3033	1685	3134	1397	0.93	0.546	0.0562
CF_4	904	437	1265	630	1.32	0.914	0.0713
SiF_4	800	260	1022	420	1.50	0.716	0.0252
$C\ell_4$	458	218	776	314	1.75	0.438	0.0331
$SiC\ell_4$	424	150	608	221	1.87	0.375	0.0157
$TiC\ell_4$	386	120	495	141	2.22	0.311	0.0100
$GeC\ell_4$	396	134	453	172	2.27	0.327	0.0125
$SnC\ell_4$	366	104	403	134	1.89	0.280	0.0075
CBr_4	267	123	672	183	1.94	0.336	0.0237
$SiBr_4$	249	90	487	137	2.06	0.292	0.0127
$GeBr_4$	234	78	328	111	2.46	0.258	0.0095
$SnBr_4$	220	64	279	88	2.08	0.228	0.0064
UI_4	(164)	(45)	(216)	(49)	2.88	(0.200)	(0.0050)
OsO_4	971	335	960	328	1.85	0.889	0.0352
SO_4^{--}	981	451	1104	613	1.48	0.907	0.0639
$C\ell O_4^-$	935	462	1102	628	1.50	0.824	0.0670
PO_4^{---}	980	363	1082	515	1.44	0.905	0.0414

*Values in parentheses are estimated.

where:

$$M_{11} = M_{21} = M_Y \quad ; \quad M_{21} = M_Y/3 \tag{B.197}$$

$$M_{31} = \frac{2\, M_X M_Y}{(1 + \sqrt{1 - F})(M_X + 4\, M_Y/3)} \tag{B.198}$$

$$M_{32} = \frac{M_X M_Y}{(1 + \sqrt{1 - F})(M_X + 8\, M_Y/3)} \tag{B.199}$$

$$M_{41} = \frac{2\, M_X M_Y}{(1 - \sqrt{1 - F})(M_X + 4\, M_Y/3)} \tag{B.200}$$

$$M_{42} = \frac{M_X M_Y}{(1 - \sqrt{1 - F})(M_X + 8\, M_Y/3)} \tag{B.201}$$

F is given by Eq. (B.190) which with (B.191) and (B.192) reads:

$$F = \frac{8\, k_1\, k_2\, M_X(M_X + 4\, M_Y)}{\left[k_1(M_X + 4\, M_Y/3) + 2\, k_2(M_X + 8\, M_Y/3)\right]^2} \tag{B.202}$$

We finally turn to octahedral XY_6 molecules such as SF_6 and UF_6. For this molecule the so-called "Coulomb-Forces Model" applied by Eucken and Sauter (Ref. 21) appears more satisfactory than either the "Central-Forces-Model" (simplest to use) or the "Valence-Forces Model." The latter model was assumed in all the relations we used so far since it appears to give better results than the Central-Forces-Model (Ref. 10).

According to Eucken and Sauter we have for the six normal vibrations of XY_6 the relations (Ref. 21):

Octahedral XY_6

$$4\pi^2\nu_1^2 = \frac{k_1}{M_Y} \tag{B.203}$$

$$4\pi^2\nu_2^2 = \frac{k_2}{M_Y} \tag{B.204}$$

$$4\pi^2\nu_3^2 = \frac{(1 + \sqrt{1 - G})\ k_3}{2\ M_Y} + \frac{(1 + \sqrt{1 - G})\ k_4}{M_X} \tag{B.205}$$

$$4\pi^2\nu_4^2 = \frac{(1 - \sqrt{1 - G})\ k_3}{2\ M_Y} + \frac{(1 - \sqrt{1 - G})\ k_4}{M_X} \tag{B.206}$$

$$4\pi^2\nu_5^2 = \frac{k_5}{M_Y} \tag{B.207}$$

$$4\pi^2\nu_6^2 = \frac{k_6}{M_Y} \tag{B.208}$$

Here:

$$G = \frac{4\ M_X(M_X + 6\ M_Y)\ k_c^2}{\{M_X\ k_3 + 2\ M_Y\ k_4\}^2} \tag{B.209}$$

Of the seven force constants k_1, k_2, k_3, k_4, k_5, k_6, and k_c only six are independent if the Coulomb-Forces-Model is assumed. In this case we have that:

$$k_3 = \left(\frac{k_1 + 2\,k_2}{3}\right) + (k_5 - k_6) = M_Y\left[\frac{\lambda_1 + 2\,\lambda_2}{3} + \lambda_5 - \lambda_6\right] =$$

$$= 0.058899 \underset{(\text{amu})}{M_Y} \underset{(\text{cm}^{-1})^2}{\left[\frac{\nu_1^2 + 2\,\nu_2^2}{3} + \nu_5^2 - \nu_6^2\right]} \;,\quad \text{dynes/cm} \;, \qquad (\text{B.210})$$

where we define

$$\lambda_i = 4\pi^2\nu_i^2 \qquad (\text{B.211})$$

and where from Eqs. (B.203), (B.204), (B.207), and (B.208), we have:

$$k_1 = M_Y\,\lambda_1 = 0.058899 \underset{(\text{amu})(\text{cm}^{-1})^2}{M_Y \quad \nu_1^2} \;,\quad \text{dynes/cm} \qquad (\text{B.212})$$

$$k_2 = M_Y\,\lambda_2 = 0.058899 \underset{(\text{amu})(\text{cm}^{-1})^2}{M_Y \quad \nu_2^2} \;,\quad \text{dynes/cm} \qquad (\text{B.213})$$

$$k_5 = M_Y\,\lambda_5 = 0.058899 \underset{(\text{amu})(\text{cm}^{-1})^2}{M_Y \quad \nu_5^2} \;,\quad \text{dynes/cm} \qquad (\text{B.214})$$

$$k_6 = M_Y\,\lambda_6 = 0.058899 \underset{(\text{amu})(\text{cm}^{-1})^2}{M_Y \quad \nu_6^2} \;,\quad \text{dynes/cm} \qquad (\text{B.215})$$

From Eqs. (B.205) and (B.206), we obtain further that:

$$k_4 = M_X \left[\frac{\lambda_3 + \lambda_4}{2} - \frac{k_3}{2\,M_Y}\right] = \underset{(\text{amu})}{M_X} \left[0.029450\underset{(\text{cm}^{-1})^2}{\left(\nu_3^2 + \nu_4^2\right)} - \underset{(\text{amu})}{\frac{k_3}{2\,M_Y}}\right] =$$

$$= 0.029450\ \underset{(\text{amu})}{M_X} \left[\nu_3^2 + \nu_4^2 - \underset{(\text{cm}^{-1})^2}{\left(\frac{\nu_1^2 + 2\nu_2^2}{3}\right)} - \nu_5^2 + \nu_6^2\right],\ \frac{\text{dynes}}{\text{cm}} \tag{B.216}$$

and:

$$k_c = M_Y\left(\frac{M_X\,\lambda_3\,\lambda_4}{M_X + 6\,M_Y}\right)^{1/2} = 0.058899\ \underset{(\text{amu})}{M_Y}\left(\frac{M_X}{M_X + 6\,M_Y}\right)^{1/2} \underset{(\text{cm}^{-1})}{\nu_3}\ \underset{(\text{cm}^{-1})}{\nu_4}\ ,\ \frac{\text{dynes}}{\text{cm}} \tag{B.217}$$

The above relations were derived from the work by Eucken and Sauter (Ref. 21), who do not use the force constants k_i but instead a set of seven basic parameters A′, B′, D′, E′, F′, H′, and J′ to which our k_i are related by:

$$k_1 = A' + 2\,D' + 4\,E' - 4\,F' \tag{B.218}$$

$$k_2 = A' + 2\,D' + 4\,E' + 2\,F' \tag{B.219}$$

$$k_3 = A' + B' + 6\,E' \tag{B.220}$$

$$k_4 = A' + 2\,B' \tag{B.221}$$

$$k_5 = 1\ B' + 4\ E' + 4\ H' + 4\ J' \tag{B.222}$$

$$k_6 = B' + 2\ E' + 4\ J' \tag{B.223}$$

$$k_3 = (A'B' + 2\ A'E' + 4\ B'E')^{1/2} \tag{B.224}$$

The existence of seven basic constants A', B', etc., for an octahedral molecule follows strictly from symmetry considerations and does not follow from any force model. To obtain definite relations between these seven constants and the six observable normal vibrations ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 , it is necessary to establish another condition(s) such as the assumption of central-forces, valence-forces, or Coulomb-like forces, so that the number of unknown constants becomes equal to or less than the number of known parameters. For the Coulomb-Force-Model which Eucken and Sauter favor, this additional condition is (Ref. 21):

$$H' = -2\ D' \tag{B.225}$$

This relation together with Eqs. (B.218) through (B.224) can be shown to reduce the number of independent k_i's from seven to six and results in the relations we gave above.

Note that we rote for convenience $k_{11} = k_1$, $k_{21} = k_2$, $k_{31} = k_{41} = k_3$, $k_{32} = k_{42} = k_4$, $k_{51} = k_5$, and $k_{61} = k_6$. In Table B-7, values of the six normal vibrational frequencies and the force constants are listed for a number of important octahedral hexafluorides. The vibrations are illustrated in Figure B-10. Note that ν_1 is non-degenerate, ν_2 is doubly-degenerate, and ν_3 , ν_4 , ν_5 , and ν_6 are each triply-degenerate.

TABLE B-7. FORCE CONSTANTS OF SELECTED OCTAHEDRAL XY_6 MOLECULES ACCORDING TO THE COULOMB-FORCES MODEL (Refs. 21, 22)

Molecule XY_6	Normal Frequencies, cm^{-1}						ℓ_{XY}, Angstrom	Force Constants, Megadynes/cm						
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6		k_1	k_2	k_3	k_4	k_c	k_5	k_6
SF_6	775	644	932	613	524	344	1.57	0.672	0.464	0.708	0.576	0.231	0.307	0.132
SeF_6	708	662	780	437	405	260	1.71	0.561	0.491	0.621	0.567	0.120	0.183	0.076
TeF_6	701	674	752	327	313	197	1.85	0.550	0.512	0.592	0.553	0.0771	0.110	0.043
MoF_6	736	641	742	269	319	240	1.84	0.606	0.459	0.523	0.351	0.0672	0.080	0.065
WF_6	769	670	712	256	322	216	1.84	0.662	0.502	0.629	0.103	0.0515	0.116	0.052
UF_6	667	533	624	186	202	134	1.99	0.499	0.317	0.401	0.250	0.0108	0.046	0.023

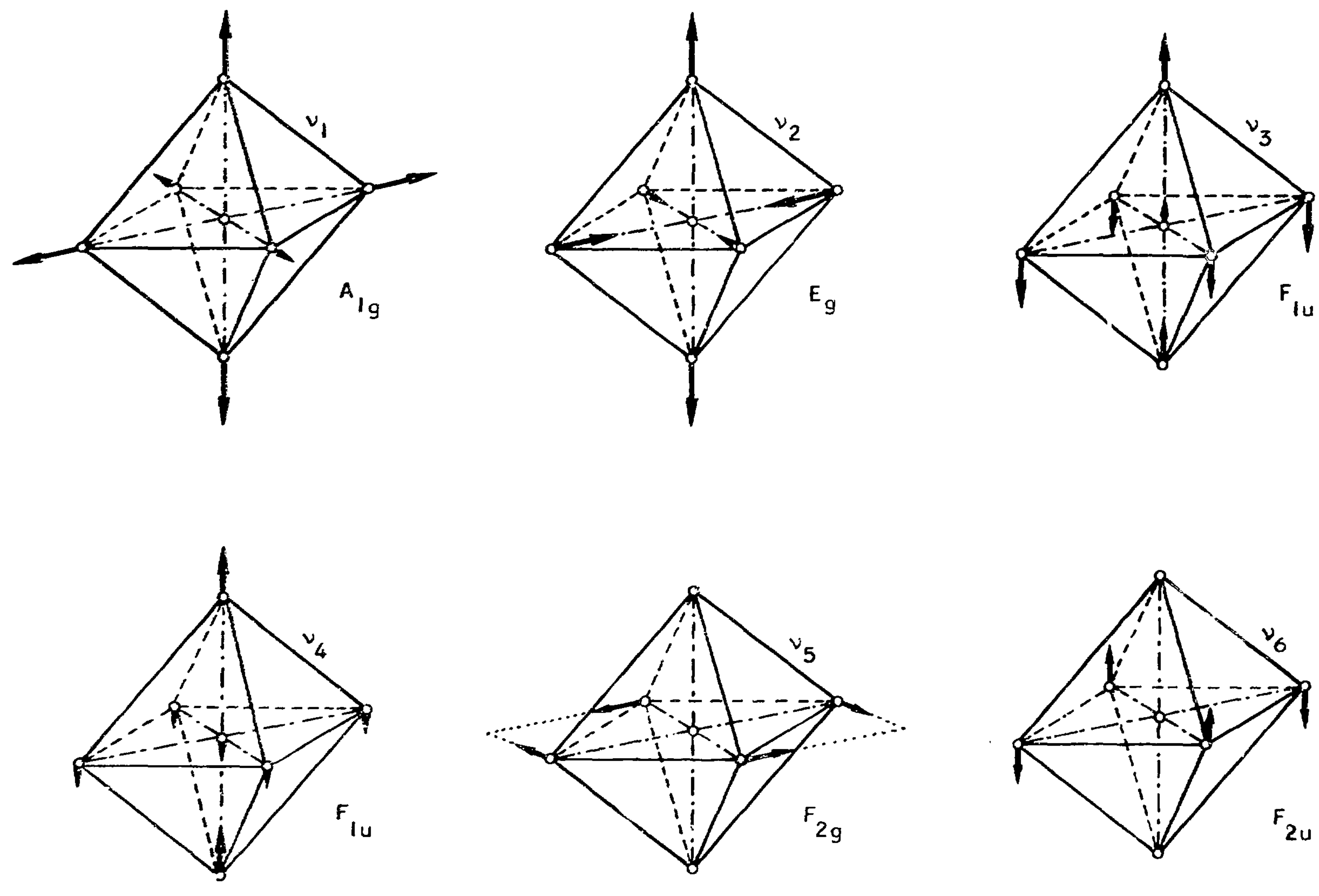

FIGURE B-10. NORMAL VIBRATIONS OF OCTAHEDRAL XY_6 MOLECULES Ref. 15

Taking proper account of the $\gamma_{\beta s}$ and $\vec{e}_{\beta s}$ by inspection of the vibrations shown in Figure B-10 and using Eq. (B.100), we find for the z_β of XY_6:

$$\boxed{z_1 = 0} \tag{B.226}$$

$$\boxed{z_2 = 0} \tag{B.227}$$

$$\boxed{z_3 = \left(\frac{(2\pi\nu_3)^{1/2}}{M_{31}^{-1/2} + M_{32}^{-1/2}}\right)\left(\frac{2\sqrt{2}\,z_{XY}}{(k_3\,M_{31})^{1/4}} + \frac{2\sqrt{2}\,z_{XY}}{(k_4\,M_{32})^{1/4}}\right)} \tag{B.228}$$

$$\boxed{z_4 = \left(\frac{(2\pi\nu_4)^{1/2}}{M_{41}^{-1/2} + M_{42}^{-1/2}}\right)\left(\frac{2\,z_{XY}}{(k_3\,M_{41})^{1/4}} + \frac{2\,z_{XY}}{(k_4\,M_{42})^{1/4}}\right)} \tag{B.229}$$

$$\boxed{z_5 = 0} \tag{B.230}$$

$$\boxed{z_6 = 0 \quad ,} \tag{B.231}$$

where:

$$M_{31} = \frac{2\,M_Y}{1 + \sqrt{1 - G}} \tag{B.232}$$

$$M_{32} = \frac{M_X}{1 + \sqrt{1 - G}} \tag{B.233}$$

$$M_{41} = \frac{2\ M_Y}{1 - \sqrt{1 - G}} \qquad (B.234)$$

$$M_{42} = \frac{M_X}{1 - \sqrt{1 - G}} \qquad (B.235)$$

Here G was given by Eq. (B.209).

If the normal frequencies and force constants of a molecule are not known, one may of course estimate the force constants k_1, k_2, etc., by comparison with similar molecules listed in Tables B-2 through B-7. From these force constants k_i and the atomic masses, one can then calculate the normal frequencies via the various model relations provided. Similarly one may also estimate values of z_{XY} by comparison. Clearly estimation by comparison can be done only if a sufficient number of different molecules with known properties are available for comparison. It is hoped that the tabular compilations of z_{XY} values and k_i factors in this Appendix will provide a reasonably broad coverage, and can be used to obtain or estimate values for z_β for most molecules of interest.

In the above we have only given model expressions of the more symmetric and simplest types of polyatomic molecules. Herzberg (Ref. 10) gives also model expressions for linear X_2Y_2, and planar XYZ_2 and X_2Y_4 molecules which have respectively five, six, and ten normal vibrations. The technique for calculating the z_β's which we gave above can be readily extended to these molecules as well.

We have not covered here methods for finding the charge constants of electric quadrupole transitions or transitions in which the second derivative of the [illegible] moment is required, that is the anharmonicity in the dipole moment [illegible]e Appendix A). As was shown at the end of Appendix A, transitions involving anharmonic dipoles are much weaker than first-order transitions and even weaker than transitions that are second- and third-order anharmonic mechanically but harmonic or first-order as far as the dipole moment is concerned. Similarly quadrupole transitions are known to be at least 10^{-6} times weaker (usually $\sim 10^{-10}$) than first-order transitions.

For mechanically-allowed transitions in which the dipole moment vanishes but a quadrupole moment exists, it may be possible to construct a model for the basic quadrupole constants of a polyatomic molecule starting with the elementary z_{XY} values of the XY bond, as we did for the dipole. However we shall not consider it further here.

APPENDIX C
ESTIMATION OF VIBRATIONAL ANHARMONIC CONSTANTS OF POLYATOMIC MOLECUES

C.1 GENERAL CONSIDERATIONS

As shown in Ref. 16, page 9, the anharmonic constant x_e for diatomic molecules may be related to the dissociation limit energy D_e of the vibration by the simple equation:

$$x_e = \frac{h\nu_e}{4D_e} = 3.09926 \times 10^{-5}\ \frac{\nu_e\,(\mathrm{cm}^{-1})}{D_e(\mathrm{eV})}\ , \tag{C.1}$$

if the vibration potential can be described by a "Morse potential curve" (see Figure C-1), which is known to approximate most molecular vibrations rather well. Here ν_e is the fundamentamental vibration frequency.

To demonstrate how well Eq. (C.1) holds, let us apply it to strongly covalent CO and strongly ionic $HC\ell$. For CO, Ref. 2 lists three possible values for D_e, namely $D_e' = 11.108$ eV ; $D_e'' = 9.605$ eV ; $D_e''' = 9.141$ eV, with preference given to $D_e' = 11.108$ eV. The measured values for x_e and ν_e for CO are $x_e = 0.00620$ and $\nu_e = 2170.21$ cm^{-1} (Ref. 2). If we use Eq. (C.1) then with the three quoted values for D_e, we get $x_e' = 0.00606$; $x_e'' = 0.00700$; $x_e''' = 0.00736$. The calculated value x_e' (with $D_e' = 11.108$ eV) does indeed agree quite well with the measured value of $x_e = 0.00620$.

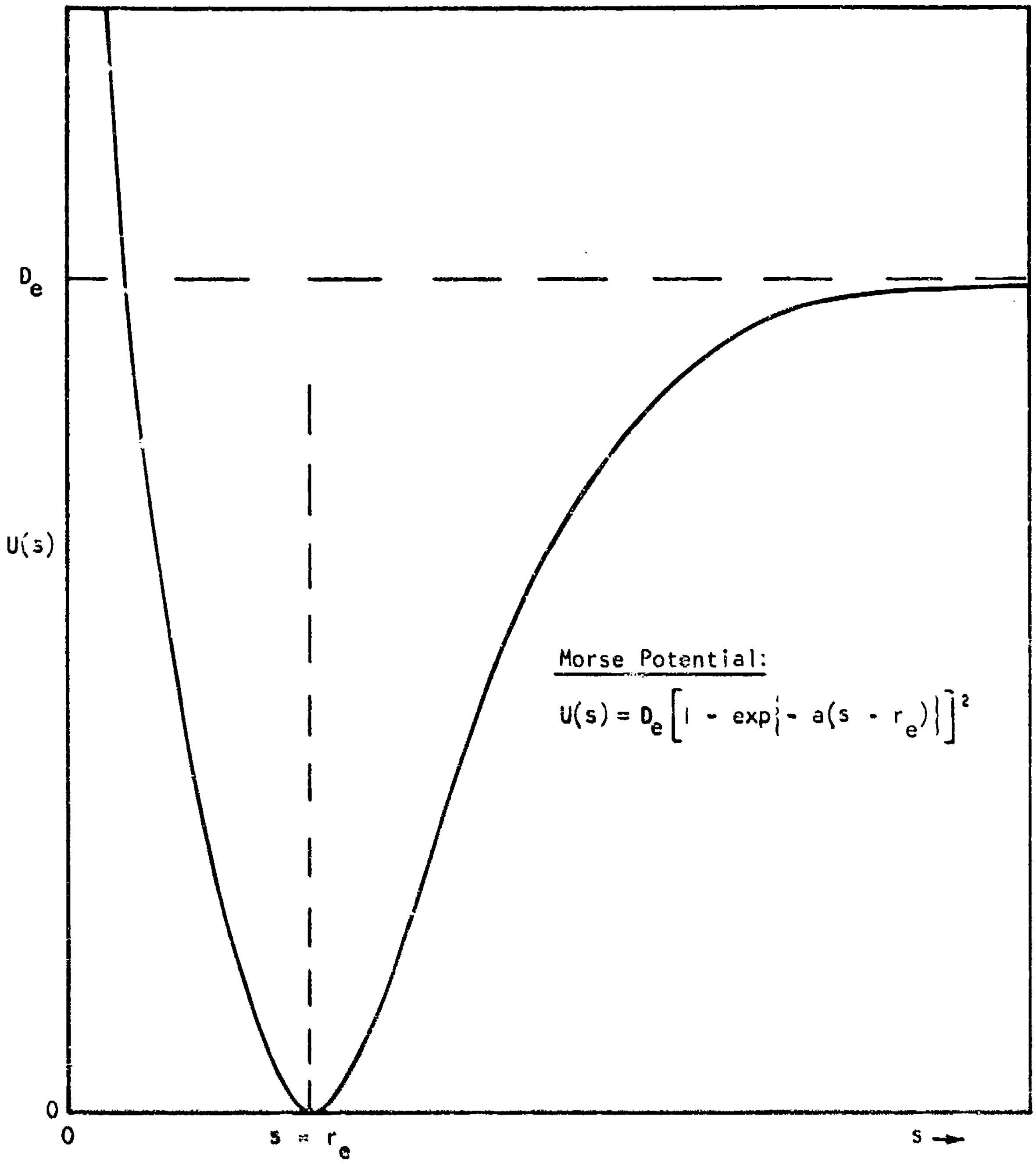

FIGURE C-1. VARIATION OF MOLECULAR POTENTIAL ENERGY U(s) WITH INTERNUCLEAR DISTANCE s

For HCℓ we find the measured values $\nu_e = 2989.74\ \mathrm{cm}^{-1}$, $x_e = 0.0174$, and $D_e = 4.430$ eV. Using formula (C.1), we get $x_e' = 0.0209$, which again does not differ too badly from the measured value $x_e = 0.0174$. We conclude that Eq. (C.1) is a good approximation for x_e if measurements of x_e are not available but D_e and ν_e are known.

For polyatomic molecules, one may expect a relation similar to (C.1) to hold for the various vibrations α, if the Morse potential is assumed:

$$x_a = \frac{h\nu_\alpha}{4D_\alpha} = 3.09926 \times 10^{-5}\ \frac{\nu_\alpha\,(\mathrm{cm}^{-1})}{D_\alpha(\mathrm{eV})} \tag{C.2}$$

However D_α is not as easily obtained experimentally as D_e is for diatomic molecules, since the actual dissociation of a polyatomic molecule takes place via a combination of processes in which all normal vibrations are participating to varying degrees. In principle of course. x_α may be determined by observing the convergence (or divergence) of the vibrational energy levels of the α vibration, which are (Ref. 16):

$$G(v_\alpha) = G_0 + \left(v_\alpha + \frac{d_\alpha}{2}\right)\nu_\alpha - \left(v_\alpha + \frac{d_\alpha}{2}\right)^2 x_\alpha\,\nu_\alpha \tag{C.3}$$

The energy levels (C.3) result for either a Morse potential or if one assumes an anharmonic potential of the form:

$$V_\alpha(y) = \frac{1}{2}\,k_\alpha y^2 - g_\alpha y^3 = \frac{1}{2}\,k_\alpha y^2 - \left[g_{\alpha\alpha} + \sum_\beta g_{\alpha\beta}\right] y^3 , \tag{C.4}$$

In (C.4), y is the normal vibration displacement coordinate, while in (C.3) v_α is the vibrational level of the normal vibration α, and d_α is the degeneracy of the normal vibration α. One can show that the anharmonic constant x_α of Eq. (C.3) is related to the anharmonic constants g_α and $g_{\alpha\beta}$ in the potential (C.4) by:

$$x_\alpha = \frac{15\, h\nu_\alpha\, g_\alpha^2}{4\, k_\alpha^3} = \frac{15\, h\nu_\alpha}{4\, k_\alpha^3} \left(g_{\alpha\alpha} + \sum_\beta g_{\alpha\beta} \right) \tag{C.5}$$

The constant k_α in (C.4) and (C.5) is the harmonic oscillator force constant of course. Thus x_α may be calculated if either D_α or g_α is given. Since D_α is usually better known or easier estimated, we shall only consider Eq. (C.2).

In the following we shall briefly consider how to calculate or estimate values of x_α for linear and planar triatomic molecules, and three-dimensional pyramidal, tetrahedral, and octahedral molecules.

C.2 TRIATOMIC MOLECULES (LINEAR AND PLANAR)

Instead of (C.3), in the presence of simultaneous excitations of various levels of other normal vibrations β, the energy equation for doubly-degenerate or non-degenerate vibrations (the only two possibilities for triatomic molecules) is often written (Ref. 10):

$$G(v_\alpha, v_\beta, \ldots.) = G_o + \sum_\beta \left(v_\beta + \frac{d_\beta}{2} \right) \nu_\beta +$$

$$- \sum_\beta \sum_\alpha \left(v_\beta + \frac{d_\beta}{2} \right) \left(v_\alpha + \frac{d_\alpha}{2} \right) x_{\alpha\beta}\, \nu_\beta + \sum_{\beta_j} \sum_{\alpha_i} \gamma_{\alpha\beta}\, \ell_{\alpha_i}\, \ell_{\beta_j}\, \nu_\beta \tag{C.6}$$

Here d_β is the degeneracy of vibration β, that is $d_\beta = 1$ for a non-degenerate vibration and $d_\beta = 2$ for a doubly-degenerate one. If $d_\beta = 2$, the ℓ_{β_i} in (C.6) are given by:

$$\underset{(d_\beta = 2)}{\ell_{\beta_i}} = v_\beta \, , \; v_\beta - 2 \, , \; v_\beta - 4 \, , \; \ldots \, , \; 1 \text{ or } 0 \tag{C.7}$$

On the other hand if there is no degeneracy, that is if $d_\beta = 1$, we have:

$$\underset{(d_\beta = 1)}{\ell_{\beta_i} = 0} \quad ; \quad \underset{(d_\beta = 1)}{\gamma_{\alpha\beta} = 0} \tag{C.8}$$

Since:

$$G(v_\alpha \, , \, v_\beta \, , \, \ldots) = G(v_\alpha) + G(v_\beta) + \ldots \; , \tag{C.9}$$

we see by comparing (C.3) with (C.6), that:

$$\left(v_\alpha + \frac{d_\alpha}{2}\right)^2 x_\alpha \nu_\alpha = \sum_\beta \left(v_\alpha + \frac{d_\alpha}{2}\right)\left(v_\beta + \frac{d_\beta}{2}\right) x_{\alpha\beta} \, \nu_\alpha \; +$$

$$- \sum_\beta \sum_{i,j} \gamma_{\alpha\beta} \, \ell_{\alpha_i} \, \ell_{\beta_j} \, \nu_\alpha \quad , \tag{C.10a}$$

or:

$$x_\alpha(v_\alpha \, , \, v_\beta \, , \, \ldots) = \frac{\sum_\beta \left[(v_\alpha + d_\alpha/2)(v_\beta + d_\beta/2) \, x_{\alpha\beta} - \sum_{i,j} \ell_{\alpha_i} \, \ell_{\beta_i} \, \gamma_{\alpha\beta} \right]}{(v_\alpha + d_\alpha/2)^2} \tag{C.10b}$$

Thus we see that x_α is not constant if other normal vibrations are also excited and depends on the v_α , v_β , ... If all other $v_\beta = 0$ except v_α , we have that:

$$\boxed{x_\alpha = x_\alpha(v_\alpha) = x_{\alpha\alpha} + \frac{\sum\limits_\beta (d_\beta \, x_{\alpha\beta}/2)}{(v_\alpha + d_\alpha/2)} - \frac{\sum\limits_{i,j} \ell_{\alpha_i} \, \ell_{\alpha_j} \, \gamma_{\alpha\alpha}}{(v_\alpha + d_\alpha/2)^2}} \tag{C.11}$$

Here of course $\gamma_{\alpha\alpha} = 0$ if $d_\alpha = 1$ according to (C.8); ℓ_{α_i} is given by (C.7) if $d_\alpha = 2$, and the two possible values of d_α are $d_\alpha = 1$ or $d_\alpha = 2$.

We note from Eq. (C.11) that x_α still depends on v_α even if all $v_\beta = 0$. For $v_\alpha = 0$, we get from (C.11) that:

$$\boxed{x_\alpha(v_\alpha{=}0) = x_{\alpha\alpha} + \sum_\beta \left(\frac{d_\beta}{d_\alpha}\right) x_{\alpha\beta} \quad ,} \tag{C.12}$$

since $\ell_\alpha = 0$, while for $v_\alpha = 1$, we obtain:

$$x_\alpha(v_\alpha{=}1) = x_{\alpha\alpha} + \frac{\sum\limits_\beta \left(\frac{d_\beta}{d_\alpha} x_{\alpha\beta}\right)}{(1 + 2/d_\alpha)} - \frac{\gamma_{\alpha\alpha}}{4} \quad , \tag{C.13}$$

since $\ell_{\alpha_i} = \ell_\alpha = 1$ (if $d_\alpha = 2$). Comparing (C.13) with (C.12), we see that the summed term is reduced by a factor of 3 if $d_\alpha = 1$, or 2 if $d_\alpha = 2$, in going from $v_\alpha = 0$ to $v_\alpha = 1$. If $d_\alpha = 1$, the term with $\gamma_{\alpha\alpha}$ is zero of course, and only if $d_\alpha = 2$ does $\gamma_{\alpha\alpha}$ have a nonzero value.

From (C.9) it is also clear that $x_\alpha \rightarrow x_{\alpha\alpha}$ when $v_\alpha \rightarrow \infty$. In most cases of interest to us however the vibrational transition element involves transitions with lower values of v_α; transitions involving high values of v_α are usually electronic and in this case the transition element is determined mainly by the electronic parameters.

Only few measurements of $x_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ of polyatomic molecules have been reported. Reference 10 gives for triatomic CO_2, N_2O, HCN, and H_2O, respectively:

$\underline{CO_2}$

$\nu_1^0 = 1351.2\ \text{cm}^{-1}$ $\quad\nu_2^0 = 672.2\ \text{cm}^{-1}$ $\quad\nu_3^0 = 2396.4\ \text{cm}^{-1}$

$x_{11} = 0.000222$ $\quad x_{21} = -0.008480$ $\quad x_{31} = 0.009139$

$x_{12} = -0.004218$ $\quad x_{22} = 0.001934$ $\quad x_{32} = 0.004590$

$x_{13} = 0.01621$ $\quad x_{23} = 0.01636$ $\quad x_{33} = 0.005216$

$\gamma_{11} = 0$ $\quad \gamma_{22} = 0.002529$ $\quad \gamma_{33} = 0$

$\underline{N_2O}$

$\nu_1^0 = 1288.2\ \text{cm}^{-1}$ $\quad\nu_2^0 = 588.0\ \text{cm}^{-1}$ $\quad\nu_3^0 = 2237.2\ \text{cm}^{-1}$

$x_{11} = 0.002445$ $\quad x_{21} = -0.007908$ $\quad x_{31} = 0.011644$

$x_{12} = -0.003610$ $\quad x_{22} = 0.003707$ $\quad x_{32} = 0.005565$

$x_{13} = 0.020262$ $\quad x_{23} = 0.02100$ $\quad x_{33} = 0.006101$

$\gamma_{11} = 0$ $\quad \gamma_{22} = 0.005051$ $\quad \gamma_{33} = 0$

HCN

$\nu_1^0 = 2041.2\ \mathrm{cm}^{-1}$ $\nu_2^0 = 711.7\ \mathrm{cm}^{-1}$ $\nu_3^0 = 3368.6\ \mathrm{cm}^{-1}$
$x_{11} = 0.025475$ $x_{21} = -0.005901$ $x_{31} = 0.004275$
$x_{12} = -0.002058$ $x_{22} = 0.003864$ $x_{32} = 0.005798$
$x_{13} = 0.007055$ $x_{23} = 0.02744$ $x_{33} = 0.016470$
$Y_{11} = 0$ $Y_{22} = 0.004426$ $Y_{33} = 0$

H_2O

$\nu_1^0 = 3693.8\ \mathrm{cm}^{-1}$ $\nu_2^0 = 1614.5\ \mathrm{cm}^{-1}$ $\nu_3^0 = 3801.7\ \mathrm{cm}^{-1}$
$x_{11} = 0.011855$ $x_{21} = 0.012388$ $x_{31} = 0.040771$
$x_{12} = 0.005414$ $x_{22} = 0.012078$ $x_{32} = 0.005208$
$x_{13} = 0.041962$ $x_{23} = 0.012264$ $x_{33} = 0.012171$
$Y_{11} = 0$ $Y_{22} =$ ——— $Y_{33} = 0$

For the above four molecules, Eq. (C.12) reads:

$$x_1^0 = x_{11} + 2\,x_{12} + x_{13} \tag{C.14a}$$

$$x_2^0 = \frac{1}{2}\,x_{21} + 2\,x_{22} + \frac{1}{2}\,x_{23} \tag{C.14b}$$

$$x_3^0 = x_{31} + 2\,x_{32} + x_{33} \tag{C.14c}$$

Then from the above parameters we calculate, using Eq. (C.14), values for $x_\alpha(v_\alpha=0) = x_\alpha^0$ as shown in Table C-1.

TABLE C-1. VALUES OF $x_\alpha(v_\alpha=0) \equiv x^0_\alpha$

	x^0_1	x^0_2	x^0_3	D^0_1(eV)	D^0_2(eV)	D^0_3(eV)
CO_2	0.007996	0.007808	0.02878	5.238	2.668	2.581
N_2O	0.01549	0.01395	0.02888	2.577	1.306	2.401
HCN	0.02841	0.0185	0.03234	2.227	1.192	3.228
H_2O	0.06465	0.03091	0.06336	1.771	1.619	1.860

Using Eq. (C.1), we can calculate values for D_α from the x_α and ν_a . The results for CO_2 , N_2O , HCN , and H_2O are shown in Table C-1.

Performing the same calculation for these molecules with $v_\alpha = 1$, we have according to (C.13) for $x_\alpha(v_\alpha=1) \equiv x^1_\alpha$.

$$x^1_1 = x_{11} + \frac{2}{3} x_{12} + \frac{1}{3} x_{13} \tag{C.15a}$$

$$x^1_2 = \frac{1}{4} x_{21} + x_{22} + \frac{1}{4} x_{23} - \frac{1}{4} Y_{22} \tag{C.15b}$$

$$x^1_3 = \frac{1}{3} x_{31} + \frac{2}{3} x_{32} + x_{33} \tag{C.15c}$$

From the data on CO_2 , N_2O , HCN , and H_2O given above then the values for the x^1_α calculated by (C.15) can be obtained as listed in Table C-2.

TABLE C-2. VALUES OF $x_\alpha(v_\alpha=1) \equiv x_\alpha^1$

	x_1^1	x_2^1	x_3^1	D_1^1(eV)	D_2^1(eV)	D_3^1(eV)
CO_2	0.002813	0.003272	0.01132	14.887	6.367	6.561
N_2O	0.006792	0.005717	0.01369	5.878	3.188	5.065
HC_N	0.02645	0.008142	0.02176	2.392	2.709	4.798
H_2O	0.04952	0.01824	0.02923	2.312	2.743	4.031

Again by means of Eq. (C.2), values for D_α^1 can be calculated as listed in Table C-2.

Finally we calculate the x_α and D_α values for $v \rightarrow \infty$. In this case we have simply:

$$x_1 = x_{11} \tag{C.16a}$$

$$x_2 = x_{22} \tag{C.16b}$$

$$x_3 = x_{33} \tag{C.16c}$$

Table C-3 lists the calculated values of x_α and D_α for the case $v_\alpha \rightarrow \infty$, for CO_2, N_2O, HCN, and H_2O.

TABLE C-3. VALUES OF x_α FOR $v_\alpha \to \infty$

	x_1^∞	x_2^∞	x_3^∞	D_1^∞, eV	D_2^∞, eV	D_3^∞, eV
CO_2	0.000222	0.001934	0.005216	188.636	10.772	14.239
N_2O	0.002445	0.003707	0.006101	16.329	4.916	11.365
HCN	0.025475	0.003864	0.005798	2.483	5.708	18.006
H_2O	0.011855	0.012078	0.012171	9.657	4.143	9.681

The measured dissociation constants of CO_2 , N_2O , HCN , H_2O , are listed in Table C-4.

TABLE C-4. MEASURED DISSOCIATION ENERGIES

Molecule XYZ	D(X + YZ) (eV)	D(XY + Z) (eV)	D(XZ + Y) (eV)	D(X + Y + Z) (eV)
OCO (CO_2)	5.453	5.453	11.481	16.561
NNO (N_2O)	4.930	1.677	4.930	10.216
HCN	5.55	9.69	9.36	13.16
HOH (H_2O)	5.113	5.113	4.987	9.463

We note from Tables (C-1) through (C-4) that except for the unusually large value D_1^∞ of 188 eV for CO_2 , all other D_α values are within a factor of two to three of the measured dissociation constants, giving us confidence that the relation (C.2) must be at least approximately correct. A comparison of Tables C-3 and C-4 shows that coarse agreement is obtained if we set:

$$D_1^\infty \approx \frac{4\,M_X\,M_Z}{(M_X + M_Z)^2}\;D_3^\infty \approx \frac{4\,M_X\,M_Z}{(M_X + M_Z)^2}\;D(X + Y + Z) \qquad (C.17)$$

$$D_2^\infty \approx D(XZ + Y) \qquad (C.18)$$

$$D_3^\infty \approx D(X + Y + Z) \qquad (C.19)$$

In most cases of interest we need values for x_α^1 and therefore values of D_α^1. By comparing Tables C-2 and C-3, we make the coarse estimates:

$$D_1^1 \approx \frac{1}{2}\,D_1^\infty = \frac{2\,M_X\,M_Z}{(M_X + M_Z)^2}\;D(X + Y + Z) \qquad (C.20)$$

$$D_2^1 \approx \frac{1}{2}\,D_2^\infty = \frac{1}{2}\,D(XZ + Y) \qquad (C.21)$$

$$D_3^1 \approx \frac{1}{2}\,D_3^\infty \approx \frac{1}{2}\,D(X + Y + Z) \qquad (C.22)$$

In Table C-5, measured values of D_α^∞ and D_α^1 and calculated values obtained from (C.17) through (C.22), are compared. Except for D_1^∞ and D_1^1 of CO_2 whose measured values appear anomalously high,* the agreement is not too bad considering the many uncertainties inherent in the measured values of both the D(X , Y , Z) and x_α parameters.

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*This anomaly is due to the Fermi-Resonance-Effect on ν_1 by the vibration $2\nu_2$ (see the discussion at the end of this Appendix).

TABLE C-5. COMPARISON OF MEASURED AND CALCULATED D_α^∞ AND D_α^1 VALUES*

	$v_\alpha = \infty$						$v_\alpha = 1$					
	Measured			Eqs.(C.17)–(C.19)			Measured			Eqs.(C.20)–(C.22)		
	D_1^∞	D_2^∞	D_3^∞	D_1^∞	D_2^∞	D_3^∞	D_1^1	D_2^1	D_3^1	D_1^1	D_2^1	D_3^1
CO_2	188.6	10.77	14.24	16.56	11.48	16.56	14.89	6.37	6.56	8.28	5.74	8.28
N_2O	16.33	4.92	11.37	10.17	4.93	10.22	5.88	3.19	5.07	5.09	2.47	5.11
HCN	2.48	5.71	18.01	3.28	9.36	13.16	2.39	2.71	4.80	1.64	4.68	6.58
H_2O	9.66	4.14	9.68	9.46	4.99	9.46	2.31	2.74	4.03	4.73	2.50	4.73

*All D values are in electronvolts (eV).

It should be realized that Eqs. (C.17) through (C.22) are mostly empirical and heuristic. Until a more precise theory becomes available however, these relations should be useful for obtaining approximate values for the anharmonic constants of polyatomic molecules, in the frequent case that such data are not available. For convenience, Tables C-6 and C-7 list values of diatomic and triatomic dissociation energies taken from Refs. 2 and 11. The dissociation energies of diatomic molecules are useful for calculating dissociation energies in polyatomic molecules such as D(X + Y + Z) which we can obtain from the equation:

$$D(X + Y + Z) = D(XY) + D(XY + Z) = D(YZ) + D(X + YZ) \qquad (C.23)$$

This relation follows of course from the energy conservation law.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)*

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
AgBr	2.6	BaF	3.8	BiF	3.2
AgCℓ	3.1	BaH	1.82	BiH	2.7
AgH	2.5	BaO	4.7	BiD	2.7
AgI	2.98	BaS	2.3	BiO	2.9
AgO	1.8	B_2	3.6	Br_2	1.971
AℓBr	2.4	BH	3.41	BrCℓ	2.26
AℓCℓ	3.1	BD	3.45	BrF	2.60
AℓF	2.5	BBr	(4.1)	BrO	2.2
AℓH	2.97	BCℓ	(4.2)	CaI	2.8
AℓD	3.00	BF	(4.3)	CaBr	2.9
AℓI	2.9	BO	9.1	CaCℓ	2.76
AℓO	3.65	BN	5.0	CaF	3.15
As_2	3.96	BeCℓ	4.3	CaH	1.70
AsN	6.5	BeF	5.4	CaO	5.0
AsO	5.0	BeH	2.2	CaS	5.2
AsF	(5.3)	$(BeH)^+$	3.2	C_2	3.6
AsCℓ	(5.5)	BeO	3.7	CI	(5.20)
AuCℓ	3.5	Bi_2	1.70	CB.	(5.50)
AuH	3.1	BiI	2.7	CCℓ	(5.95)
BaBr	2.8	BiBr	2.74	CF	(7.14)
BaCℓ	2.7	BiCℓ	3.0	CN	7.6

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)*
(Continued)

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
CO	11.108	$(C\ell_2)^+$	4.4	GaBr	2.7
$(CO)^+$	9.9	CℓF	2.616	GaCℓ	3.7
CS	7.8	CℓO	1.9	GaF	(3.5)
CP	6.9	CrO	3.8	GaO	2.9
CSe	6.8	Cs_2	0.45	GdO	5.9
CH	3.47	CsI	3.27	GeI	(2.8)
CD	3.52	CsBr	3.90	GeBr	3.0
$(CH)^+$	3.6	CsCℓ	(4.11)	GeCℓ	4.0
Cd_2	0.087	CsF	5.55	GeF	4.9
CdI	1.6	CsH	1.9	GeO	6.9
CdBr	3.3	Cu_2	0.17	GeS	5.6
CdCℓ	2.8	CuI	3.0	GeSe	4.1
CdF	(5.04)	CuBr	2.5	GeTe	3.2
CdH	0.678	CuCℓ	3.0	H_2	4.4763
CdD	0.704	CuF	3.0	HD	4.5112
$(CdH)^+$	2.0	CuH	2.89	D_2	4.5526
CdO	(6.23)	CuD	2.93	HT	4.5241
CdS	3.9	CuO	4.5	T_2	4.5881
CdSe	3.2	F_2	2.65	$(H_2)^+$	2.6481
CeO	7.7	FeO	4.8	HI	3.0564
$C\ell_2$	2.475	GaI	2.88	$(HI)^+$	3.11

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)* (Continued)

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
HBr	3.754	HgO	(2.2)	LaO	9
$(HBr)^+$	3.50	HgS	2.8	Li_2	1.03
HCℓ	4.430	HgSe	2.7	LiI	3.48
DCℓ	4.481	HgTℓ	0.031	LiBr	4.53
$(HC\ell)^+$	4.48	I_2	1.5417	LiCℓ	5.1
$(DC\ell)^+$	4.53	IBr	1.8170	LiF	6.6
HF	6.40	ICℓ	2.152	LiH	2.5
DF	6.42	IO	1.9	LiD	2.5
HS	2.77	InI	2.7	LuO	5.3
HO	4.35	InBr	3.3	MgI	3.0
$(He_2)^*$	2.6	InCℓ	4.54	MgBr	3.35
$(He_2)^+$	3.1	InF	(4.2)	MgCℓ	3.2
Hg_2	0.060	InH	2.48	MgF	4.2
HgI	0.36	InO	1.3	MgH	2.49
HgBr	0.7	K_2	0.514	MgD	2.49
HgCℓ	1.0	KI	3.33	$(MgH)^+$	2.1
HgF	1.8	KBr	3.96	MgO	3.7
HgH	0.376	KCℓ	4.42	MgS	2.9
HgD	0.398	KF	5.9	MnI	2.7
$(HgH)^+$	2.3	KH	1.76	MnBr	2.9
$(HgD)^+$	2.4	KD	1.79	MnCℓ	3.3

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)* (Continued)

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
MnF	3.9	NaK	0.621	PbI	2.84
MnH	2.4	NaRb	0.57	PbBr	2.87
MnO	4.4	NiBr	(6.4)	PbCℓ	3.12
MoO	(4.80)	NiCℓ	7.3	PbF	3.37
MoF	(3.79)	NiF	(8.1)	PbH	1.59
N_2	9.756	NiO	(9.7)	PbO	4.3
NH	3.8	NiH	3.1	PbS	4.7
ND	3.9	O_2	5.080	PbSe	4.7
NI	(2.9)	$(O_2)^+$	6.48	PbTe	3.5
NBr	3.0	OH	4.35	Rb_2	0.49
NCℓ	(3.4)	OD	4.39	RbI	3.29
NF	(4.0)	$(OH)^+$	4.45	RbBr	3.93
NO	6.477	P_2	5.031	RbCℓ	3.96
$(NO)^+$	10.6	PH	(3.6)	RbF	5.35
NS	5.9	PD	(3.6)	RbO	(8.25)
Na_2	0.73	PN	6.3	RbH	1.9
NaI	3.16	PO	6.2	S_2	4.4
NaBr	3.85	PF	(6.8)	SO	5.146
NaCℓ	3.58	PCℓ	(7.1)	SF	(3.6)
NaF	5.3	PBr	(6.3)	Sb_2	3.7
NaH	2.2	Pb_2	0.7	SbI	(3.3)

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)* (Continued)

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
SbBr	(4.0)	$(SiO)^+$	(12)	Te_2	3.18
SbCℓ	4.6	SiS	5.6	TeO	3.453
SbF	4.2	SiSe	5.8	TeF	(2.6)
SbBi	3.0	SiTe	5.5	TeH	(2.10)
SbN	4.8	SnI	(2.8)	TiCℓ	1.0
SbO	3.8	SnBr	3.0	TiF	(5.5?)
ScO	7	SnCℓ	3.6	TiO	6.90
ScF	(6.5)	SnF	3.9	TiH	3.94
Se_2	3.55	SnH	3.2	TℓI	2.64
SeO	5.4	SnO	5.6	TℓBr	3.19
SeF	(3.8)	SnS	3.0	TℓCℓ	3.75
SeH	(2.47)	SnSe	4.6	TℓF	4.70
Si_2	(0.5)	SnTe	4.2	TℓH	2.18
SiI	(3.5)	SrI	2.2	UO	(5.85)
SiBr	3.7	SrBr	2.8	UI	(2.3)
SiCℓ	4.0	SrCℓ	3.0	UF	(4.15)
SiF	4.8	SrF	3.5	VO	6.40
SiH	(1.8)	SrH	1.68	VF	(4.61)
SiD	(1.8)	SrD	1.70	WO	(5.00)
SiN	4.5	SrO	4.5	WF	(3.75)
SiO	7.4	SrS	2.7	Y_bF	(1.42)

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-6. DISSOCIATION ENERGIES OF DIATOMIC MOLECULES (After Ref. 2)* (Continued)

Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)	Molecule XY	D_{XY}(eV)
YbCℓ	1.20	ZnBr	(2.7)	ZnS	4.4
YbO	(2.02)	ZnCℓ	3.0	ZnSe	(3.9)
YO	9	ZnF	(5.6)	ZnTe	2.2
YF	(7.2)	ZnH	0.851	ZrO	7.8
Zn_2	0.25	$(ZnH)^+$	2.5	ZnF	(5.6)
ZnI	2.0	ZnO	(7.8)	ZrH	(4.5)

*Values in parentheses are estimates; if a value of D is not found for XY, try looking under YX.

TABLE C-7. DISSOCIATION ENERGIES OF SOME TRIATOMIC XYZ MOLECULES (Ref. 11)*

(All Energies in Electronvolts (eV))

Molecule XYZ	D(X + YZ)	D(XY + Z)	D(XZ + Y)	D(X + Y + Z)
OCO (CO_2)	5.453	5.453	11.481	16.561
SCS (CS_2)	3.70	3.70	7.10	11.50
SCO (OCS)	3.71	5.38	8.85	14.00
NNO (N_2O)	4.930	1.677	4.930	10.216
HCN	5.55	9.69	9.36	13.16
ICN	(5.3)	(9.7)	(12.1)	(15.0)
BrCn	(5.6)	(9.7)	(12.3)	(15.3)
CℓCN	(5.7)	(9.7)	(12.0)	(15.4)
SCN	(3.7)	(9.7)	(7.5)	(13.4)
HOH (H_2O)	5.113	5.113	4.987	9.463
DOD (D_2O)	5.160	5.160	5.25	9.80
HSH (H_2S)	(3.26)	(3.26)	(1.55)	(6.03)
DSD (D_2S)	(3.27)	(3.27)	(1.49)	(6.04)
HSeH (H_2Se)	(2.90)	(2.90)	(0.89)	(5.37)
DSeD (D_2Se)	(2.91)	(2.91)	(0.83)	(5.38)
HCH (CH_2)	4.20	4.20	3.19	7.67
OSO (SO_2)	5.613	5.613	5.68	10.76
ONO (NO_2)	3.114	3.114	4.505	9.591
FOF (F_2O)	(2.8)	(2.8)	(2.3)	(5.0)
CℓOCℓ ($C\ell_2O$)	2.5	2.5	1.9	4.4

*Values in parentheses are estimated.

C.3 PYRAMIDAL AND PLANAR XY_3 MOLECULES

To estimate anharmonic constants for pyramidal molecules via Eq. (C.2), it is advantageous to consult the normal vibration diagrams of this molecule shown in Figure B-5 of Appendix B. On the basis of these diagrams it appears that we can set:

$$D_1^{\infty} \approx D(X + 3\ Y) \tag{C.24}$$

$$D_2^{\infty} \approx D(X + 3\ Y) \approx D_1^{\infty} \tag{C.25}$$

$$D_3^{\infty} \approx D(X + Y_3) \tag{C.26}$$

$$D_4^{\infty} \approx D(XY + Y_2) \tag{C.27}$$

On the basis of our results with triatomic molecules, we shall further assume that:

$$D_{\alpha}^{\prime} \approx D_{\alpha}^{\infty}/2\ , \tag{C.28}$$

from which it follows according to Eq. (C.2) that:

$$x_{\alpha}^{\prime} \approx 2\ x_{\alpha}^{\infty} \tag{C.29}$$

Admittedly the relations (C.24) through (C.29) are rather crude, but in the absence of a more refined theory or measured data, they should be quite helpful and yield values of x_{α}^{∞} or $x_{\alpha}^{\prime}$ via Eq. (C.2) that should be accurate within a factor of 3 or better.

In Table C-8 values for $D(X + 3\ Y)$, $D(X + Y_3)$, and $D(XY + Y_2)$ are listed, obtained or estimated from data given in the literature (mostly Ref. 11).

TABLE C-8. ESTIMATED DISSOCIATION LIMIT ENERGIES OF SOME PLANAR AND PYRAMIDAL XY_3 MOLECULES

Molecule XY_3	$D(X + 3\,Y)$ (eV)	$D(X + Y_3)$ (eV)	$D(XY + Y_2)$ (eV)	$D(Y + XY_2)$ (eV)
Planar				
BF_3	13.5	9.9	6.5	4.4
$BC\ell_3$	13.0	10.2	6.3	4.3
BBr_3	12.4	10.1	6.3	4.2
SO_3	18.0	11.8	7.7	5.0
CO_3^{--}	26	19.8	9.9	9.0
NO_3^-	17	10.8	5.4	6.5
Pyramidal				
NH_3	14.2	9.6	5.9	4.28
ND_3	14.5	9.9	6.0	4.3
PH_3	11.8	6.7	3.7	3.8
PD_3	11.9	6.8	3.7	3.8
PF_3	21.5	17.8	12.0	7.0
$PC\ell_3$	22.0	18.5	12.4	7.2
PBr_3	20.0	17.0	11.7	6.5
AsF_3	17.2	13.5	9.2	5.6
$AsC\ell_3$	18.0	14.5	10.0	5.8
$SbC\ell_3$	16.1	12.6	9.0	4.8
$BiC\ell_3$	10.4	6.9	4.9	3.2
UI_3	8.3	6.1	4.4	2.5

C.4 TETRAHEDRAL XY_4 MOLECULES

For tetrahedral XY_4 molecules, the normal vibrations are shown in Figure B-6 of Appendix B. To estimate values for the anharmonic constants of a XY_4 molecule we shall again assume Eq. (C.2), setting the dissociation limit energies D_1^∞, D_2^∞, D_3^∞, and D_4^∞ of the four normal vibrations equal to:

$$D_1^\infty \approx D(X + 4\,Y) \tag{C.30}$$

$$D_2^\infty \approx D(X + 2\,Y_2) \tag{C.31}$$

$$D_3^\infty \approx D(X + Y_4) \tag{C.32}$$

$$D_4^\infty \approx D(X + 2\,Y + Y_2) \tag{C.33}$$

Table C-9 gives estimated values for the various D(X, Y) dissociation limit energies of some selected molecules. To obtain D'_α and x'_α we shall assume relations (C.28) and (C.29) to hold also for tetrahedral molecules.

C.5 OCTAHEDRAL XY_6 MOLECULES

The dissociation-limit energies D_1^∞, D_2^∞, D_3^∞, D_4^∞, D_5^∞, and D_6^∞ for the six normal vibrations of octahedral XY_6, we estimate to be approximately given by:

$$D_1^\infty \approx D(X + 6\,Y) \tag{C.34}$$

$$D_2^\infty \approx D(XY_4 + 2\,Y) \tag{C.35}$$

TABLE C-9. ESTIMATED DISSOCIATION-LIMIT ENERGIES OF SELECTED TETRAHEDRAL XY_4 MOLECULES

Molecule XY_4	$D(X + 4\ Y)$ (eV)	$D(X + 2\ Y_2)$ (eV)	$D(X + Y_4)$ (eV)	$D(X + 2\ Y + Y_2)$ (eV)	$D(XY_3 + Y)$ (eV)
CH_4	16.2	7.2	10.5	11.7	3.7
CD_4	16.3	7.2	10.6	11.7	3.7
SiH_4	10.1	1.1	4.4	5.6	2.3
NH_4^+	21.0	12.0	15.3	16.5	5.2
CF_4	29.6	24.2	26.0	26.9	7.3
SiF_4	21.5	16.1	17.9	18.8	5.1
$C\ell_4$	26.6	21.6	23.2	24.1	6.2
$SiC\ell_4$	17.8	12.8	14.4	15.3	4.2
$TiC\ell_4$	9.2	4.2	5.8	6.7	2.1
$GeC\ell_4$	16.8	14.3	13.4	11.8	4.1
$SnC\ell_4$	15.9	13.4	12.5	10.9	3.8
CBr_4	24.0	20.0	21.1	22.0	5.8
$SiBr_4$	16.8	12.8	13.9	14.8	4.0
$GeBr_4$	15.5	11.5	12.6	13.5	3.5
$SnBr_4$	14.2	10.2	11.3	12.2	3.3
UI_4	10.8	7.8	8.4	9.3	2.5
OsO_4	28.5	18.3	22.0	23.4	6.8
SO_4^{--}	24.0	13.8	17.5	18.9	5.4
$C\ell O_4^-$	11.3	1.1	4.8	6.2	2.5
PO_4^{---}	27.5	17.3	21.0	22.4	6.5

$$D_3^\infty \approx D(XY_2 + Y_4) \tag{C.36}$$

$$D_4^\infty \approx D(XY_4 + Y_2) \tag{C.37}$$

$$D_5^\infty \approx D(XY_2 + 2\ Y_2) \tag{C.38}$$

$$D_6^\infty \approx D(XY_2 + 2\ Y_2) \tag{C.39}$$

Table C-10 lists estimated values of the various D(X, Y) dissociation-limit energies for some selected octahedral XY_6 molecules. With the aid of Eq. (C.2) and Eqs. (C.34) through (C.39), anharmonic constants for these molecules may then be estimated. Again we shall assume (C.28) and (C.29) to hold for obtaining D_α^1 and x_α^1 .

C.6 FERMI-RESONANCE-EFFECTS

Whenever the value of the frequency $\nu_\beta\nu_\beta$ of a normal vibration β is close to the value of the frequency $\nu_\alpha\nu_\alpha$ of a normal vibration α in a polyatomic molecule, the so-called "Fermi-Resonance-Effect" occurs in which vibrational energy can be fed back and forth between the two vibrational levels internally in the molecule. The anharmonic constant can be expected to be strongly effected in this case by the "cross-feeding" between these two levels. A well-known example is the Fermi-Resonance between ν_1 and $2\nu_2$ in CO_2 which is probably the cause for the high value of the dissociation energy D_1 in CO_2 discussed earlier.

In a more refined theory for the calculation of x_α , a treatment of Fermi-Resonance must clearly be included. We shall not go further here

TABLE C-10. ESTIMATED DISSOCIATION-LIMIT ENERGIES OF SELECTED OCTAHEDRAL XY_6 MOLECULES

Molecule XY_6	$D(X + 6\ Y)$ (eV)	$D(XY_4 + 2\ Y)$ (eV)	$D(XY_2 + Y_4)$ (eV)	$D(XY_4 + Y_2)$ (eV)	$D(XY_2 + 2\ Y_2)$ (eV)	$D(XY_5 + Y)$ (eV)
SF_6	23.3	7.8	19.7	20.6	17.9	3.8
SeF_6	16.5	8.2	12.9	13.8	11.1	4.0
TeF_6	17.3	5.8	13.7	14.6	11.9	2.8
MoF_6	23.9	8.0	20.3	21.2	18.5	3.9
WF_6	24.1	8.0	20.5	21.4	18.7	3.9
UF_6	26.3	8.8	22.7	23.6	20.9	4.3

except to state that in the case of a Fermi-Resonace it appears that a higher value for D_α must be used in Eq. (C.2) than the value for D_α obtained by the simple recipe that we gave above.