

AD 728 164

91-17

Contract No. DAHCO4-69-C-0077
ARPA Order No. 1442, Amendment No. 2
Program Code No. 9E30

MOLECULAR SPECTRA AND THE RAMAN EFFECT
A SHORT REVIEW

by

Samuel Lederman



POLYTECHNIC INSTITUTE OF BROOKLYN

DEPARTMENT
of
AEROSPACE ENGINEERING
and
APPLIED MECHANICS

JUNE 1971

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

Distribution of this
document is unlimited.

PIBAL REPORT NO. 71-15

56

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Polytechnic Institute of Brooklyn
Dept. of Aerospace Eng. and Applied Mechanics
Route 110, Farmingdale, New York 11735

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

MOLECULAR SPECTRA AND THE RAMAN EFFECT - A SHORT REVIEW

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Research Report

5. AUTHOR(S) (First name, middle initial, last name)

Samuel Lederman

6. REPORT DATE

June 1971

7a. TOTAL NO. OF PAGES

47

7b. NO. OF REFS

14

8a. CONTRACT OR GRANT NO.

DAHCO4-69-C-0077

9a. ORIGINATOR'S REPORT NUMBER(S)

PIBAL Report No. 71-15

b. PROJECT NO.

9b. OTHER REPORT NO(S) (Any of this report)

:s that may be assigned

c. ARPA Order No. 1442, Amendment 2

d. Program Code No. 9E30

10. DISTRIBUTION STATEMENT

1. This document has been approved for public release and sale;
its distribution is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

U.S. Army Research Office-Durham
Box CM, Duke Station
Durham, North Carolina 27706

13. ABSTRACT

A short review of the fundamentals of molecular spectroscopy is given. The basic underlying principles of the rotational and vibrational spectra as well as the principle of the Raman effect are presented. The common relations of the Raman spectra with the rotational and vibrational spectra are pointed out. The distinguishing features between the respective spectra are indicated. The governing equations and their interpretations are discussed.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rational and vibrational spectra Raman effect Raman shift Stokes and Anti-Stokes lines Polarizability Molecular invariants Line intensity						

MOLECULAR SPECTRA AND THE RAMAN EFFECT

A SHORT REVIEW

by

Samuel Lederman

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by the U.S. Army Research Office-Durham, under Contract No. DAHCO4-69-C-0077.

Reproduction in whole or in part is permitted for any purpose of the United States Government.

POLYTECHNIC INSTITUTE OF BROOKLYN

Department

of

Aerospace Engineering and Applied Mechanics

June 1971

PIBAL Report No. 71-15

BLANK PAGE

MOLECULAR SPECTRA AND THE RAMAN EFFECT

A SHORT REVIEW[†]

by

Samuel Lederman^{*}

Polytechnic Institute of Brooklyn
Preston R. Bassett Research Laboratory
Farmingdale, New York

ABSTRACT

A short review of the fundamentals of molecular spectroscopy is given. The basic underlying principles of the rotational and vibrational spectra as well as the principle of the Raman effect are presented. The common relations of the Raman spectra with the rotational and vibrational spectra are pointed out. The distinguishing features between the respective spectra are indicated. The governing equations and their interpretations are discussed.

[†]This research was supported by the Advanced Research Projects Agency, The Department of Defense and was monitored by U.S. Army Research Office-Durham, Box CM, Duke Station, North Carolina 27706, under Contract No. DAHCO4-69-C-0077.

^{*}Associate Professor of Aerospace Engineering.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I Introduction	1
II Fundamentals of Radiation	3
III The Essentials of Band Spectroscopy	9
IV The Raman Effect	17
V Line Intensities of Infrared and Raman Spectra	23
VI Some Applications	30
VII Conclusions	32
References	33
Table I	35
Table II - Some Calculated Molecular Constants	36

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	The Bohr Orbits of Hydrogen and Energy Level Representations of the Transitions Producing the Lyman, Balmer and Paschen Series	37
2	The Dumbbell Model of the Rigid Rotator	38
3	Schematic of the Energy Level of a Rigid Rotator and the Resulting Equidistant Line Spectrum	39
4	Energy Level Diagram of a Rigid and Non-Rigid Rotator	40
5	Energy Level Diagram for the Raman and Rayleigh Transitions	41
6	Schematic of the Energy Level of a Rigid Rotator and the Resulting Equidistant Raman Line Spectrum	42
7	Number of Molecules N_J in the Rotational Level J of the Lower Vibrational State	43
8a	Temperature Dependence of the Raman Intensity. Raman Frequency Shift as a Parameter	44
8b	Temperature Dependence of the Raman Intensity. Raman Frequency Shift as a Parameter	45
8c	Temperature Dependence of the Raman Intensity. Raman Frequency Shift as a Parameter	46
9	Ratio of the Stokes to Anti-Stokes Intensity as a Function of Gas Temperature	47

A_{nm}	Einstein's transition probability of spontaneous emission
B	$\frac{h}{8\pi^2 c I}$ =rotational constant
B_{nn}	Einstein's transition probability of absorption
c	velocity of light
d_m, d_n	degeneracy
D	$\frac{4B^3}{\omega^2}$ =rotational constant
e	electron charge value
E	energy
F	rotational term value
G	vibrational term value
h	Boltzmann constant
i	$\sqrt{-1}$
I	line intensity
j	rotational quantum number
J	total angular momentum of the electrons of an atom
m	mass
M	electric dipole moment
n	principal atomic quantum
N	number of atoms or molecules
P	induced dipole moment
Q	partition function
R	Rydberg constant
R^{nm}	matrix elements of the electric dipole moment
S	line strength factor
t	time
T	total term value
v	vibrational quantum number
V	potential energy

x_e anisotropic scattering defined by Eq. (72a)
 Z atomic number
 α polarizability (spherical part)
 γ polarizability (anisotropic part)
 λ wavelength
 μ reduced mass
 ν wavenumber
 ν' frequency
 ψ amplitude of wave
 Ψ wave function
 ω wavenumber
 j atomic quantum number

Subscripts

e equilibrium
 v vibration
 n, m energy states of molecules
 r rotation

BLANK PAGE

I. INTRODUCTION

It has long been recognized that the ensemble of wavelengths emitted or absorbed by any substance is determined by the atoms or molecules it contains. The theory and practice of molecular spectra, their recording and interpretation, has been treated in numerous books, scientific articles and reports for scores of years. It is, however, believed that a short introduction into the field of spectroscopy, and particularly into the field of the Raman spectroscopy, of a tutorial nature, could be of some value to researchers who are outside the circle of spectroscopists and who would still like to take advantage of the latest developments in this particular field and the special features it possesses.

In connection with the above, for the sake of clarity, it must be distinguished between the applications spectroscopists make of the spectra they obtain and the use intended in this work for those spectra. Again, in describing the use spectroscopists make of the spectra, this topic can only be dealt with in very broad terms. A detailed description is outside the scope of this work. It is clearly not the purpose or place to go here into details. In general, it can only be said that molecular spectra provide the physicist and chemist with one of the most important tools for investigating molecular structure. From the given spectra, the various energy levels of a given molecule can be determined. These, in turn, provide detailed information about the motion of the electrons, the vibrations and rotations of the nuclei in a

molecule. The motions of the electrons provide information on the chemical valences. The vibrational frequencies provide information of the interatomic forces, and it is also possible to determine with great accuracy the heats of dissociation. The rotational frequencies, on the other hand, provide extremely accurate values of the internuclear distances as will be shown in some examples later. This is only a very small indication of the knowledge one is able to obtain from the molecular spectra. One additional thing must be mentioned about the information obtainable from spectra. In recent years, a whole new field of astrophysics emerged. It is possible from the spectra to obtain not only information about the structure of distant planets, but also their composition and chemical changes going on in these planets, enlarging the knowledge of the universe enormously.

The above phenomena of such great interest are not, however, the purpose of this work. In this work the concern is focussed on a very simple and possibly minor portion of work of the spectroscopists. To make it clear, it is not the purpose of this work to expand on the theory of spectroscopy, but rather to apply one portion of this field to detection measuring and monitoring molecules without trying to determine from their spectra the construction, chemical properties or physical forces keeping them together. This is proposed with the use of the Raman effect. In this work, after a short introduction into the fundamentals of radiation and the essentials of infrared spectroscopy, it is proposed to present

the fundamental properties of the Raman effect, without going into the complicated derivations of working equations. These will be presented in a rather simple form referring the interested reader to the proper references. The connection with the infrared spectra will be pointed out. A short discussion of Raman active and infrared active molecules and some specific examples of molecules will be given. It should be pointed out here that the application of these methods, besides the ability to resolve multi-particle mixtures, is capable of detecting air pollution from distances instantaneously, is capable of detecting chemical compounds which might be hidden from normal detection, and has a multitude of applications which could be of major importance for civilian as well as military use.

II. FUNDAMENTALS OF RADIATION

Niels Bohr suggested that an atom or molecule cannot exist in states having any arbitrary energy, but only in certain discrete energy states called stationary states. These are selected according to certain rules from a continuous range of classically passible states¹. According to Bohr, electromagnetic radiation is not emitted while an electron is orbiting around the nucleus (as it should according to classical electrodynamics), but only when the electron is going from an energy level E_1 to another energy level E_2 . The energy emitted is in the form of a photon of energy

$$E_1 - E_2 = h\nu' = h\nu c \quad (1)$$

This is Bohr's frequency condition. The wave number of the emitted or absorbed radiation becomes

$$\nu = \frac{E_1}{hc} - \frac{E_2}{hc} \quad (2)$$

which becomes

$$\nu = RZ^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad n_1 > n_2 \quad (3)$$

where $R = R'/hc = 2\pi^2\mu e^4/ch^3$ is the Rydberg constant, and n_1 and n_2 are the principal quantum numbers of the two energy states concerned. It should be noted here that the spectrum thus obtained is the so-called line spectrum of atoms in contrast to band spectra of molecules. The essential point of the Bohr theory, that is, the discrete stationary energy states, is retained in wave mechanics. While the Bohr theory starts out from classical laws of motion and by means of certain quantum conditions selects only some of the possible orbits, wave mechanics, by using the fundamental idea of De Broglie which states that the motion of any corpuscle of matter is associated with a wave motion of wavelength

$$\lambda = \frac{h}{mv} \quad (4)$$

becomes more comprehensive and agrees quantitatively with experiments while the values calculated by Bohr's theory do not. The governing wave equation for the nonrelativistic case is, according to Schrodinger

$$\begin{aligned} & - \frac{h^2}{8\pi^2} \sum \frac{1}{m_k} \left(\frac{\partial^2 \Psi}{\partial x_k^2} + \frac{\partial^2 \Psi}{\partial y_k^2} + \frac{\partial^2 \Psi}{\partial z_k^2} \right) + V\Psi \\ & = i \frac{h}{2\pi} \frac{\partial \Psi}{\partial t} \end{aligned} \quad (5)$$

where $\Psi = \psi e^{-2\pi i \nu' t}$

A solution for a single particle could be obtained by solving Schrödinger's wave equation which, in terms of its amplitude of the wave motion, ψ is given by:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E-V) \psi = 0 \quad (6)$$

and which, in case of multiple particles, becomes

$$\sum_k \frac{1}{m_k} \left(\frac{\partial^2 \psi}{\partial x_k^2} + \frac{\partial^2 \psi}{\partial y_k^2} + \frac{\partial^2 \psi}{\partial z_k^2} \right) + \frac{8\pi^2}{h^2} (E-V) \psi = 0 \quad (7)$$

The solutions of the above equations are treated in numerous references and are not going to be treated here. It is sufficient to point out that solutions for particular cases can be found in Refs. 1-4.

For the purposes of this review, the particular solutions do not contribute enough to be discussed and complicate matters. The complete solution of the Schrödinger equation yields not only the eigenvalues, that is the energy values E of the stationary states, but also the corresponding eigenfunctions $\Psi = \psi \exp[-2\pi i \frac{E}{h} t]$ where $\frac{E}{h} = \nu'$. Frequently, there are several different eigenfunctions associated with one and the same eigenvalue. In that case, we have a degenerate state. The degeneracy is d -fold if there are d linearly independent eigenfunctions for a given eigenvalue. These d eigenfunctions are not uniquely determined by the wave equation, since any linear combination of the eigenfunctions belongs to the same eigenvalue.

If the interaction with an electromagnetic field is introduced into the Schrödinger equation of an atomic system, it is found that a non-zero probability arises of finding the

system in a state E_n , if originally it was in a state E_m and if radiation of wave number $\nu = [E_n - E_m]/hc$ is present. If $E_n < E_m$ radiation of this wave number is emitted, on the other hand, $E_n > E_m$ radiation of this wave number is absorbed by the atomic system.

The intensity of a spectral line in emission I_{em}^{nm} is defined (Ref. 5) as the energy emitted by the source per second. If there are N_n atoms in the initial state and if A_{nm} is the fraction of atoms in the initial state carrying out the transition to m per second, then

$$I_{em}^{nm} = N_n h c \nu_{nm} A_{nm} \quad (8)$$

where A_{nm} is the Einstein transition probability of spontaneous emission which is related in the case of dipole radiation to the matrix element as follows:

$$A_{nm} = \frac{64\pi^4 \nu^3}{3h} |R^{nm}|^2 \quad (9)$$

that the intensity becomes

$$I_{em}^{nm} = \frac{64\pi^4 \nu^4 c N_n}{3} |R^{nm}|^2 \quad (10)$$

where

$$R^{nm} = \int \psi_n^* M \psi_m d\tau \quad (11)$$

If the vector quantity R^{nm} , the matrix element of the electric dipole moment, differs from zero for two states n and m , the two states combine with each other with a certain probability with emission or absorption of radiation. If it is zero, the transition under consideration is forbidden as a dipole transition. It does follow certain selection rules as, for example, the selection rule in the case of a one-electron

system, $\Delta l = \pm 1$.

In the case of absorption, the intensity is given by

$$I_{\text{abs}}^{\text{nm}} = \rho_{\text{nm}} N_m B_{mn} \Delta x h c \nu_{\text{nm}} \quad (12)$$

If $I_0^{\text{nm}} = e \rho_{\text{nm}}$ is the intensity of the incident radiation, the last equation can be written as:

$$I_{\text{abs}}^{\text{nm}} = I_0^{\text{nm}} N_m B_{mn} h \nu_{\text{nm}} \Delta x \quad (13)$$

where N_m is the number of atoms in the initial lower state m and B_m is the Einstein transition probability of absorption,

$$B_{mn} = \frac{8\pi^3}{3h^2 c} |R^{\text{nm}}|^2 \quad (14)$$

this implies that

$$B_{nm} = \frac{1}{8\pi h c \nu_{\text{nm}}} A_{nm} \quad (15)$$

thus,

$$I_{\text{abs}}^{\text{nm}} \sim \nu_{\text{nm}} |R^{\text{nm}}|^2 \quad (16)$$

and

$$I_{\text{em}}^{\text{nm}} \sim \nu_{\text{nm}}^4 |R^{\text{nm}}|^2$$

Absorption is thus proportional to the incident frequency, whereas emission is proportional to the 4th power of the incident frequency of illumination.

It should be noted that Eqs. (9) and (14) are valid in the case of transitions between non-degenerate levels only. In case of transition between two degenerate levels of degeneracy d_n and d_m , those equations should be replaced by the following:

$$A_{nm} = \frac{64\pi^4 \nu^3 \sum |R_{i^m k^n}|^2}{3h d_n} \quad (17)$$

$$B_{nm} = \frac{8\pi^3}{3h^3 c} \sum |R_{nm}|^2 \quad (18)$$

and Eq. (15) appropriately by

$$B_{nm} = \frac{1}{8\pi h c \nu_{nm}^3} \frac{d_n}{d_m} A_{nm} \quad (19)$$

As indicated above, Eq. (2), the wave numbers are expressed in terms of the differences between energy states of the atom, which in turn is identified with the orbits of the electrons in the atom. These orbits are associated with the quantum numbers n and l and are responsible for the so-called line spectra. In addition to the line spectra due to emission of radiation by atoms, there is another type of spectrum due to radiation by molecules, the so-called band spectra. A band is characterized by a head, either on the violet or red side, the lines there being usually so close as to be indistinguishable and becoming more widely spaced and fainter towards the tail end. Heavy molecules have their bands more closely spaced than light molecules. It must also be noted here that a third kind of spectrum is observed, that is, a continuous spectrum. Two types of continuous spectra can be distinguished. The first obtained from liquids and solids as a result of very close packing of the atoms and the interaction of the atoms and molecules with each other. This kind of continuous spectrum is more a result of the revolving power of the spectrographs and also, what is more important, the broadening of the spectral lines for the above-mentioned reasons. The second kind, the so-called "continuous term" spectrum is a result of dissociation (molecules) and/or

ionization (atoms). With the usual zero-point of the energy scale ($n=\infty$), all stable discrete quantum states of an atom with one outer electron have negative energy values. A positive value of energy E corresponds to an electron which moves in a hyperbolic orbit about the nucleus. It, of course, goes only once through such an orbit. The energy can assume all positive values of E . Therefore, from the limit $E=0$ of a discrete energy spectrum of an atom, there is a continuous region of possible energy values, the so-called "continuous term spectrum". Figure 1 presents a simplified energy level diagram of hydrogen where the above is indicated. Included in the figure is a circular Bohr orbit diagram for hydrogen showing the Lyman, Balmer and Paschen series.

III. THE ESSENTIALS OF BAND SPECTROSCOPY

As indicated above, the term "band spectrum" is used to designate a spectrum originating from emission or absorption of molecules. As such, it must be distinguished from a line spectrum which is the designation of a spectrum originating in the atom. The optical radiant energy identified with molecular spectra is distributed over a very wide range of frequencies, extending from the ultraviolet to the microwave region.

The essential difference between atomic and molecular spectra is that the atomic spectra are completely explained by the quantized changes in the energy associated with the outer electronic structure, whereas the molecular spectra

include not only this energy but also contributions of energy resulting from the vibrations of the component atom relative to each other and from rotation of the molecule as a whole about an axis through the center of gravity.

The total energy of the system may be represented by the sum of all the above-mentioned contributions,

$$E_{\text{tot}} = E_e + E_v + E_r \quad (20)$$

which, in terms of the wave number units (term values), can be written as

$$T = T_e + G + F \quad (21)$$

In Eq. (20), $E_e = E^{el} + V_n$ is the electronic energy of the state and represents the potential in the Schrödinger equation under whose action the nuclei are moving. E^{el} is the total energy in the Schrödinger equation for a case where the electrons are moving in the field of fixed nuclei and having a potential V_e . In the case of a diatomic molecule V , the Coulomb potential, as is well known, is given by

$$V_n = \frac{z_1 z_2 e^2}{r} \quad (22)$$

The development of the quantum theoretical explanation of the features of molecular spectra is generally started with diatomic molecules. This introduces a relatively greater degree of simplicity because one is dealing with a two-body problem. Furthermore, the full details of diatomic spectra

are frequently completely observable, whereas the complexity of the spectra of polyatomic molecules is, in general, so great that details are resolved only in relatively few instances, usually where symmetry considerations permit simplification of the model. Generally, the features of polyatomic molecules are explained by extending the concepts of diatomic molecules.

The simplest model of a diatomic molecule is thought of as a dumbbell structure, the two atoms rigidly joined by a line, with an axis of rotation perpendicular to the line joining the nuclei, at the center of mass of the two atoms, Fig. 2. The solution of the Schrödinger equation appropriate to the problem results in the following energy eigenvalues:

$$E_{\text{rot}} = \frac{h^2 J(J+1)}{8\pi^2 \mu r^2} = \frac{h^2 J(J+1)}{8\pi^2 I} \quad (23)$$

$$\frac{E_{\text{rot}}}{hc} = F(J) = BJ(J+1) \quad (24)$$

where $B = \frac{h}{8\pi^2 c I}$ is called the rotational constant. μ = the reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$, I = the moment of inertia and J = the rotational quantum number related to the total angular momentum \bar{J} of the electrons in an atom, by $|\bar{J}| = \sqrt{J(J+1)} \left(\frac{h}{2\pi}\right) \approx J \frac{h}{2\pi}$. Thus, J gives approximately the angular momentum in units of $\frac{h}{2\pi}$. Each rotational energy state is characterized by one of these J values, which can take on a series of integers from 0, 1, 2, The quantum mechanics leads to a selection rule for transition between energy states

$$\Delta J = \pm 1 \quad (25)$$

These transitions account for the spectral lines whose wave number is given by

$$\nu = F(J+1) - F(J) = 2B(J+1) \quad (26)$$

leading to a series of equidistant lines, which are observed in the far infrared region, Fig. 3. The actual frequency of rotation of the rigid rotator is given by

$$\nu_{\text{rot}} = C2B [J(J+1)]^{\frac{1}{2}} \approx C2BJ \quad (27)$$

Since, in actuality, the molecules are not strictly rigid, Eq. (24) for the rotational term values is generally modified to

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \quad (28)$$

where $D = \frac{4B^2}{\omega^2}$ is always very small and for the present applications, insignificant. The effect of this modification is shown in Fig. 4, where the rigid rotator lines are plotted as a reference. It is evident that at low rotational quantum numbers, it is negligible.

The same dumbbell model considered as a harmonic oscillator would result in

$$\nu_{\text{osc}} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \quad (29)$$

where μ is the reduced mass defined previously. Again, a solution of Schrödinger's equation results in the vibrational energy states,

$$E(v) = h\nu_{\text{osc}}(v + \frac{1}{2}) \quad (30)$$

where v is the vibrational quantum number which takes on

integral values 0,1,2,... and again the selection rules for permitted energy transition are

$$\Delta v = \pm 1 \quad (31)$$

In terms of energy term values, Eq. (30) can be written

$$G(v) = \frac{E(v)}{hc} = \frac{\nu_{osc}}{c} (v + \frac{1}{2}) = \omega (v + \frac{1}{2}) \quad (32)$$

Since emission and absorption of radiation takes place as a result of a transition from a higher to a lower state or from a lower to a higher state, the wave number of the emitted or absorbed radiation is given by

$$\nu = \frac{E(v')}{hc} - \frac{E(v'')}{hc} = G(v') - G(v'') \quad (33)$$

Using Eqs. (32) and (33), one obtains

$$\nu = G(v+1) - G(v) = \omega \quad (34)$$

indicating that the quantum mechanically derived frequency is equal to the classical frequency for all transitions.

As in the case of the rotational term values, the expression for the vibrational term values must be modified to correct for the assumption of a harmonic oscillator. In fact, the finer details of the spectra can only be accounted for if the molecule is considered as an anharmonic oscillator. For small anharmonicities, which is generally the case, the term values are given by

$$G(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3 \quad (35)$$

instead of by Eq. (32).

The zero point energy is obtained from Eq. (35) by

setting $v=0$; thus

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e \dots \quad (36)$$

If the energy levels are referred to this lowest level as zero, then using Eqs. (35) and (36):

$$G_0(v) = \omega_0 v - \omega_0 x_0 v^2 + \omega_0 y_0 v^3 \quad (37)$$

where

$$\begin{aligned} \omega_0 &= \omega_e - \omega_e x_e + 3/4 \omega_e y_e + \dots \\ \omega_0 x_0 &= \omega_e x_e - 3/2 \omega_e y_e \\ \omega_0 y_0 &= \omega_e y_e \end{aligned} \quad (38)$$

In both Eqs. (35) and (36), $\omega_e \gg \omega_e x_e$ and $\omega_e x_e \gg \omega_e y_e$. Neglecting cubic terms in Eq. (35), the separation of successive absorption bands is given by

$$\Delta G_{v+1/2} = G(v+1) - G(v) = \omega_e - 2\omega_e x_e - 2\omega_e x_e v \quad (39)$$

The frequency ω_e is thus from the first band (1-0)

$$v(1-0) = \Delta G_{1/2} = \omega_e - 2\omega_e x_e = \omega_0 - \omega_0 x_0 \quad (40)$$

One important feature must be pointed out. Whereas the selection rule for the non-rigid rotator remained the same as for the rigid rotator, $\Delta J = \pm 1$, the selection rule for the anharmonic oscillator is changed. Δv can now assume, besides the values of ± 1 , which give the most intense transitions, also values of $\pm 2, \pm 3$ even so with rapidly decreasing intensity.

The combined effect of these modifications results in the term values for the vibrating rotator,

$$\begin{aligned} T = G(v) + F(J) &= \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \dots \\ &+ B_v J(J+1) - D_v J^2(J+1)^2 + \dots \end{aligned} \quad (41)$$

where $B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots$ with $\alpha_e \ll B_e$ since the change in internuclear distance during the vibration is small compared to the internuclear distance itself, and $D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots$ with $\beta_e \ll D_e$ on the same grounds as α_e . In this context, B_v and D_v signify the rotational constants for the vibrating rotator, the subscript v to be distinguished from the vibrational quantum numbers v . If a particular vibrational transition from v_1 to v_2 is considered, then according to Eq. (41), neglecting the rotational constant D_v , the wave numbers become

$$\nu = \nu_0 + B'_v J'(J'+1) - B''_v J''(J''+1) \quad (42)$$

where $\nu_0 = G(v') - G(v'')$ is the wave number of the pure vibrational transition neglecting rotation ($J'=J''=0$). If, in Eq. (42) $\Delta J=1$ and $\Delta J=-1$, and the interaction between rotation and vibration is neglected, then $B'_v = B''_v = B$ and Eq. (42) result in

$$\nu_R = \nu_0 + 2B + 2BJ \quad J=0, 1, \dots \quad (43)$$

$$\nu_P = \nu_0 - 2BJ \quad J=1, 2, \dots \quad (44)$$

These last two equations represent two series of lines called the R and P branches, respectively. In the above, the effect of the electrons surrounding the nuclei on the angular momentum has been neglected. If the angular momentum of the electrons about the internuclear axis is designated by $\Lambda = \lambda \frac{h}{2\pi}$, where λ is the quantum number of this angular momentum, then for $\lambda=0$, we get $\Delta J = \pm 1$ as in (43) and (44). If, however, $\lambda \neq 0$, then $\Delta J = 0, \pm 1$ and for $\Delta J=0$, we obtain

$$\nu_e = \nu_0 + F'(J) - F''(J) \quad (45)$$

called the Q-branch.

As indicated previously, (Eq. (21)), the total energy of a system of molecules in terms of its term values consists of the term values of Eq. (41) and a term T_e representing the electronic transition. Thus,

$$\nu = (T'_e - T''_e) + (G' - G'') + (F' - F'') \quad (46)$$

is the wave number of the given system.

Using Eq. (35) and neglecting the rotational term values, the wave number becomes, according to (45),

$$\begin{aligned} \nu = & \nu_e + \omega'_e (v' + \frac{1}{2}) - \omega'_e x'_e (v' + \frac{1}{2})^2 + \omega'_e y'_e (v' + \frac{1}{2})^3 + \dots \\ & - [\omega''_e (v + \frac{1}{2}) - \omega''_e x''_e (v + \frac{1}{2})^2 + \omega''_e y''_e (v + \frac{1}{2})^3 + \dots] \quad (47) \end{aligned}$$

The last equation represents all possible transitions between the different vibrational levels of two participating electronic states. There is no strict selection rule for the vibrational quantum number ν for electronic transitions. Thus, in principle, each vibrational state of an upper electronic state can combine with each vibrational state of a lower electronic state, resulting in a large number of lines (hence, band spectra).

In an analogous way, the principles of the Raman spectra and their relation to the infrared spectra is presented in the following section.

IV. THE RAMAN EFFECT

The Raman Effect is the phenomenon of light scattering from a material medium, whereby the light undergoes a wavelength change and the scattering molecules an energy change in the scattering process. The Raman scattered light has no phase relationship with the incident radiation. The phenomenon was predicted in 1923 by Smekal and experimentally observed in 1928 by Raman and Krishnan, in liquids and solids, and by Landsberg and Mandelstam in crystals. The Raman shifts correspond to energy differences between discrete stationary states of the scattering system. Classically, the Raman effect can be described as the modulation of the scattered light by the internal motions of the scattering molecules. In this kind of analogy, the Raman lines would correspond to the side bands, and the Rayleigh light to the carrier frequency. This, of course, would result in the Stokes lines having the same intensity, which is not the case. Quantum theoretically, the incident photons collide elastically or inelastically with the molecules to give Rayleigh and Raman lines, respectively, with the inelastic process much less probable than the elastic. When an inelastic collision occurs with the incident photon furnishing energy to the molecule raising it to a higher energy level, the scattered photon being of lower energy, gives rise to the Stokes line. If the scattering molecule gives up energy to the impinging photon and moves to a lower energy state, the scattered photon gives rise to the anti-Stokes line. Since the anti-Stokes

line must originate in molecules of higher energy level, which are less abundant at normal temperatures, the anti-Stokes lines would be expected to be much weaker than the Stokes lines. The process of light scattering can thus be visualized, as the absorption of an incident photon of energy E by a molecule of a given initial state, raising the molecule to a "virtual" state, from which it immediately returns to a final stationary state emitting a photon of the difference energy between the two states and incident energy E . The process is illustrated in Fig. 5. A quantum theoretical derivation of the intensity of the scattered radiation utilizing the perturbation theory of wave mechanics and also utilizing the polarizability theory of Placzek is given in Refs. 5,6,7 and 12. In this short review following the outline of Section III, the Raman lines of a rigid rotator, harmonic oscillator and vibrating rotator will be presented.

The rotational Raman spectrum is governed by a selection rule which is different than the selection rule for the infrared spectrum as expressed in Eq. (25); namely,

$$\Delta J = 0 \pm 2 \quad (48)$$

When molecules with different J values are present, the rotational Raman spectrum consists of a number of lines. $\Delta J = 0$ corresponds to the undisplaced line. The transition $J \rightarrow J+2$ results in a shift to longer wavelength (Stokes lines) and the transition $J+2 \rightarrow J$ results in a shift to shorter wavelength (anti-Stokes lines). Using Eq. (24), the magnitude of the frequency shift can be found,

$$\begin{aligned}\Delta\nu &= F(J+2) - F(J) \\ &= B(J+2)(J+3) - BJ(J+1) = 4B(J+3/2)\end{aligned}\tag{49}$$

Eq. (49) represents a series of equidistant Raman lines on either side of the undisplaced line. These small Raman displacements can, therefore, be identified as the rotational Raman spectrum, Fig. 6.

From the matrix elements of the polarizability, it is found that in the case of a harmonic oscillator, the same selection rule holds for the Raman as for the infrared spectrum,

$$\Delta\nu = \pm 1\tag{50}$$

Thus, a transition can take place only to the adjacent vibrational state. The frequency shift using Eq. (32) becomes

$$\Delta\nu = G(v+1) - G(v) = \omega\tag{51}$$

this shift occurring to either side of the illuminating radiation frequency. As mentioned previously, at ordinary temperatures most of the molecules are in the lowest energy state ($v=0$) and only a very small fraction of the molecules is in the higher state ($v=1$). As a result, the intensity of the Stokes-Raman lines which correspond to a transition $0 \rightarrow 1$ is much greater than the intensity of the anti-Stokes lines which correspond to a transition $1 \rightarrow 0$.

A comparison of Eqs. (34) and (51) reveals a very important relationship between the infrared and Raman spectra. It is seen that the infrared vibrational frequencies agree exactly with the Raman frequency shifts. This can be seen

in Table I, where a number of infrared frequencies and Raman displacements have been tabulated for several molecules for which both spectra have been observed. The Raman spectra can, therefore, be regarded as an infrared spectrum shifted into the visible or ultraviolet region.

The selection rules for the Raman spectrum of the anharmonic oscillator are the same as those for the anharmonic oscillator of the infrared spectrum. Therefore, the Raman shifts can be represented by the same equations as the frequency of the anharmonic oscillator, Eq. (40).

As in the case of the infrared spectrum, the Raman spectrum of the vibrating rotator, governed by the vibrational selection rules, $\Delta v = \pm 1$ and rotational selections rules, $\Delta J = 0, \pm 2$, consists of three branches, the S-branch, Q-branch, and O-branch. Their equations can be obtained from

$$\Delta v = \Delta v_0 + B'_v J'(J'+1) - B''_v J''(J''+1) \quad (52)$$

analogous to Eq. (42) for the infrared spectrum, by substituting $J' = J'' + 2$ (S-branch), $J' = J'' - 2$ (O-branch) and $J' = J''$ (Q-branch) and using $J' = J$.

$$(\Delta v)_S = \Delta v_0 + 6B'_v + (5B'_v - B''_v)J + (B'_v - B''_v)J^2 \quad J=0,1,\dots \quad (53)$$

$$(\Delta v)_O = \Delta v_0 + 2B'_v - (3B'_v + B''_v)J + (B'_v - B''_v)J^2 \quad J=2,3,\dots \quad (54)$$

$$(\Delta v)_Q = \Delta v_0 + (B'_v - B''_v)J + (B'_v - B''_v)J^2 \quad J=0,1,\dots \quad (55)$$

For the 0-1 vibrational transition, the difference between B'_v and B''_v is very small. The lines of the Q-branch are, therefore, very close to each other and are usually not resolved, giving rise to an intense line. The S- and O-branches

are much weaker since their lines are not superimposed. The above are similar to the R and P branches of the infrared spectrum. In most cases considered in the measurements of Ref. 7, the observed Raman lines of large displacements represented the unresolved Q-branches of the Raman rotation-vibration bands.

As mentioned previously, the Raman displacements of some molecules can be regarded as the infrared vibrational spectrum shifted into the visible or ultraviolet region. This should not be regarded as a general law governing the relation between the Raman spectrum and infrared spectrum, or vice-versa. It should be noted that not all Raman active molecules are infrared active, and not all infrared active molecules are Raman active. The infrared and Raman activity are dependent on the structure and symmetry of the given molecule. Since in unsymmetrical molecules every normal vibration is associated with a change of the dipole moment, all normal vibrations of such molecules are infrared active. Symmetrical molecules, on the other hand, may have vibrations during which a change of the dipole moment is zero, and therefore, those molecules are infrared inactive. As an example, the symmetrical molecule CO_2 is infrared inactive for the vibration ν_1 and active for ν_2 and ν_3 . On the other hand, the nonlinear symmetric molecule H_2O has all three normal vibrations associated with a change of the dipole moment and is infrared active.

In the case of Raman spectra, the amplitude of the dipole

moment induced by the incident radiation must change during the vibration considered. According to the polarizability theory, Ref. 12, the amplitude of the induced dipole moment is given by

$$|P| = \alpha |E| \quad (56)$$

where α is the polarizability and E the electric vector of the incident radiation of frequency ν . In an unsymmetric molecule, during all normal vibrations, a periodic change of the polarizability takes place. The induced dipole moment changes and the molecules are, therefore, Raman active. For symmetrical molecules this is not always the case, although it is possible for a linear symmetrical molecule to be infrared inactive and Raman active. The linear symmetric molecule CO_2 is infrared inactive in its first normal vibration ν_1 , but Raman active. The same molecule is infrared active for ν_2 and ν_3 and Raman inactive for these vibrations. It should be noted here that all homonuclear diatomic molecules like O_2 , H_2 , N_2 , ... are infrared inactive while they are all Raman active. This is a result of the fact that the dipole moment and its change are zero for homonuclear diatomic molecules, whereas the polarizability, its change, and the resulting amplitude change in the induced dipole moment do not vanish. This description of the Raman and infrared activity of the molecules is of a very elementary nature. For a detailed treatment of the subject, Refs. 5 and 13 should be consulted.

V. LINE INTENSITIES OF INFRARED AND RAMAN SPECTRA

In the foregoing, some fundamental relations of molecular infrared and Raman spectra as well as the relations between those spectra, the selection rules for rotational and vibrational lines of both have been discussed. One of the fundamental measurable quantities is the intensity of the given line both in the infrared and Raman spectra. As indicated in Section II, Eqs.(10) and (16) and Ref. 7, the intensity of a spectral line depends not only on the frequency and transition probability but also on the number of molecules in a given state. For a theoretical determination of the intensity of a given line, it is necessary to know the distribution of the molecules in the various initial states and the transition probabilities (Ref. 7). Since most infrared and Raman spectra are observed under conditions of thermal equilibrium, the distribution of the molecules over the different quantum states in thermal equilibrium need be considered. According to the Maxwell-Boltzmann distribution, the number of molecules in each of the vibrational states is proportional to

$$N_v \sim e^{-\frac{E}{kT}} = e^{-\frac{G_0(v)hc}{kT}} = e^{-\frac{G_0(v)}{.6952T}} \quad (57)$$

where the zero point energy level (Eq. 36) has been left out. To add this to the exponent would mean only adding a constant factor to all the vibrational levels including the zero level. Thus, the exponential gives the relative numbers of molecules in the different vibrational levels, referred to the number

of molecules in the lowest vibrational level. In order to obtain the number of molecules in a particular energy level referred to the total number of molecules N , the state sum or partition function

$$Q_v = 1 + \exp\left[-\frac{G_0(1)hc}{kT}\right] + \exp\left[-\frac{G_0(2)hc}{kT}\right] + \dots \quad (58)$$

must be utilized.

The number of molecules in the state v is, therefore,

$$N_v = \frac{N}{Q_v} \exp[-G_0(v)hc/kT] \quad (59)$$

Evaluation of Eqn. (59) can be most tedious. Since successive terms in Eqn. (59) decrease very rapidly and in most cases the exponential terms in Eqn. (58) are small compared to unity Eqn. (59) can be written as:

$$N_v = N \exp[-G_0(v)hc/kT] \quad (60)$$

In the case of the thermal distribution of the rotational levels, the problem is somewhat more complicated. It is not given by the Boltzmann factor $\exp(-E/kT)$ above. According to the quantum theory each state of an atomic system with a total angular momentum J consists of $(2J+1)$ levels which coincide in the absence of an external field. The state has a $(2J+1)$ fold degeneracy. The frequency of its occurrence is $(2J+1)$ times that of the state $J=0$. The number of molecules N_J in the rotational level J of the lowest vibrational state at a temperature T is proportional to:

$$N_J (2J+1) \exp[-F(J)hc/kT] = (2J+1) \exp[-BJ(J+1)hc/kT] \quad (61)$$

The behavior of this function for a fixed B is shown in Figure 7 . It is seen that the number of molecules does not decrease with the increase of the rotational quantum number J but goes through a maximum. This maximum is

$$J_{\max} = \left(\frac{kT}{2Bhc} \right)^{\frac{1}{2}} - \frac{1}{2} = .5896 \left(\frac{T}{B} \right)^{\frac{1}{2}} - \frac{1}{2} \quad (62)$$

Proceeding in an analogous way, as in the vibrational state, the number of molecules in the rotational state J is

$$N_J = \frac{N}{Q_r} (2J+1) \exp[-BJ(J+1)hc/kT] \quad (63)$$

where

$$Q_r = 1 + 3\exp\left[-\frac{2Bhc}{kT}\right] + 5\exp\left[-\frac{6Bhc}{kT}\right] + \dots \quad (64)$$

which can be replaced by

$$Q_r = \int_0^{\infty} (2J+1) e^{-\frac{hcBJ(J+1)}{kT}} dJ = \frac{kT}{hcB} \quad (65)$$

so that Eqn. (63) becomes

$$N_J = N \frac{hcB}{kT} (2J+1) \exp\left[-\frac{BJ(J+1)hc}{kT}\right] \quad (66)$$

For the higher vibrational levels

$$N_J \sim (2J+1) \exp[-(G(v)+F(J))hc/kT] \quad (67)$$

with the factor $\exp[-G(v)hc/kT]$ separated, only the rotational levels remain, which are considerably smaller than the lowest vibrational level. The individual line intensities in a rotation-vibration band are proportional to N_J as given by Eqn. (63) as a function of J. Using Eqns. (10,12,16,19) and 63, the intensities of the lines of the rotation-vibration bands with $d_n = 2J'+1$ and $d_m = 2J''+1$ is

$$I_{em} = \frac{64\pi^4 \nu^4 c N}{3Q_r} \left(\sum_{ik} |R_{i m_k}|^2 \right) \exp\left[\frac{-B' J' (J'+1) hc}{kT}\right] \quad (68)$$

$$= \frac{2C_{em} \nu^4}{Q_r} S_J \exp\left[\frac{-B' J' (J'+1) hc}{kT}\right]$$

$$I_{abs} = \frac{I_o 8\pi^3 \nu N}{3hc_r} \left(\sum_{ik} |R_{i m_k}|^2 \right) \exp\left[\frac{-B'' J'' (J''+1) hc}{kT}\right] \quad (69)$$

$$= \frac{2C_{abs} \nu}{Q_r} S_J \exp\left[\frac{-B'' J'' (J''+1) hc}{kT}\right]$$

It must be noted that the J value of the initial state must be used in the exponential term, that is, the value of the higher state J' for emission and the value of the lower state J'' for absorption as in (68) and (69) respectively. The line strength S_J is that part of $\sum |R_{i m_k}|^2$ that depends on J . A constant factor corresponding to the magnitude of the dipole moment or its change is included in C_{em} and C_{abs} , respectively. In the case of a rotation ($\Delta=0$) an evaluation of the matrix elements $R_{i m_k}$ results (Ref. 5) in:

$$\begin{aligned} \text{for } \Delta J = +1 & \quad S_J = J+1 \\ \text{for } \Delta J = -1 & \quad S_J = J \end{aligned} \quad (70)$$

Eq. (68) holds for the Raman spectra. According to Placzek the line strength factors S_J are for $\Delta=0$

$$\begin{aligned} \text{for } \Delta J = +2 & \quad S_J = \frac{3(J+1)(J+2)}{2(2J+3)} \\ \text{for } \Delta J = -2 & \quad S_J = \frac{3(J-1)J}{2(J-1)} \\ \text{for } \Delta J = 0 & \quad S_J = a_0 (2J+1) + \frac{J(J+1)(2J+1)}{(2J-1)(2J+3)} \end{aligned} \quad (71)$$

where a_0 is a constant.

Eqs. (68) and (71) define the intensity of a Raman line

in the case where the vibrational contribution has been separated, with the last expression in Eq. (71) corresponding to a Q-branch line. The intensity of an individual Q-branch line including the vibrational contribution is given (Ref. 10) by

$$I_{em} = \frac{64\pi^4 (\nu_o - \nu)^4 \cdot c}{3Q_r Q_v} \cdot (V_{k+1}) \exp\left[-\frac{hc\nu}{kT} V_k\right] \times$$

$$\times [NE_o^2 d_j (2J+1) \exp\left[-J(J+1) \frac{hCB}{kT}\right] \frac{h}{8\pi^2 c \nu}] \times \quad (72)$$

$$\times \left[\alpha'^2 + \frac{7}{45} \gamma'^2 \frac{J(J+1)}{(2J-1)(2J+3)}\right]$$

for vertically polarized incident radiation and transverse observation. In most applications of interest in the context of this work, the intensity of the Q-branch of the vibration-rotation part of the spectra is observed. In order to obtain an expression for the intensity of the Q-branch, Eq. (72) must be summed over all V_k and J values. The summation over V_k of the vibrational contribution $(V_{k+1}) \exp\left[-\frac{hc\nu}{kT} V_k\right]$ converges to Q_v^2 and the summation over J of the expression

$$\frac{1}{Q_r} \sum d_j (2J+1) \exp\left[-\frac{J(J+1)hBe}{kT}\right] \times$$

$$\times \left[\alpha'^2 + \frac{7}{45} \gamma'^2 \frac{J(J+1)}{(2J-1)(2J+3)}\right] = \alpha'^2 + \frac{7}{45} \gamma'^2 X$$

where

$$X = \frac{1}{Q_r} \sum d_j (2J+1) \exp\left[-\frac{J(J+1)hBc}{kT}\right] \frac{J(J+1)}{(2J-1)(2J+3)} \quad (72a)$$

Eq. (72) thus becomes:

$$I_{em} = \frac{64\pi^4 (\nu_o - \nu)^4}{3} \frac{h}{8\pi^2 \nu} Q_v NE_o^2 \left(\alpha'^2 + \frac{7}{45} X \gamma'^2\right) \quad (73)$$

Substituting the expressions for E_o and Q_r and combining terms, Eq. (73) can be written in the more familiar form (Ref. 11)

$$I = \frac{2^7 \pi^5}{135} k N b^2 d_j (45 \alpha'^2 + 7 X Y'^2) I_o \quad (74)$$

where $k = (\nu_o - \nu)^4 (1 - e^{-\frac{h c \nu}{k T}})^{-1}$

$$b^2 = h / 8 \pi^2 c \nu \quad (75)$$

and d_j is a degree of degeneracy. Equations (73) and (74) are both valid for observation at a unit distance. In case of remote observation of the scattered radiation, the factor $1/R$ must be included; thus, Eq. (74) becomes:

$$I = \frac{2^7 \pi^5}{135} k_j N b_j^2 d_j \left(\frac{45 \alpha'^2 + 7 X Y'^2 I_o}{R^2} \right) \quad (76)$$

Generally, the Raman intensity can be expressed (Ref. 7) for both Stokes and Anti-Stokes lines as

$$I_{S,A} = C (\nu_o \pm \nu)^4 N \frac{b^2}{\mu} I_o (45 \alpha'^2 + 7 X Y'^2) \Omega \quad (77)$$

The ratio of the Stokes to Anti-Stokes intensity utilizing the Boltzmann distribution to determine the number of molecules in each vibrational state, is given by:

$$\frac{I_S}{I_A} = \frac{(\nu_o - \nu)^4}{\nu_o^4} \exp \left[\frac{h \nu}{k T} \right] \quad (78)$$

The Raman Stokes to Rayleigh intensity for vertically polarized incident radiation is given by:

$$\frac{I_S}{I_R} = \frac{(\nu_o - \nu)^4}{\nu_o^4} \frac{h}{8 \pi^2 \mu \nu} \frac{(45 \alpha'^2 + 7 X Y'^2)}{(45 \alpha^2 + 7 X Y'^2)} \quad (79)$$

From Eqs. (75) and (76) the dependence of the Raman intensity on the ambient temperature can be obtained. An inspection of Eq. (75) indicates that this dependence is relatively weak at low temperatures. Figure 8 presents a family of curves with the Raman shift as a parameter, indicating the dependence of the Raman intensity on the temperature. It is clearly evident from these figures that the temperature and the Raman frequency shift have a pronounced effect on the Raman intensity. An increase in either increases the Raman intensity. Thus the effective Raman scattering cross-section is increased with the increase in temperature and molecules whose Raman frequency shift is larger have essentially a higher scattering cross-section. At low temperatures, however, the dependence of the scattering intensity on the temperature is very weak (Fig. 8a). It is quite evident, therefore, that the weak dependence on the temperature, at room or near room temperature, makes this effect a very useful tool in gas dynamic diagnostics as well as measurements of atmospheric pollutants. Equation (78) provides a means of measuring the vibrational temperature of a given gas, as well as the temperature of gases of different temperatures.

In Fig. 9 a plot of the ratio of Stokes to Anti-Stokes intensities as a function of temperature for several molecules of interest is shown. It is evident that by measuring the ratio of the scattered intensity of each specie, the individual temperatures can be determined. This was shown experimentally in Ref. 7, where the temperature of O_2 was determined using this method.

VI. SOME APPLICATIONS

As indicated previously, the infrared and Raman spectra contain a vast source of information relating to the atomic, molecular and electronic structure of matter, from which various properties of individual molecules, their physical and chemical properties can be obtained, predicted or understood. Some of the fundamental properties of molecules, as for example, the internuclear distance and force constant are obtainable from the observed infrared spectra. In the following, several examples are given on the application of the spectra in their most fundamental relations.

From a given spectrum of CN, the line separation was observed to be 3.7992 cm^{-1} . If this were a rotational spectrum, then according to Eq. (26)

$$\nu = 2B(J+1)$$

this value 3.7992 cm^{-1} must be equal to $2B$. Thus $B = 1.8996 \text{ cm}^{-1}$.

Since $B = h/8\pi^2 cI$, the moment of inertia $I = 14.7 \times 10^{-40} \text{ gm cm}^2$.

Since $I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$, the internuclear distance r becomes with $\mu = 10.8 \times 10^{-24} \text{ gm}$, $r = 1.17 \times 10^{-8} \text{ cm}$. The frequency of rotation in the quantum states $J=1,2,3$ is, according to Eq. (27), 1.14×10^{11} , 2.28×10^{11} , $3.42 \times 10^{11} \text{ c/sec.}$, respectively, and the periods of rotation $8.78 \times 10^{-12} \text{ sec.}$, 4.39×10^{-12} and $2.93 \times 10^{-12} \text{ sec.}$

In the near infrared, CN has an intense line at 2042.4 cm^{-1} . If this represents the vibrational line, then according to Eq. (34), $J=2042.4$. Therefore, $\nu_{\text{osc}} = \omega \cdot c = 6.11 \cdot 10^{13} \text{ c/sec.}$

The period of vibration is therefore, 1.64×10^{-14} sec.
Using Eq. (29) one finds $k=1.59 \times 10^6$ dynes/cm. In Table II the results of similar calculations as above have been compiled for several molecules, and those results compared with data available from calculations utilizing more sophisticated theories. As can be seen, the differences are within reasonable error. The application of the first order theory to obtain order of magnitude molecular data can thus be justified.

VII. CONCLUSIONS

The fundamentals of radiation, band spectroscopy and the Raman effect have been presented. In addition, the expressions for the line intensities of both the infrared and Raman spectra are given. The section on applications, while incomplete and of very fundamental nature, provides the reader unfamiliar with spectroscopy a glimpse into the data obtainable utilizing this branch of science. It must be emphasized that with the advent of very powerful coherent monochromatic radiation sources, spectroscopy and in particular, Raman spectroscopy has great potentials for remote identification, measurement, three dimensional mapping and uncovering of species in mixtures, inaccessible before.

REFERENCES

1. Bohm, David: Quantum Theory. Prentice Hall, Inc., New York, 1951.
2. Pauling, L. and Wilson, E.B.: Introduction to Quantum Mechanics. McGraw Hill Book Company, New York, 1935.
3. Slater, J.C.: Quantum Theory of Matter. McGraw Hill Book Company, New York, 1951.
4. Shiffe, L.: Quantum Mechanics. McGraw Hill Book Company, New York, 1955.
5. Hersberg, G.: "Molecular Spectra and Molecular Structure", D. Van Nostrand, Princeton, New Jersey, 1963.
6. Mizushima, S.I.: "Raman Effect", Handbuch der Physik, Vol. XXVI, Springer-Verlag, 1958.
7. Lederman, S. and Widhopf, G.: "Species Concentration Measurements Utilizing Raman Scattering of a Laser Beam", Polytechnic Institute of Brooklyn, PIBAL Report No. 69-46, AD 701343, November 1969.
8. Leighton, R.B.: Principles of Modern Physics. McGraw Hill Book Company, New York, 1959.
9. Standsbury, E.J., Crawford, M.F. and Welsh, H.L.: "Determination of Rates of Change of Polarization from Raman and Rayleigh Intensities", Canadian Journal of Physics, 31, 954, 1953.
10. Golden, D.M. and Crawford, B.: "Absolute Raman Intensities I. Method for Molecules in the Gas Phase", Journal of Chemical Physics, 36, 6, 1964.

11. Schooter, H.W. and Bernstein, H.J.: "Intensity of the Raman Effect", Journal of Molecular Spectroscopy, 12, 1-17, 1964.
12. Placzek, G.: "Rayleigh Streuung und der Raman Effect", Handbuch der Radiologie Leipzig Akademische Verlagsgesellschaft, VI, 1934.
13. Herzberg, G.: "Infrared and Raman Spectra of Polyatomic Molecules", 2, D. Van Nostrand Co., 1945.
14. Bauman, R.P.: "Absorption Spectroscopy", John Wiley (ed.) New York, 1962.

TABLE I

Gas	Raman Displacement $\Delta\nu$	Infrared Frequency ν_o
HCl	2886.0	2885.9
NO	1877.	1875.9
CO	2145.	2143.2
N ₂ O	1285 2223.5	1285. 2223.5
H ₂ O	3651.7	3651.7

Molecule	B cm ⁻¹	λ cm ⁻¹	tab. r(cm) 10 ⁻⁸	r(cm) 10 ⁻⁸	ν_{ROT} J=1 c/sec. 10 ⁻¹¹	ν_{ROT} J=1 sec. 10 ⁻¹²	ν_{ROT} J=2 1/sec. 10 ⁻¹¹	ν_{ROT} J=2 sec. 10 ⁻¹²	ν_{ROT} J=3 1/sec. 10 ⁻¹¹	ν_{ROT} J=3 sec. 10 ⁻¹²	$\nu_{\text{VIB.}}$ 1/sec. 10 ⁻¹³	$\nu_{\text{VIB.}}$ (sec.) 10 ⁻¹⁴	K dynes/cm ⁵ 10 ⁵
NO	1.7046	1890	1.1508	1.145	1.021	9.8	2.04	4.9	3.06	3.26	5.664	1.76	15.7
OH	18.871	3569.6	0.9706	0.97	11.3	0.884	22.6	0.442	33.9	0.295	10.69	0.935	7.06
CH	14.457	2723	1.1198	1.12	8.665	1.15	17.33	0.577	25.99	0.385	6.16	1.22	4.02
CN	1.8996	2042	1.1718	1.17	1.138	8.98	2.276	4.39	3.414	2.93	6.11	1.64	15.8
CO	1.9313	2184	1.1281	1.12	1.158	8.62	2.316	4.32	3.474	2.88	6.55	1.53	19.4
HCl	10.5909	2885	1.2746	1.27	6.35	1.57	13.7	0.73	20.05	0.499	8.64	1.16	7.8
CS	0.8205	1272	1.534	1.45	0.492	20.3	0.984	10.2	1.476	6.78	3.81	2.62	9.16
HBr	8.473	2559.25	1.413	1.41	5.06	1.96	10.16	0.984	15.24	0.656	7.67	1.30	3.82

TABLE II SOME CALCULATED MOLECULAR CONSTANTS

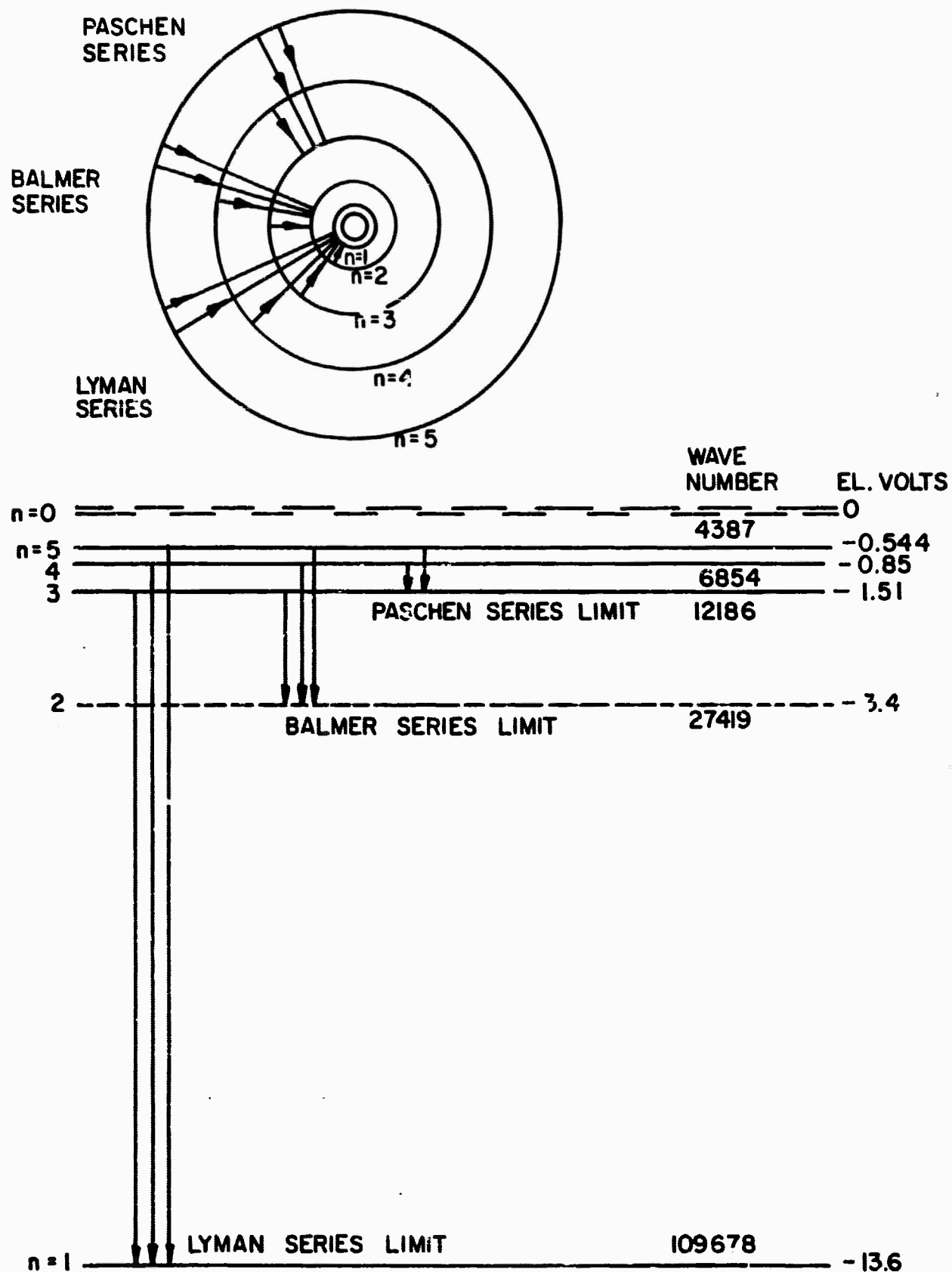
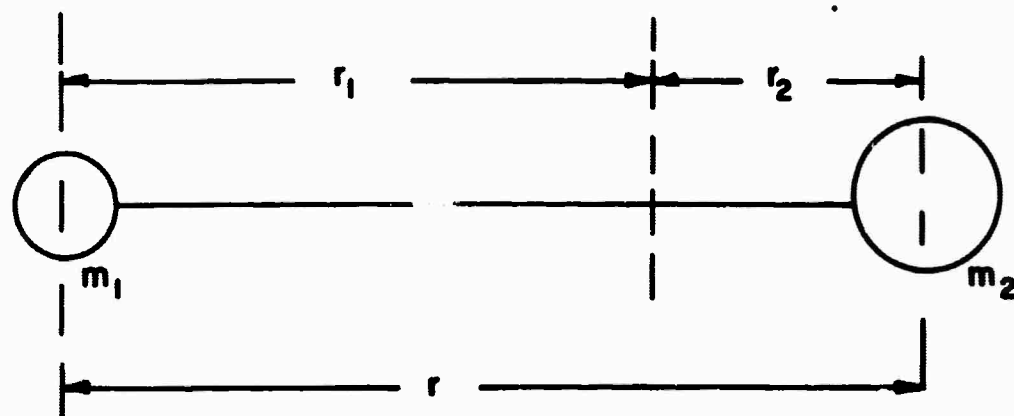


FIG. 1 THE BOHR ORBITS OF HYDROGEN AND ENERGY LEVEL REPRESENTATIONS OF THE TRANSITIONS PRODUCING THE LYMAN, BALMER AND PASCHEN SERIES



$$E_{\text{ROT}} = \frac{1}{2} I \omega^2 \quad \omega = 2 \pi \nu_{\text{ROT}}$$

$$I = \sum m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2$$

$$r_1 = \frac{m_2}{m_1 + m_2} r$$

$$r_2 = \frac{m_1}{m_1 + m_2} r$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$I = \mu r^2$$

FIG. 2 THE DUMBELL MODEL OF THE RIGID ROTATOR

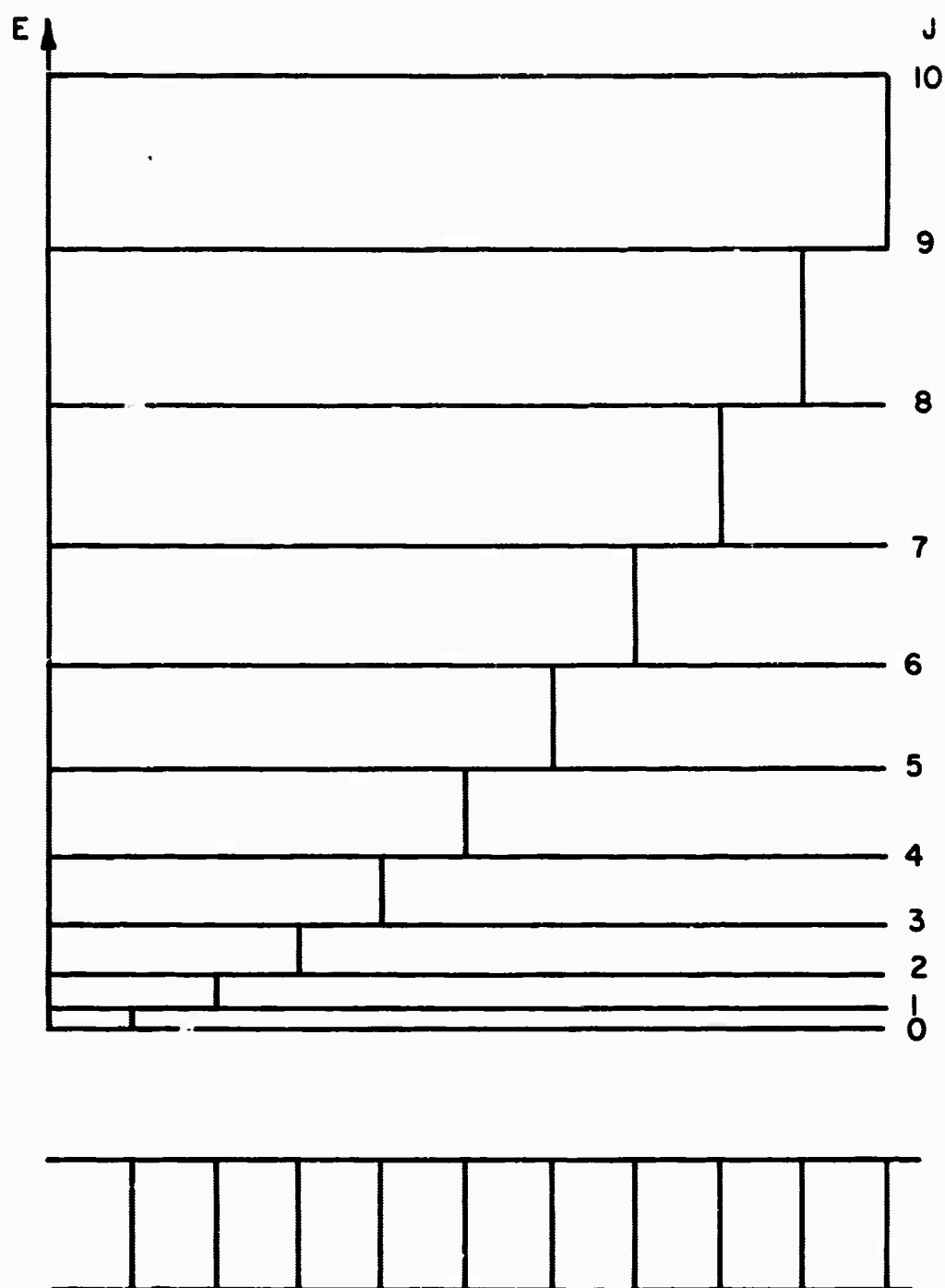


FIG.3 SCHEMATIC OF THE ENERGY LEVEL OF A RIGID ROTATOR AND THE RESULTING EQUIDISTANT LINE SPECTRUM

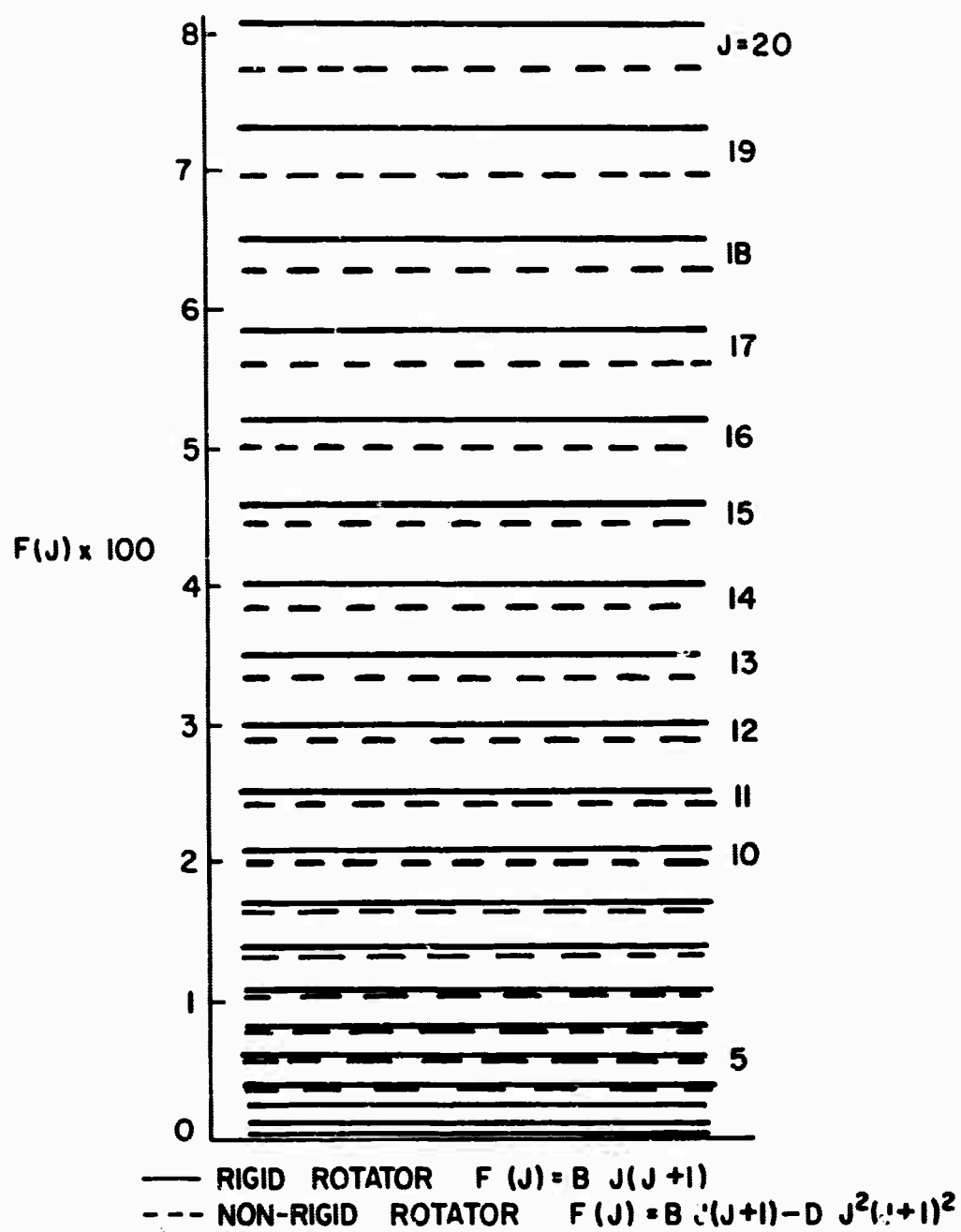


FIG.4 ENERGY LEVEL DIAGRAM OF A RIGID AND NON-RIGID ROTATOR

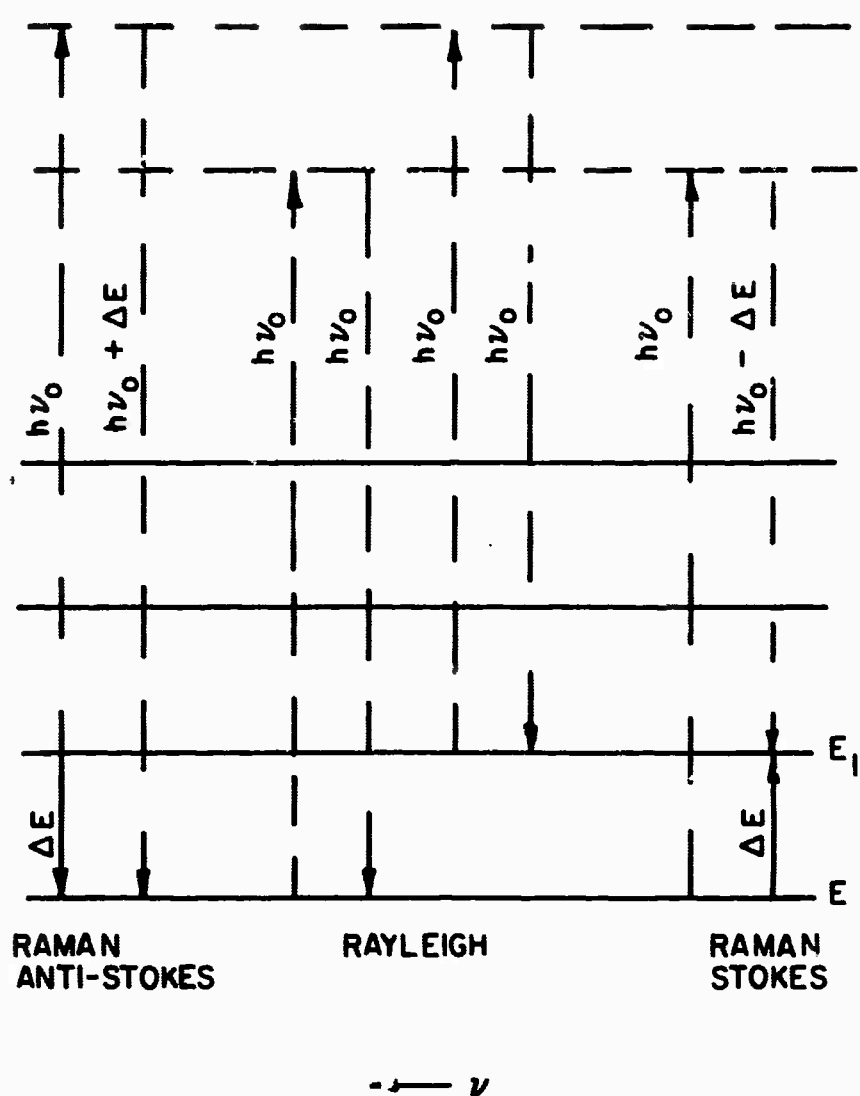


FIG. 5 ENERGY LEVEL DIAGRAM FOR THE RAMAN AND RAYLEIGH TRANSITIONS

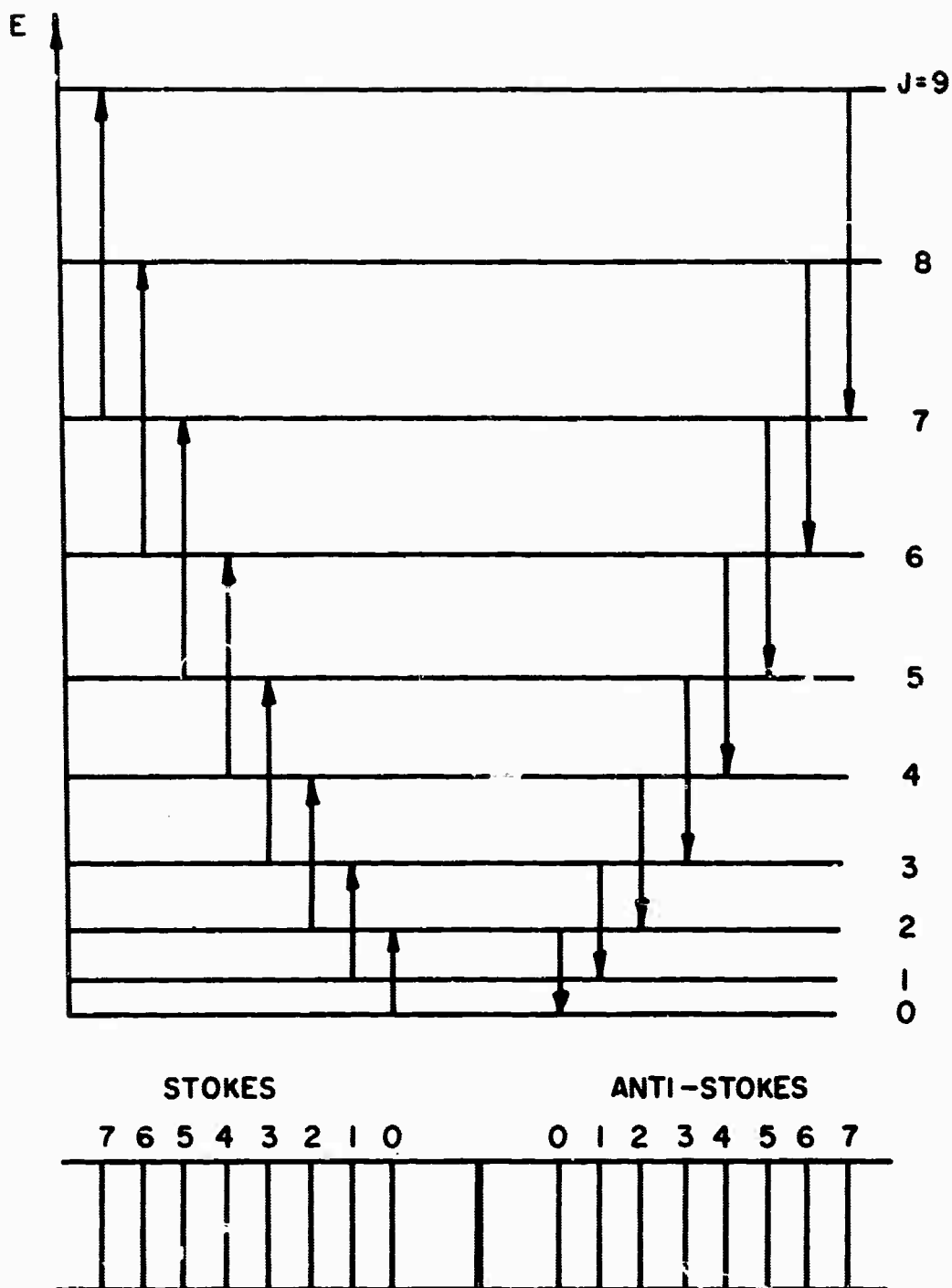


FIG. 6 SCHEMATIC OF THE ENERGY LEVEL OF A RIGID ROTATOR AND THE RESULTING EQUIDISTANT RAMAN LINE SPECTRUM

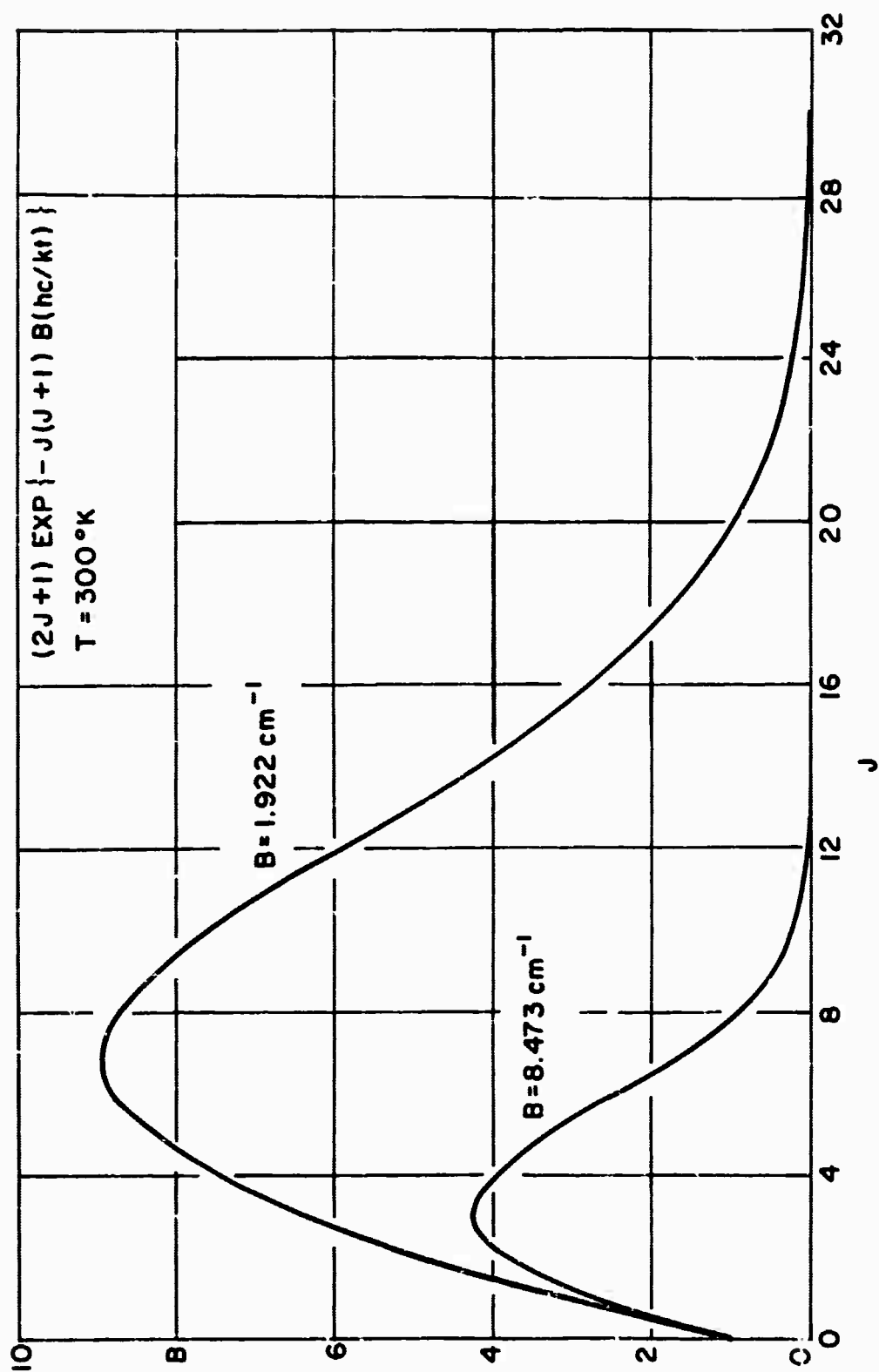


FIG. 7 NUMBER OF MOLECULES N_J IN THE ROTATIONAL LEVEL J OF THE LOWER VIBRATIONAL STATE

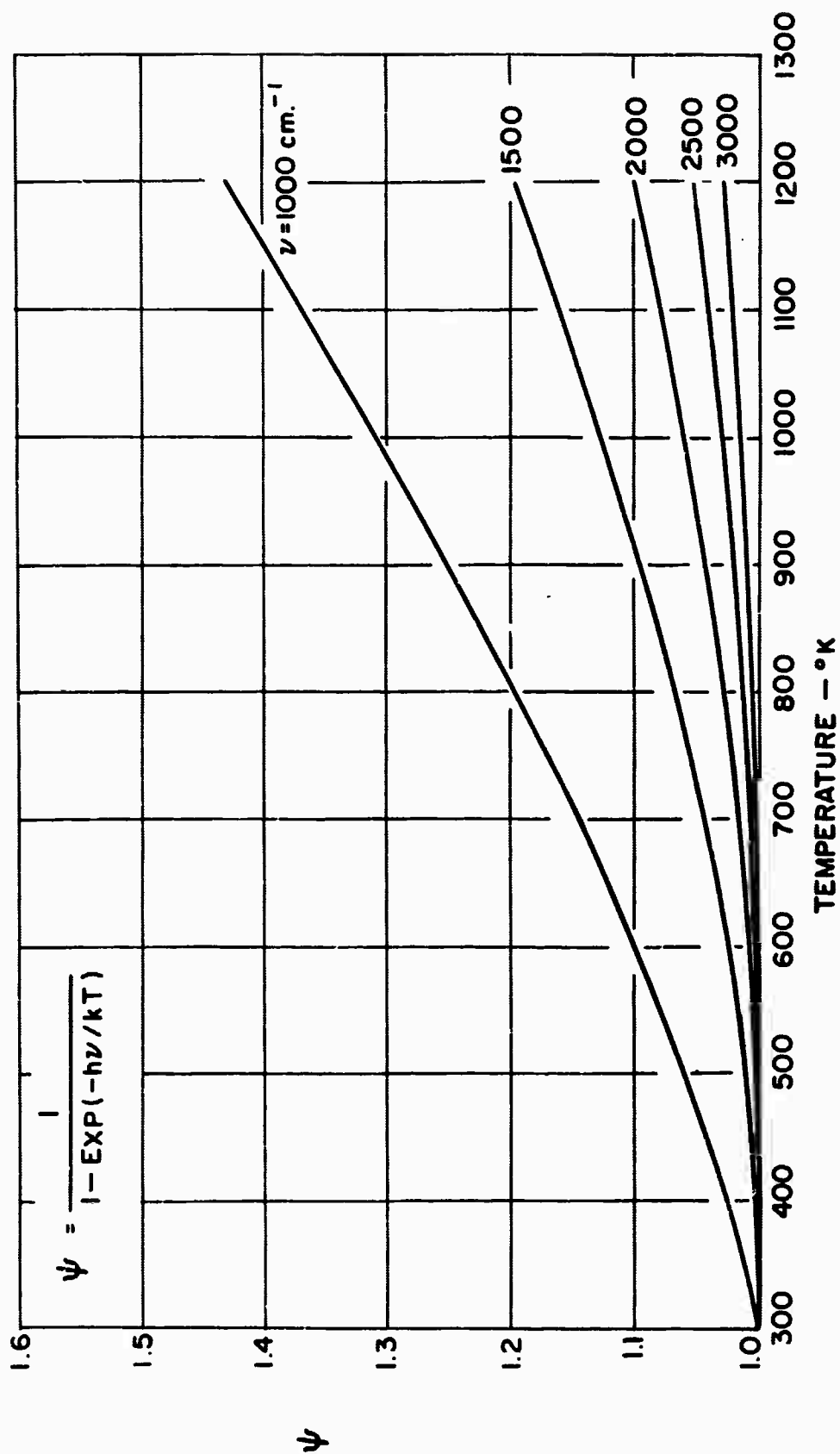


FIG. 8a TEMPERATURE DEPENDENCE OF THE RAMAN INTENSITY.
RAMAN FREQUENCY SHIFT AS A PARAMETER

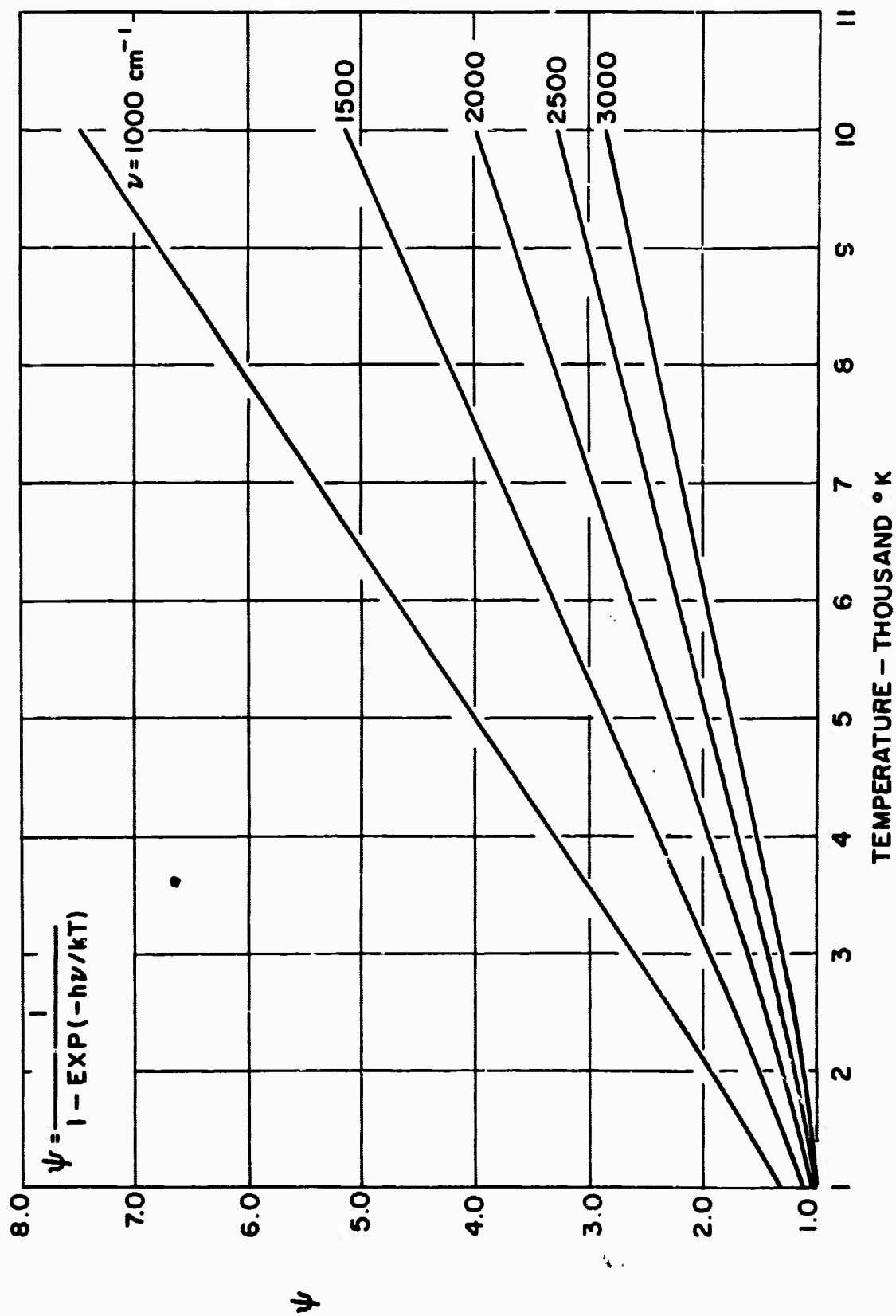


FIG. 8b TEMPERATURE DEPENDENCE OF THE RAMAN INTENSITY. RAMAN FREQUENCY SHIFT AS A PARAMETER

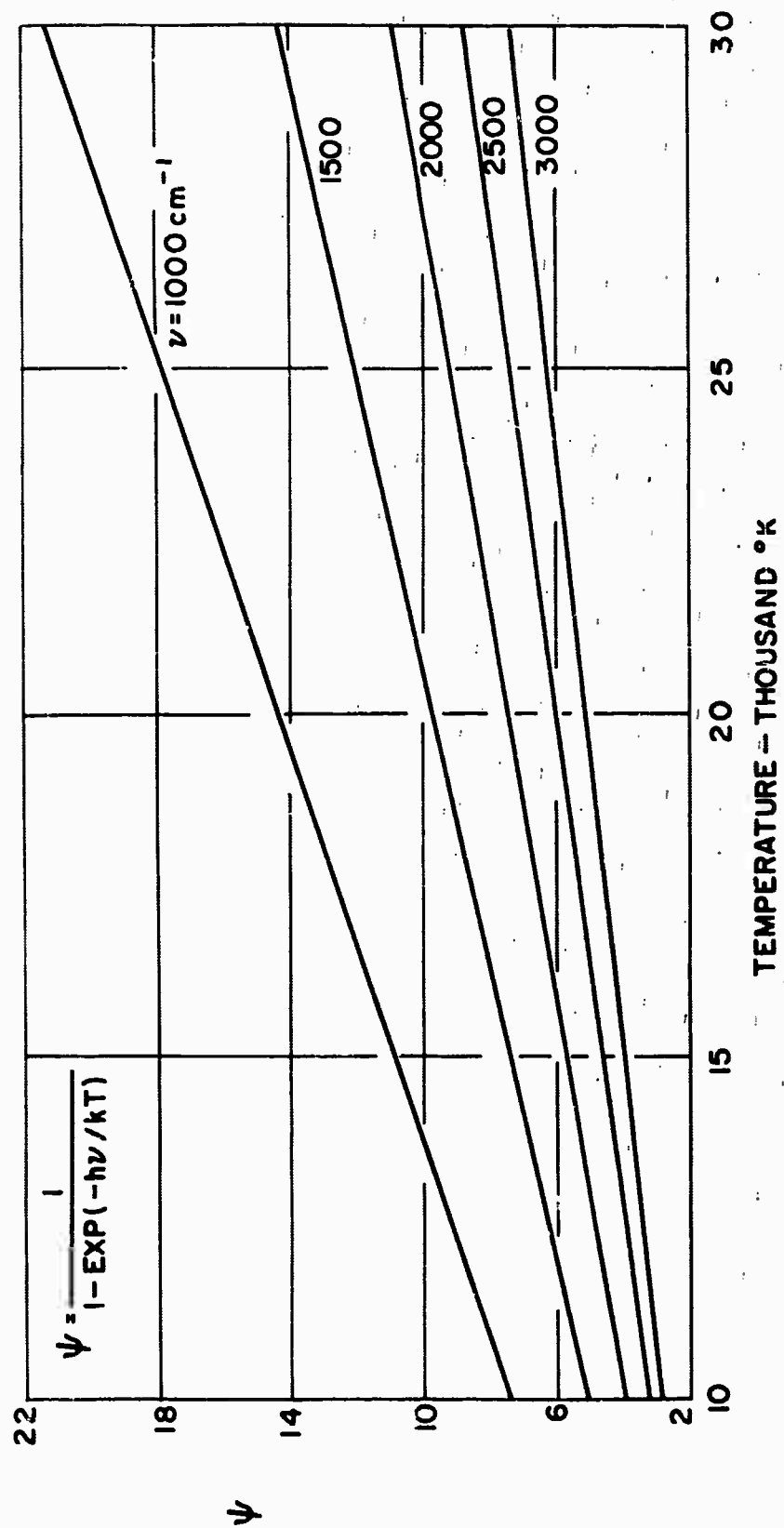


FIG. 8c TEMPERATURE DEPENDENCE OF THE RAMAN INTENSITY.
RAMAN FREQUENCY SHIFT AS A PARAMETER

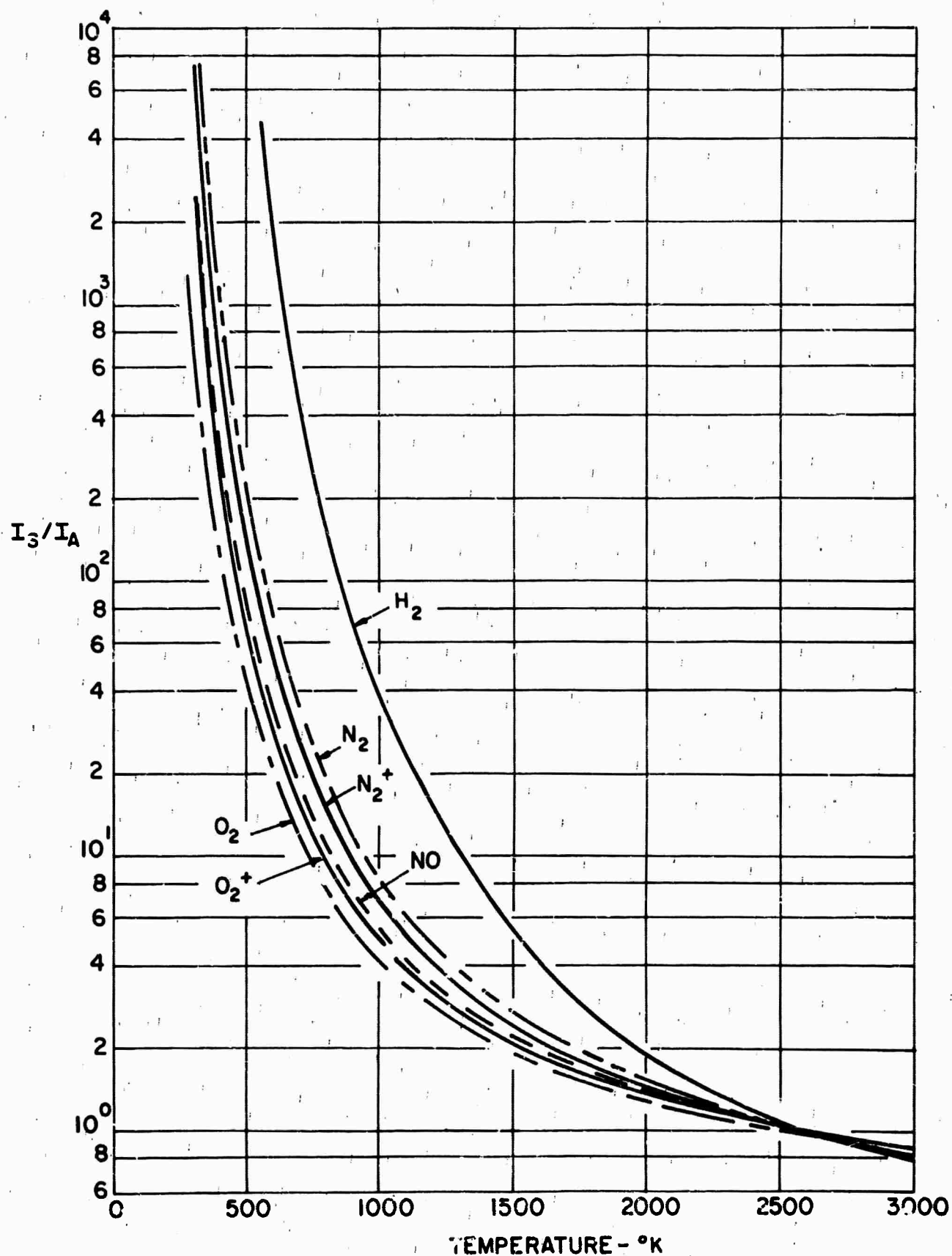


FIG.9 RATIO OF THE STOKES TO ANTI-STOKES INTENSITY AS A FUNCTION OF GAS TEMPERATURE

AD-728164

September 1, 1971

POLYTECHNIC INSTITUTE OF BROOKLYN
Department of Aerospace Engineering
and Applied Mechanics

ERRATA

MOLECULAR SPECTRA AND THE RAMAN EFFECT
A SHORT REVIEW

by

Samuel Lederman

PIBAL Report No. 71-15
June 1971

Page 7, Eq. (17): ν^3 should read ν_{nm}^3

" 12, Eq. (27): C should be replaced with c

" 13, Eq. (35) should read: $G(\nu) = \omega_e(\nu + \frac{1}{2}) - \omega_e x(\nu + \frac{1}{2})^2 + \omega_e y_e(\nu + \frac{1}{2})^3 + \dots$

" 16, Eq. (47): $-\omega_e''(\nu + \frac{1}{2})$] should read $-\omega_e''(\nu'' + \frac{1}{2})$]

" 19, Eqs. (49) and (51): $\Delta\nu$ should read $|\Delta\nu|$

" 24, Eq. (61): $N_J(2J+1)$ should read $N_J \sim (2J+1)$

" 26, Eq. (69): $I_{abs} = \frac{I_o 8\pi^3 \nu N}{3hc r}$ should read $I_{abs} = \frac{I_o 8\pi^3 \nu N}{3hc Q_r}$

" 28, Eq. (76) should read: $I = \frac{2^7 \pi^5}{135} k_j N b_j^2 d_j \frac{(45\alpha'^2 + 7X\gamma'^2)}{R^3} I_o$