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HIGH INTENSITY LASER PROPAGATION IN THE ATMOSPHERE

FINAL REPORT

1 NOVEMBER 1965 - 28 FEBRUARY 1967

Prepared under
Contract N00014-66-C0022
for
OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
Washington, D. C.

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Subject: Contract N00014-66-C0022
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HIGH INTENSITY LASER PROPAGATION IN THE ATMOSPHERE

Final Report
1 November 1965 - 28 February 1967

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TABLE OF CONTENTS

INTRODUCTION AND SUMMARY

This report is concerned with phenomena which may limit the transmission of a laser beam through the atmosphere. We have considered two salient types of limitations and the specific contributing processes. The first limitation corresponds to a self-defocusing instability of the laser beam which can result in an undesirable decrease in the delivered power density. The instability results from photon absorption leading to atmospheric heating and consequently to a local decrease in the refractive index; the result is a lens effect which causes the beam to diverge. The second limitation to beam transmission is imposed by the stimulated Raman effect. This process involves inelastic photon scattering, and at sufficiently large power levels results in the amplification of the beam of scattered photons in a laser-like fashion. The amplification of the scattered photon beam can produce a serious depletion of the laser beam.

Chapters 1, 2, and 3 are concerned with the heating mechanisms that lead to the self-defocusing instability. In Chapter 1 the far wings of pressure-broadened molecular absorption lines are studied. The motivation is the need for a reliable theory to compensate for the absence of experimental data. The distance from the line center beyond which the usual pressure-broadening theory becomes invalid has been ascertained, and it has been found that beyond this point the line profile falls exponentially. This conclusion has particular significance with regard to an earlier calculation of the absorption in the window at 1.0468 microns, where the assumption of Lorentzian line shapes led to the conclusion that the absorption coefficient was just at the threshold for the self-defocusing instability. In the aforementioned calculation it was assumed that the absroption is due only to the molecular resonance lines. The present research indicates that because of the exponential fall-off, the absorption due to the molecular resonance lines is actually substantially smaller, and consequently may be ignored with respect to the self-defocusing instability at 1.0468 microns. However, it has been pointed out that atmospheric absorption in the spectral neighborhood of 1.0468 microns is actually dominated, not by contributions from the wings of molecular resonance lines, but by a continuous absorption band due to the existence of $(O_2)_2$ complexes. Earlier inferences from experimental data indicated that the absorption coefficient due to $(O_2)_2$

is about two orders of magnitude above the threshold for the self-defocusing effect. In Chapter 2 we report the results of a detailed study of the photon absorption mechanism of the $(O_2)_2$ complex itself and the relaxation mechanisms by which the absorbed energy is subsequently converted into heat. It is concluded that, during a laser pulse of about one millisecond duration, only one-sixth of the absorbed photon energy is converted into heat so that the estimate of the effective absorption coefficient for $(O_2)_2$ at 1.0468 microns must be reduced by a factor of six. Moreover, the study suggests that the desired additional reduction in the net absorption coefficient can be accomplished by a shift to slightly higher frequencies, i.e., somewhere in the region 1.030 to 1.037 microns.

Another process which contributes to the residual absorption in what is otherwise considered to be a transmission window is collision-induced absorption. This is a phenomenon in which absorption takes place by virtue of a transient dipole moment which exists only during an intermolecular collision. It is characterized spectrally by broad continuous bands having widths of the order of several hundred wave numbers. These bands are superposed upon internal transition lines which may even be forbidden for the isolated molecule.

The energy of the absorbed photon is partitioned into an internal excitation of one of the molecules and kinetic energy of the colliding pair. The energy taken up by the translational component corresponds to an instantaneous heating, which contributes to the beam instability regardless of the laser pulse duration. The translational band contributes to the magnitude of the absorption in a valley between resonance lines, and may dominate over the far wing contributions of resonance lines.

In Chapter 3 we consider the photon absorption which occurs during a collision between two rare gas atoms. The analysis is somewhat simplified in this case because of the absence of rotational and vibrational modes; the absorbed energy goes entirely into translational energy of the atoms. Theoretical work in this field has been meager and has been principally confined to the calculation of frequency integrated absorption coefficients. Relatively little has been done regarding the frequency dependence of the collision induced absorption coefficient and even this work is quite recent. The studies which have been made were not concerned with the far wings and cannot be extrapolated into the far wing regions with confidence; the present chapter contains a discussion of these calculations.

We have performed a quantum mechanical analysis of this problem which is capable of yielding the absorption coefficient as a function of frequency even in the far wings of the absorption band, where no experimental determination has as yet been possible. It is these unmeasurable, far wing absorptions which extend into the atmospheric windows, and provide instantaneous heating. They must be determined theoretically in order to evaluate the self-defocusing heating instability. The mathematical analysis leading to the expression for the absorption coefficient has been completed, and only a number of independent numerical integrations remain to be performed. Preparations are currently in progress for evaluation by digital computer.

In Chapter 4 laser beam depletion by stimulated Raman scattering is investigated by solving rate equations describing this process. The particular effects which are analyzed in great detail are (a) the interaction of competing Raman lines, (b) multiple order Stokes wave generation, (c) the amplification of Raman backscattered light, and (d) the effect of pressure dependence upon the propagation of a beam vertically through the atmosphere. In each of the above the intensities of both the Raman radiation and primary laser beam are obtained as a function of distance from the laser.

It is found that the maximum intensity of laser light which can be transmitted vertically through the atmosphere without frequency change due to Raman scattering is critically sensitive to the laser line width. The maximum intensity is calculated for representative values of the laser line width and other pertinent parameters. Another conclusion is that the amplified backscattered beam has a significant deleterious effect if the magnitude of the backscattered cross section is greater than ninety-two percent of the forward cross section, and the laser pulse duration is greater than 5×10^{-5} seconds. If either of these conditions fails to prevail, then Raman backscattering is inconsequential as a loss mechanism.

An analysis is reported which describes the propagation of a pulse of radiation moving through and antiparallel to the laser beam. The frequency of the backward propagating pulse is that which corresponds to the Stokes shifted frequency. It is found that this pulse may be amplified at the expense of the laser beam to a peak intensity many times greater than that of the laser beam itself, and that in fact most of the energy in the laser beam can be concentrated into this backward moving pulse.

Chapter 1.

FAR WING PRESSURE BROADENING

In this chapter, some model-type studies on the far wing pressure broadening of molecular vibrational lines will be reported. The most elementary system of interest is that of a diatomic heteropolar molecule in collision with a monatomic perturber. For the sake of definiteness, the optical transition will be assumed to connect the vibrational state with the first excited (vibrational) state of the diatomic molecule $(0 \leftrightarrow 1)$.

The physical picture motivating the treatment derives from earlier work[1] by one of the present authors; it may be described briefly as follows. When the optical frequency, ω, is sufficiently close to the unperturbed transition frequency, ω_o — specifically when $(\omega-\omega_o)\tau_c < 1$, with τ_c an appropriately defined collision time, one may expect the impact theory to be valid; the line shape will therefore correspond to the wing of a Lorentz-type line shape $(\sim\gamma_p/(\omega-\omega_o)^2)$. If, on the other hand, the frequency shift $(\omega-\omega_o)$ is so large that $(\omega-\omega_o)\tau_c > 1$, the spectral profile will follow the predictions of the so-called statistical theory. In this theory, one focuses attention on the collision-induced perturbation of the instantaneous transition frequency. Two possibilities then arise. If during a collision event, the perturbed transition frequency, $\omega_o+\omega_p$, momentarily coincides with the optical frequency, ω, the spectral intensity, $I(\omega)$, will be proportional to the occurrence probability of the perturbed transition frequency — i.e., the probability that $\omega_o+\omega_p$ lie within a unit differential frequency range about the spectral frequency, ω. If, on the other hand, there are no collisions which are able to provide a coincidence of $\omega_o+\omega_p$ with ω, one may expect the spectral intensity, $I(\omega)$, to decrease exponentially[2] with increasing frequency shift, $\omega-\omega_o$.

The particular problem upon which the present studies are focused is the absorption on the violet side of a given vibrational line, at distances of the order of[3] 600-1000 cm^{-1} from the unperturbed frequency. (The corresponding shift in units of circular frequency is $\omega-\omega_o \sim 1.2\text{x}10^{14} - 2\text{x}10^{14}\text{sec}^{-1}$.) From the above discussion it then becomes clear that the absorption at such extreme distances from the unperturbed line will be exponentially small unless (a) the collision time is $\lesssim 10^{-14}\text{sec}^{-1}$ -- with atomic velocities $\sim 10^5\text{cm/sec}$, such a limitation could be met only with very short range interactions $(\sim 10^{-9}\text{cm})$ and/or (b) the collision-induced shift in the momentary vibrational frequency is positive and $\gtrsim$ 600-1000 cm^{-1}. Whether or not such extreme conditions can be met, one may infer that they will be approached most closely by the standard short-range repulsive interatomic interactions generally taken to have the form[4]

$$V(r) = V_o \ell^{-\alpha r} , \tag{1.1}$$

rather than the longer range, multipole-type interactions of the form, C/r^n (with n a number varying roughly from 3 → 6). It is therefore proposed to consider the basic interaction responsible for the far-wing absorption to be a sum of two terms, each of the form (1.1) — describing the interaction between the colliding atom and each of the two atomic constituents of the absorbing molecule. Moreover, in order to avoid complications which — in the opinion of the present authors — do not appear to be essential for the physics of the problem, the following further "model-type" simplifications are introduced:

(1) the rotational motion of the molecule is ignored, and
(2) the collision is assumed to be collinear.

Concerning the first simplification, it may be remarked that, on the scale of the above mentioned frequency shift (600 - 1000 cm^{-1}), rotational frequencies are quite small,[5] so that (a) there is certainly no question of the existence of any rotational component of the line in the far-wing spectral region of interest and (b), in considering the partition of the excess energy into translational and rotational motion, it would seem quite legitimate to ignore the discrete structure of rotational energy levels.[6] Once this is done, rotation and translation may both be considered as comparable types of essentially unquantized motion.[7] For a detailed quantitative calculation, both, of course, must be taken into account. For a semiquantitative study which, like the present one, is aimed at a first look at the gross features of the far-wing broadening problem, it is felt that a model-type treatment which takes explicit account of energy conversion into one type of unquantized motion, namely translation, while ignoring the rotational component, is basically adequate.

The assumption of collinear collisions is introduced because it is susceptible to a relatively straight-forward analysis. It is hoped that the insight gained in studying this special case will permit at least semiquantitative extensions to the more general case.

It may finally be stated that both of the above discussed simplifications are contained in essentially all treatments of the related problem of collision-induced vibrational deactivation of diatomic molecules.[8]

With these preliminary considerations out of the way, let us proceed to the formulation of the model Hamiltonian of the problem. In the absence of the external (optical) electromagnetic field it takes the form

$$H = \frac{P_X^2}{2\mu_v} + \frac{1}{2}\mu_v\omega_o^2 X^2 + \frac{P_R^2}{2M} + V(R,X) \ . \tag{1.2}$$

In this expression $X \equiv r - r_e$ (with r the internuclear separation and r_e its equilibrium value) is the vibrational coordinate, $P_X \equiv \frac{\hbar}{i}\frac{\partial}{\partial X}$ the associated canonical momentum, $\mu_v \equiv \frac{M_A M_B}{M_A+M_B}$ the reduced mass for vibrational motion (letters A and B will be used to designate quantities associated with the constituent atoms of the diatomic molecule, whereas the letter C will refer to the colliding monatomic species), R denotes the distance between the center of gravity of the molecule and the colliding atom (C), $P_R \equiv \frac{\hbar}{i}\frac{\partial}{\partial R}$ is the associated canonical momentum (with $M \equiv \frac{(M_A+M_B)M_C}{M_A+M_B+M_C}$ the reduced mass for the relative motion of atom C with respect to the center of gravity of the molecule). The first two terms in (1.2) are the kinetic and potential energy for vibrational motion of the molecule (ω_o = vibrational frequency). The third term is the kinetic energy for the relative motion of the colliding partners. Finally, V(R,X) is the interaction between the colliding atom C and the molecule. It is here assumed to have the form

$$V(R,X) = V_o \exp\{-\alpha[R-\lambda r]\} = V_o \exp\{-\alpha[R-\lambda(r_e+X)]\} \ , \tag{1.3}$$

where

$$\lambda \equiv \frac{M_A}{M_A+M_B} \ . \tag{1.4}$$

Expression (1.3) follows from (1.1) and the fact that, in a collinear collision, the interaction of colliding atom C with only one atom of the molecule (say, B) need be considered (cf numerical estimate of α given in Ref. 4 and the tables of values of r_e in Herzberg's book[5]).

The presence of the optical electromagnetic field gives rise to an additional term in the Hamiltonian. It has the form

$$H_{em} = -\mu(X)\, \mathcal{E} e^{-i\omega t} + C\cdot C , \tag{1.5}$$

in which $\mathcal{E}$ is the amplitude of the electromagnetic field of the incident light and $\mu(X)$ is that part of the molecular dipole moment which depends upon the vibrational coordinate, X; as is usual, it will be assumed that this dependence is linear, so that the optical selection rule for the change in vibrational quantum number $\Delta v = \pm 1$.

In the absence of the electromagnetic perturbation, represented by (1.5), there exist stationary solutions, $\psi_i(X,R)$ of the time-independent Schroedinger equation

$$H\, \psi_i(X,R) = E_i \psi_i(X,R) , \tag{1.6}$$

which are asymptotically ($R \to \infty$) of the form

$$\psi_i(X,R) \to \phi_o(X) \sin(k_i R + \delta) , \tag{1.7}$$

where $\phi_o(X)$ is the ground state Harmonic oscillator wave function and $k_i \equiv \sqrt{2ME_i/\hbar^2}$ is the incident wave vector of relative motion. In what follows, $\psi(X,R)$ will be approximated by a product function

$$\psi_i(X,R) \approx \phi_o(X)\, \psi_o(R) , \tag{1.8}$$

where $\psi_o(R)$ is that solution of the equation

$$E_i \psi_o(R) = \left[\frac{P_R^2}{2M} + V_{oo}(R)\right] \psi_o(R) , \tag{1.9}$$

$$V_{oo}(R) \equiv \int \phi_o^2(X)\, V(R,X)\, dX , \tag{1.10}$$

which obeys (1.7).[9]

In the presence of the electromagnetic field, the wave function of the system will be augmented by a term, $\psi_1(X,R)$, which may be computed from first-order time-dependent perturbation theory. The relevant equation is[10]

$$i\hbar\frac{\partial\psi_1}{\partial t} - H\psi_1 = H_{em}\,\psi_i(X,R)\,\exp\{-(it/\hbar)(E_i + \hbar\omega_o/2)\}, \tag{1.11}$$

with H_{em} given by (1.5). The steady-state solutions of (1.11) will consist of two terms, $\psi^{(+)}$ and $\psi^{(-)}$ with time-dependences of the form $\exp\{-(it/\hbar)(E_i + \hbar\omega_o/2 + \hbar\omega)\}$ and $\{-(it/\hbar)(E_i + \hbar\omega_o/2 - \hbar\omega)\}$ respectively; of these, only the former (describing the absorption of a photon of energy $\hbar\omega$ is of interest). The equation determining this term is

$$\left(E_i + \frac{\hbar\omega_o}{2} + \hbar\omega - H\right)\psi^{(+)} = -\mu(X)\mathcal{E}\psi_i(X,R). \tag{1.12}$$

At this point, a considerable simplification can be achieved by resorting to the (already employed) distorted-wave approximation. This may be done as follows. Substituting the expansion

$$\psi^{(+)} = \sum_m \chi_m^{(+)}\phi_m(X) \ , \tag{1.13}$$

(where the $\phi_n(X)$ are the eigenstates of the vibrational part, $H_{vib} = \frac{P_X^2}{2\mu} + \frac{1}{2}\mu_v\omega_o^2X^2$, with eigenvalues $\hbar\omega_o\left(n + \frac{1}{2}\right)$) multiplying on the left by $\phi_n(X)$, and integrating with respect to X, one has [upon using (1.2) and (1.8)]

$$\left(E_i + \hbar\omega - n\hbar\omega_o - \frac{P_R^2}{2M} - V_{nn}(R)\right)\chi_n^{(+)}(R) + \sum_{m\neq n} V_{nm}(R)\chi_m^{(+)}(R) = -\mathcal{E}\mu_{no}\psi_o(R), \tag{1.14}$$

where

$$\mu_{nm} \equiv \int \phi_n(X)\mu(X)\phi_n(X)\,dX \ , \tag{1.15}$$

$$V_{nm}(R) \equiv \int \phi_n(X)V(R,X)\phi_m(X)\,dX \ . \tag{1.16}$$

The distorted-wave approximation consists in ignoring the sum on the l.h.s. of (1.14), (i.e., terms containing the coefficients V_{nm}, with $m \neq n$). One then has, in place of (1.14)

$$\left[E_i + \hbar(\omega-\omega_o) - \frac{P_R^2}{2M} - V_{11}(R)\right]\chi_1^{(+)}(R) = -\mathcal{E}\mu_{10}\psi_o(R) , \qquad (1.17)$$

since, with $\mu(X)$ assumed to be linear in X, μ_{no} differs from zero only for $n = 1$.

It is now convenient to write $\chi_1^{(+)}(R)$ in the form

$$\chi_1^{(+)}(R) = -\frac{\mathcal{E}\mu_{10}\psi_o(R)}{\hbar(\omega-\omega_o)} + \chi_{sc}(R) ; \qquad (1.18)$$

upon substituting (1.18) into (1.17) and making use of (1.9), one obtains for $\psi_{sc}(R)$ the equation

$$\left[E_i + \hbar(\omega-\omega_o) - \frac{P_R^2}{2M} - V_{11}(R)\right]\chi_{sc}(R) = \frac{\left[V_{11}(R)-V_{oo}(R)\right]}{h(\omega-\omega_o)}\mathcal{E}\mu_{10}\psi_o(R). \qquad (1.19)$$

Before proceeding further, some comments on the physical significance of the two terms on the r.h.s. of (1.18) are in order. Briefly, it is claimed that the second term, $\chi_{sc}(R)$, represents the amplitude of the process under study here — namely, the energy-conserving process whereby a quantum of energy, $\hbar\omega$, is absorbed, with a final translational energy (of relative motion), $E_f = E_i + \hbar(\omega-\omega_o)$ (as shown by the form of the l.h.s. of (1.19)). By way of contrast, the first term on the r.h.s. of (1.18) represents the virtual absorption of a quantum (in a 0 → 1 vibrational transition); in particular, from (1.8) one sees that, since the R dependence is contained entirely in the factor $\psi_o(R)$, the kinetic energy associated with this state is the initial E_i [rather than $E_f = E_i + \hbar(\omega-\omega_o)$]. The virtual character of the transition described by the first term of (1.18) is thus manifest; it will therefore be discarded without further ado.

From a "technical" standpoint, it may be remarked that Eq. (1.19) for $\chi_{sc}(R)$ is rather more suitable for scattering studies than the corresponding

Eq. (1.17) for $\chi_1^{(+)}(R)$. The reason is, basically, that, in contrast to (1.17), the driving term of (1.18) contains the factor $\left[V_{11}(R) - V_{oo}(R)\right]$, which differs from zero only in the immediate neighborhood of the collision region ($R \sim$ interatomic distance). Outside this region, $\chi_{sc}(R)$ satisfies the homogeneous wave equation; the usual boundary condition of scattering theory — namely, that as $R \rightarrow \infty$, $\chi_{sc}(R)$ takes the form of an outgoing wave $\left(\sim \ell^{ik_f R}\right)$ is then straightforwardly applied, as will now be done.

One multiplies both sides of (1.19) by that solution, $\psi_1(R)$, of the homogeneous equation:

$$\left[E_f - \frac{P_R^2}{2M} - V_{11}(R)\right]\psi_1(R) = 0 \, , \tag{1.20}$$

which has the asymptotic form

$$\psi_1(R) \xrightarrow{R \rightarrow \infty} \sin\left[k_f R + \delta\right] \, , \tag{1.21}$$

and integrates from zero to R. Performing the approximate integrations by parts, and using (1.20), one readily obtains $\left(\text{with } P_R^2 \equiv -\hbar^2 \partial^2/\partial R^2\right)$

$$\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)} \int_o^R \psi_1(R')\left[V_{11}(R') - V_{oo}(R')\right] \psi_o(R')dR' = \frac{\hbar^2}{2M}\left[\chi_{sc}(R) \frac{d\psi_1(R)}{dl} - \psi_1(R)\frac{d}{dR} \chi_{sc}(R)\right] . \tag{1.22}$$

For sufficient large R, the upper integration-limit on the l.h.s. of (1.21) may be replaced by infinity; at the same time, one may introduce (1.21) and the asymptotic expression

$$\chi_{sc}(R) \xrightarrow{R \rightarrow \infty} A_{sc}\ell^{ik_f R} \, , \tag{1.23}$$

into (1.22). This procedure yields an explicit expression for the scattering amplitude, A_{sc}, viz:

$$A_{sc} = \frac{2M}{\hbar^2 k_f} \frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)} \int_o^\infty \psi_1(R) \left[V_{11}(R)-V_{oo}(R)\right] \psi_o(R)\, dR. \qquad (1.24)$$

The outgoing particle flux is given by the relation

$$I_{out} = v_f |A_{sc}|^2 = \frac{\hbar k_f}{M} |A_{sc}|^2 . \qquad (1.25)$$

Introducing (1.24) into (1.25) and dividing by the incident flux,

$$I_{in} = v_i/4 = \hbar k_i/4M , \qquad (1.26)$$

one obtains a quantity

$$P_{10} = \frac{4k_f}{k_i} \frac{4M^2}{\hbar^4 k_f^2} \frac{\mathcal{E}^2 \mu_{10}^2}{\hbar^2(\omega-\omega_o)^2} \left| \int_o^\infty \psi_1(R)\psi_o(R)\left[V_{11}(R)-V_{oo}(R)\right] dR \right|^2 , \qquad (1.27)$$

which may be regarded as the probability that, in a collision of the special type under consideration — namely, a collinear collision — a (0 → 1) vibrational transition occurs (with, of course, simultaneous absorption of a quantum, $\hbar\omega$, of electromagnetic energy).

In order to proceed further, it is desirable to write down explicit expressions for $V_{11}(R)$ and $V_{oo}(R)$. From (1.3), one has

$$V_{oo}(R) = V_i e^{-\alpha R} , \qquad (1.28a)$$

$$V_{11}(R) = V_f e^{-\alpha R} , \qquad (1.28b)$$

where

$$V_i = V_o \exp(\alpha\lambda\gamma_e) \int_{-\infty}^{+\infty} \phi_o^2(x)\, e^{\alpha\lambda x}\, dx \;, \tag{1.29a}$$

and[11]

$$V_f \equiv V_o \exp(\alpha\lambda\gamma_e) \int_{-\infty}^{+\infty} \phi_1^2(x)\, e^{\alpha\lambda x}\, dx \;. \tag{1.29b}$$

One now inserts (1.28a) and (1.28b) into (1.19) and (1.20) respectively, obtaining

$$\frac{d^2\psi_o}{dR^2} + \left(k_i^2 - b_i^2\, e^{-\alpha R}\right)\psi_o = 0 \;, \tag{1.30a}$$

$$\frac{d^2\psi_1}{dR^2} + \left(k_f^2 - b_f^2\, e^{-\alpha R}\right)\psi_1 = 0 \;, \tag{1.30b}$$

where

$$b_{i,f} \equiv \frac{2M}{\hbar^2} V_{i,f} \,. \tag{1.30c}$$

These equations are both of the form

$$\frac{d^2\psi}{dR^2} + \left(k^2 - b^2\, e^{-\psi R}\right)\psi = 0 \,, \tag{1.31}$$

which, via the introduction of a new independent variable

$$\xi \equiv (2b/\alpha)\, e^{-\alpha R/2} \,, \tag{1.32}$$

becomes

$$\frac{d^2\psi}{d\xi^2} + \frac{1}{\xi}\frac{d\psi}{d\xi} + \left(\frac{\psi k^2}{\alpha^2\xi^2} - 1\right)\psi = 0 \; ; \qquad (1.33)$$

this equation is to be supplemented by the boundary conditions

$$\psi \xrightarrow{\xi \to \infty} 0 \, , \qquad (1.34a)$$

$$\psi \xrightarrow{\xi \to 0} \sin\left(\frac{2k}{\alpha} \log \frac{2k}{\alpha\xi} + \delta\right) \, . \qquad (1.34b)$$

The required solution is

$$\psi = \left[(2k/\alpha\pi) \sinh 2\pi k/\alpha\right]^{1/2} K_{2ik/\alpha}(\xi) \, , \qquad (1.35)$$

where

$$K_\nu(\xi) \equiv \frac{\pi}{2} \, \frac{I_{-\nu}(\xi) - I_\nu(\xi)}{\sin \pi\nu} \, , \qquad (1.36)$$

is (in standard notation) the Bessel function of imaginary argument which obeys condition (1.34a). To see that (1.34b) is satisfied one notes that, from (1.36) and Eq. (2), section 3.7 (p.77) of Watson's treatise on Bessel functions,

$$K_{2ik/\alpha}(\xi) \xrightarrow{\xi \to 0} \frac{\pi}{2i \, \sinh\frac{2\pi k}{\alpha}} \left[\frac{(2/\xi)^{2ik/\alpha}}{\Gamma(1-2ik/\alpha)} - \frac{(2/\xi)^{-2ik/\alpha}}{\Gamma(1+2ik/\alpha)}\right]$$

$$= \left[\frac{\pi}{(2k/\alpha) \sinh 2\pi k/\alpha}\right]^{1/2} \sin\left[(2k/\alpha) \log(2/\xi) + \delta'\right] \, , \qquad (1.37)$$

the equality following from the standard formula

$$|\Gamma(1+iy)|^2 = \pi y/\sinh \pi y \, ,$$

[with $\delta' \equiv \arg \Gamma(1+iy)$]. From (1.37), it is clear that (1.35) satisfies (1.34b).

Eq. (1.35) is now utilized to provide explicit expressions for both $\psi_o(R)$ and $\psi_1(R)$ in Eq. (1.27); the result is

$$P_{10} = \left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)}\right]^2 \frac{(V_f-V_i)^2}{V_f V_i} (4/\pi^2) \sinh \frac{2\pi k_f}{\alpha} \sinh \frac{2\pi k_f}{\alpha} |\mathcal{X}|^2 , \tag{1.38}$$

where

$$\mathcal{X} = \beta \int_o^\infty K_{2ik_f/\alpha}(z) z K_{2ik_i/\alpha}(\beta z) dz , \tag{1.39}$$

with (cf (1.30c) and Ref. 11)

$$\beta^2 \equiv \frac{b_i^2}{b_f^2} = \frac{V_i}{V_f} = \frac{1+\alpha^2\lambda^2\hbar/\psi\mu_v\omega_o}{1+3\alpha^2\lambda^2\hbar/\psi\mu_v\omega_o} \tag{1.40}$$

It is indeed fortunate that the integral on the r.h.s. of (1.39) has been explicitly evaluated. Specifically, one has [cf *Tables of Integral Transforms*, Bateman Manuscript Project, Vol. I, p. 334, No. (47)].

$$\beta \int_o^\infty K_\mu(z) K_\nu(\beta z) z dz = \frac{1}{2} \left(\frac{\beta^{\nu+1}}{\Gamma(2)}\right) \Gamma\left(\frac{2+\mu+\nu}{2}\right) \Gamma\left(\frac{2-\mu+\nu}{2}\right) \Gamma\left(\frac{2+\mu-\nu}{2}\right) \Gamma\left(\frac{2-\mu-\nu}{2}\right)$$

$$\times {}_2F_1\left(\frac{\mu+\nu}{2} + 1, \frac{\nu-\mu}{2} + 1; 2; 1-\beta^2\right) , \tag{1.41}$$

where ${}_2F_1(a,b,c;z)$ is the hypergeometric function which, for $|z| < |$, is defined by the series

$${}_2F_1(a,b,c;z) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} \sum_{n=o}^\infty \frac{\Gamma(a+n)\Gamma(b+n)}{\Gamma(c+n)\ n!} z^n . \tag{1.42}$$

It possesses the integral representation (cf Handbook of Mathematical Functions, Applied Mathematics, Series 55, U.S. Department of Commerce, National Bureau of Standards, p.558, Eq. 15.3.1)

$$ {}_2F_1(a,b,c;z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^1 \frac{t^{b-1}(1-t)^{c-b-1}}{(1-tz)^a}\, dt \,, \qquad (1.43) $$

valid when

$$ Rc > Rb > 0 \,. \qquad (1.44) $$

In the case at hand

$$ a = \frac{\nu+\mu}{2} + 1 \,, \qquad (1.45a) $$

$$ b = \frac{\nu-\mu}{2} + 1 \,, \qquad (1.45b) $$

$$ c = 2 \,, \qquad (1.45c) $$

$$ z = 1-\beta^2 \,, \qquad (1.45d) $$

and one notes that [cf (1.39) and (1.41)] with μ and ν imaginary, (1.44) is obeyed. Substituting (1.43) and (1.45) into (1.41), one then has

$$ \beta\int K_\mu(z)K_\nu(\beta z)zdz = \frac{1}{2}\,\beta^{\nu+1}\Gamma\left(1+\frac{\nu+\mu}{2}\right)\Gamma\left(1-\frac{\mu+\nu}{2}\right) $$

$$ \times \int_0^1 \left(\frac{t}{1-t}\right)^{\frac{\nu-\mu}{2}} \frac{dt}{\left[1-t(1-\beta^2)\right]^{(\mu+\nu)/2\,+\,1}} \,, $$

which, by virtue of the relationship

$$ \Gamma(1+z)\Gamma(1-z) = z\pi/\sin \pi z \,, $$

may be written as

$$\beta \int K_{\mu}(z)K_{\nu}(\beta z)zdz = \frac{(\mu+\nu)\pi/2}{\sin(\mu+\nu)\pi/2}\,\frac{1}{2}\,\beta^{\nu+1}$$

$$\times \int_{0}^{1} \left(\frac{t}{1-t}\right)^{\frac{\nu-\mu}{2}} \frac{dt}{\left[1-t(1-\beta^{2})\right]^{(\mu+\nu)/2+1}} . \tag{1.46}$$

It is expedient to transform the r.h.s. of (1.46) via the introduction of a new integration variable, $x = 1/t$; the result is [cf (1.39)]

$$\mathcal{X} = \frac{1}{2}\,\frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{\sin\pi(\mu+\nu)/2} \int_{1}^{\infty} \frac{dx\,x^{(\mu+\nu)/2}(x-1)^{(\mu-\nu)/2}}{x\left[x-(1-\beta^{2})\right]^{(\mu+\nu)/2+1}} , \tag{1.47}$$

where

$$\mu \equiv 2ik_{f}/\alpha , \tag{1.48a}$$

and

$$\nu \equiv 2ik_{i}/\alpha . \tag{1.48b}$$

The stage has now been reached where the various limiting cases outlined in the introduction may be studied. Let us first consider the domain of the statistical theory. From the previous work[1] (cited in the introduction) it may be inferred that this domain corresponds to those values of the parameters μ, ν, and β for which (1.47) may be evaluated by the method of steepest descents. Let us therefore carry out such an evaluation; besides yielding concrete results for the statistical limit, the treatment will serve to delineate the range of values of μ, ν, and β, for which this limit constitutes a good approximation.

For the purpose of the steepest descent evaluation of (1.47), it is convenient to write it in the form

$$\mathcal{X} = \frac{1}{2}\frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{\sin\pi(\mu+\nu)/2}\int_1^\infty \frac{d\,x\,e^{F(x)}}{x(x-c)}\ , \tag{1.49}$$

where

$$c \equiv 1 - \beta^2\ , \tag{1.50}$$

and

$$F(x) = \frac{\mu+\nu}{2}\ \log x + \frac{\mu-\nu}{2}\log\,(x-1) - \frac{\mu+\nu}{2}\log\,(x-c)$$

$$\equiv \frac{\mu+\nu}{2}\left[\log x + \gamma\log\,(x-1) - \log\,(x-c)\right]\ , \tag{1.51}$$

with

$$\gamma \equiv \frac{\mu-\nu}{\mu+\nu}\ . \tag{1.52}$$

Under the conditions

$$\left|\frac{\mu+\nu}{2}\right| \gg 1\ , \tag{1.53a}$$

$$\left|\frac{\mu-\nu}{2}\right| \gg 1\ , \tag{1.53b}$$

the factor $e^{F(x)}$ is a rapidly varying function of x, except in the vicinity of the generally complex saddle point, z_s, defined by the relation

$$0 = F'(z_s) = \frac{\mu+\nu}{2}\left[\frac{1}{z_s} + \frac{\gamma}{z_s-1} - \frac{1}{z_s-c}\right]\ , \tag{1.54}$$

(1.54) constitutes a quadratic equation in the unknown saddle point, z_s.

The two solutions are

$$z_s = \frac{c}{2}\left(1 + \frac{1}{\gamma}\right) \pm \sqrt{\frac{c^2}{4}(1+1/\gamma)^2 - c/\gamma} \quad . \tag{1.55}$$

The task of demonstrating that the original integration contour of (1.49) (namely, along the real axis from 1 to ∞) may be deformed into one whose principal contributions occur at the saddle points is relegated to a future report. Preliminary studies show that (a) if the saddle points [given by (1.55)] are complex, the major contribution to (1.49) occurs along a steepest-descent contour in the immediate vicinity of that saddle point which is located in the upper half of the complex plane, and (b) if the saddle points are real and greater than unity (this latter property holding when $c < 1$, as will hereinafter be assumed to be the case), contributions to (1.49) occur in the neighborhoods of both saddle points. In both cases, the evaluation of these contributions requires computing $F''(z_s)$. For algebraic convenience, it is desirable to write (1.54) in the form

$$F'(z_s) = \frac{\mu+\nu}{2z_s} g(1/z_s) = 0 , \tag{1.56}$$

where

$$g(y) = 1 + \frac{\gamma}{1-y} - \frac{1}{1-cy} \quad . \tag{1.57}$$

One then has (upon using (1.56) and introducing the notation $y_s = 1/z_s$)

$$F''(z_s) = \frac{\mu+\nu}{2} y_s^3 \left[\frac{\gamma}{(1-y_s)^2} - \frac{c}{(1-cy_s)^2}\right] \quad . \tag{1.58}$$

The solution of (1.56) in terms of y_s reads

$$y_s = \frac{1+\gamma}{2} \pm \Delta , \tag{1.59a}$$

where

$$\Delta = \left[\left(\frac{1+\gamma}{2}\right)^2 - \frac{\gamma}{c}\right]^{1/2} \quad . \tag{1.59b}$$

Upon introducing (1.59a), (1.58), and eliminating c by the use of (1.59b), one has (after some algebraic manipulation)

$$F''(z_s) = \pm \left(\frac{\mu+\nu}{2}\right) 2\Delta\gamma \left[\frac{\frac{1+\gamma}{2} \pm \Delta}{\frac{1-\gamma}{2} \mp \Delta}\right]^2 . \tag{1.60}$$

At this point, it may parenthetically be noted that, by similar manipulation, the factor $\frac{1}{z(z-c)}$, present in the integrand of (1.49), may (for $z = z_s$) be brought into the form

$$\frac{1}{z_s(z_s-c)} = \left[\frac{\frac{1+\gamma}{2} \pm \Delta}{\frac{1-\gamma}{2} \mp \Delta}\right] \left[\left(\frac{1+\gamma}{2}\right)^2 - \Delta^2\right] = \left[\frac{\frac{1+\gamma}{2} \pm \Delta}{\frac{1-\gamma}{2} \mp \Delta}\right] \frac{\gamma}{c} . \tag{1.61}$$

The insertion of (1.60) and (1.61) into the expression for the saddle point integrals yield (as will be seen immediately below) numerically equal contributions when the saddle points are on the real axis, a feature which will receive physical interpretation.

In the case of real saddle points (Δ real) $F''(z_s)$ [as given by (1.60)] is manifestly imaginary (μ, and ν are imaginary); hence the contour of steepest descents is inclined at an angle of $\pi/4$ or $3\pi/4$ with respect to the real axis [depending on the sign of $F''(z)$]. The saddle point integrals are then of the form [cf.(1.49)].

$$\mathcal{X}_s = \frac{1}{2} \frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{\sin(\mu+\nu)\pi/2} \frac{\exp(\pm i\pi/4)\exp\big(F(z_s)\big)}{z_s(z_s-c)} \int_{-\infty}^{+\infty} \exp(|F''(z_s)|\eta^2/2)\, d\eta$$

$$= \frac{1}{2} \frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{\sin(\mu+\nu)\pi/2} \frac{\exp(\pm i\pi/4)\exp\big(F(z_s)\big)}{z_x(z_s-c)} \left(\frac{2\pi}{|F''(z_s)|}\right)^{1/2} ,$$

which, with the use of (1.60) and (1.61), may be written as

$$\mathcal{X}_s = \frac{1}{2} \frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{c \sin(\mu+\nu)\pi/2} \exp(\pm i\pi/4) \exp\big(F(z_s)\big) \left|\frac{2\pi\gamma}{(\mu+\nu)\Delta}\right|^{1/2} . \tag{1.62}$$

Bearing in mind that (a), $F(z_s)$ is imaginary for real saddle points and (b) in an eventual energy integration, the relative phase of $F(z_s)$ at the two saddle points will undergo many oscillations, let us simply ignore the interference term which results from the substitution of

$$\mathcal{X} = \sum_{s=1,2} \mathcal{X}_s \, , \tag{1.63}$$

into (1.38). One then has

$$P_{10} = \left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)}\right]^2 \frac{(V_f-V_i)^2}{V_fV_i} \left(4/\pi^2\right) \sinh\frac{2\pi k_i}{\alpha} \sinh\frac{2\pi k_f}{\alpha} \left[|\mathcal{X}_1|^2 + |\mathcal{X}_2|^2\right] , \tag{1.64}$$

where, with use of (1.50), (1.48a,b), (1.40), and (1.59b), one obtains (after some algebraic manipulation)

$$\begin{aligned} |\mathcal{X}_1|^2 = |\mathcal{X}_2|^2 &= \frac{1}{2}\left(\frac{\beta}{1-\beta^2}\right)^2 \frac{|\mu+\nu|\pi^3/4}{\sinh^2(|\mu+\nu|\pi/2)} \frac{\gamma}{\Delta} \\ &= \frac{1}{2} \frac{V_iV_f}{(V_f-V_i)^2} \frac{k_f^2-k_i^2}{\kappa\alpha} \frac{\pi^3/4}{\sinh^2\left[\frac{\pi}{\alpha}(k_f+k_i)\right]} \, , \end{aligned} \tag{1.65}$$

where

$$\kappa^2 \equiv k_f^2 - \frac{k_f^2-k_i^2}{1-V_i/V_f} \, . \tag{1.66}$$

A brief digression on the physical significance of the quantity, κ is now in order. From Eqs. (1.30a,b,c) and (1.28a,b), one notes that

$$\kappa_i(R) \equiv \left(k_i^2-b_i^2\, e^{-\alpha R}\right)^{1/2} , \tag{1.67a}$$

and

$$\kappa_f(R) \equiv \left(k_f^2-b_f^2\, e^{-\alpha R}\right)^{1/2} , \tag{1.67b}$$

are "local" wave vectors for translational motion along the potential curves $V_{oo}(R)$ and $V_{11}(R)$ respectively, (with, of course, total energies E_i and E_f, respectively). The condition that these two local wave vectors shall coincide at some common value, κ, i.e.,

$$\kappa_i(R) = \kappa_f(R) \equiv \kappa \ , \tag{1.68}$$

is readily shown to be equivalent to (1.66). It is thus seen that the principal contributions to (1.65) [i.e., to the matrix element for the transition, as given by (1.27)] obey a modified Franck-Condon Principle, in which the instantaneous position and velocity of relative translational motion are conserved.

The above remarks lead to a simple physical interpretation for the occurrence of the factor, κ, in the denominator of (1.65). Bearing in mind that

$$\kappa = \frac{Mv_{in}}{\hbar} \ , \tag{1.69}$$

(where v_{in} is the common instantaneous velocity of relative motion in the initial and final states), one sees that the $1/\kappa$ dependence is simply an expression of the usual $1/v$ law for the occurrence-probability distribution. This interpretation will be developed more explicitly immediately below.

Proceeding with the calculation one has, upon inserting (1.65) into (1.64), and utilizing the conservation-of-energy relation

$$\hbar(\omega-\omega_o) = \hbar^2\left(k_f^2-k_i^2\right)/2M \ , \tag{1.70}$$

together with (1.69) one has

$$P_{10} = \frac{\mathcal{E}^2\mu_{10}^2}{\hbar^2}\ \frac{2\pi}{v_{in}\alpha(\omega-\omega_o)}\left\{\frac{\left[1-\exp(-4\pi k_i/\alpha)\right]\left[1-\exp(-4\pi k_f/\alpha)\right]}{\left[1-\exp(-2\pi(k_f+k_i)/\alpha)\right]^2}\right\} \ . \tag{1.71}$$

In discussing the relationship of (1.71) to the prediction of the statistical theory, let us first note that, by virtue of conditions (1.53a,b) [which define the domain of validity of (1.71)], the curly bracketed factor may be approximately unity. Then apart from the basic absorption matrix element, $\mathcal{E}\mu_{10}$ (and Planck's constant), one has

$$P_{10} \propto \frac{1}{v_{in}\alpha(\omega-\omega_o)} . \qquad (1.72)$$

It will now be shown that the r.h.s. of (1.72) is equal to the time during which the collision produces a momentary vibrational frequency perturbation, ω_p, which lies within a unit differential range about the spectral shift, $\omega-\omega_o$. One notes, from (1.16) (and Bohr's frequency condition) that

$$\omega_p = \frac{1}{\hbar}\left[V_{11}(R) - V_{oo}(R)\right] , \qquad (1.73)$$

which, with use of (1.28a) and (1.28b), becomes

$$\omega_p = (\omega_f-\omega_i)\, e^{-\alpha R} , \qquad (1.74)$$

with

$$\omega_{i,f} = V_{i,f}/\hbar , \qquad (1.75)$$

A "frequency-coincidence"

$$\omega_p(R) = \omega-\omega_o ,$$

is achieved at a value of R given by[12]

$$R_\omega = \frac{1}{\alpha} \log \frac{\omega_f-\omega_i}{\omega-\omega_o} . \qquad (1.76)$$

The differential range, dR_ω in which $\omega_p(R)$ will lie with a differential frequency-range, $d\omega$ is clearly

$$dR_\omega = d\omega/\alpha(\omega-\omega_o) \quad ; \tag{1.77}$$

correspondingly, the time, dt, during which $\omega_p(R)$ will be contained within a unit frequency-range about $\omega-\omega_o$ is

$$\frac{dt}{d\omega} = \frac{1}{v_{in}} \frac{dR_\omega}{d\omega} = \frac{1}{v_{in}\alpha(\omega-\omega_o)} , \tag{1.78}$$

q.e.d. The coincidence of (1.72), and hence (1.71), with the prediction of the statistical theory is thus established.

Further detailed discussion of the statistical theory will be abandoned for the time being. The motivation for this decision is that, as will now be shown, it appears that, under most circumstances the frequency perturbations required for the far-wing absorption of interest in these studies (600-1000 cm^{-1}) are simply not attainable.

The consideration begins by noting that [as given, e.g., by (1.66)], κ be real, i.e., $\kappa^2 > 0$. Applying this condition to the r.h.s. of (1.66) one readily obtains the inequality

$$\frac{V_f}{V_i} > \frac{k_f^2}{k_i^2} = \frac{\hbar(\omega-\omega_o)+E_i}{E_i} ,$$

or, from (1.40)

$$\frac{\hbar(\omega-\omega_o)+E_i}{E_i} < \frac{1+3\alpha^2\lambda^2\hbar^2/4\mu_v\omega_o}{1+\alpha^2\lambda^2\hbar/4\mu_v\omega_o} . \tag{1.79}$$

From (1.79), it is clear that for the determination of the domain of applicability of the statistical theory, the value of the parameter

$$\xi \equiv \frac{\alpha^2\lambda^2\hbar}{2\mu_v\omega_o} , \tag{1.80}$$

is of decisive importance.

In order to estimate ξ, let us consider HCl as a representative diatomic molecule. For this case, if it is considered that atoms A and B (referred to in e.g. (1.4) and following text) are respectively Cl and H, one may take $\lambda \approx 1$. Moreover, μ_v may be identical with the mass of the hydrogen atom; thus $\mu_v = 1.6\text{x}10^{-24}$g. For ω_o, Herzberg's tables[13] yield

$$\omega_o \cong 2\pi c\ 3\text{x}10^3 \text{sec}^{-1} .$$

Finally, for α, let us use, as a representative value, the mean of those quoted in Chapter 3, page 71 of this report (α is denoted there by the symbol $\lambda/2$)

$$\alpha = 4\text{x}10^8 \text{cm}^{-1} .$$

One then obtains

$$\xi \approx 1/12 . \qquad (1.81)$$

Introducing this value into (1.79) yields

$$\hbar(\omega-\omega_o) ; \qquad (1.82)$$

taking $E_i \sim \kappa\tau \sim 300\ \text{cm}^{-1}$, it is clear that one obtains for the frequency range of applicability of the statistical theory, a value $\lesssim 30\ \text{cm}^{-1}$.

Without proceeding further, it should nevertheless be pointed out that the contributions of superthermal incident energies should not be dismissed out-of-hand. Although adversely weighted by the Boltzmann factor, $\exp(-E_i/\kappa\tau)$, they may still make a respectable showing in comparison with the other (thermal) contributions, which fall outside the range of the statistical theory; as shown in the following paragraphs, these are also of exponential smallness in the frequency shift.

After these remarks let us explore the case in which [referring to Eq. (1.44)] there are no saddle points on the real axis (from $x=1$ to $x=\infty$). Physically this case corresponds to the situation described at the end of section I, in which the collision-induced vibrational-frequency perturbation is too small to provide the momentary coincidence with the spectral shift, $\omega-\omega_o$, which is required by the statistical theory.

For the case of saddle points off the real axis, it can be shown[14] that the integration contour can be deformed so that the principal contribution to the integral occurs in the vicinity of the saddle point in the upper half of the complex plain; from Eq. (1.55) this saddle point is given by

$$z_s = \frac{c}{2}(1+1/2) + i\left[c/\gamma-(c^2/4)(1+1/\gamma)^2\right]^{1/2} . \tag{1.83}$$

The calculation of the saddle-point integral proceeds quite analogously to the case of real saddle points. The final result is [compare with (1.62)]

$$\mathcal{K} \cong \frac{1}{2} \frac{\beta^{\nu+1}(\mu+\nu)\pi/2}{c \sin\left[(\pi/2)(\mu+\nu)\right]} \exp\left(F(z_s)\right) \left|\frac{2\pi\gamma}{\Delta(\mu+\nu)}\right|^{1/2} , \tag{1.84}$$

where [cf. (1.51) and (1.83)]

$$\mathcal{R}e\, F(z_s) = -\left|\frac{\mu+\nu}{2}\right| f = -(k_f+k_i)f/\alpha \tag{1.85a}$$

$$f = \tan^{-1}\left[\frac{2\delta}{c(1+1/\gamma)}\right] - \tan^{-1}\left[\frac{2\delta}{c(1/\gamma-1)}\right] + \gamma \tan^{-1}\left[\frac{2\delta}{c(1+1/\gamma)-2}\right] , \tag{1.85b}$$

and

$$\delta = \left[c/\gamma - (c^2/4)(1+1/\gamma)^2\right]^{1/2} . \tag{1.85c}$$

From (1.50), (1.48a,b), (1.40), and (1.59b) one obtains [by algebraic manipulations similar to those which led to (1.65)]

$$\mathcal{K} = \frac{1}{2} \frac{V_i V_f}{(V_f-V_i)^2} \frac{\pi^3/4}{\sinh^2(\pi/\alpha)(k_f+k_i)} \left(\frac{k_f^2-k_i^2}{\kappa\alpha}\right) \exp[-2(k_f+k_i)f/\alpha] , \tag{1.86}$$

where

$$|\kappa|^2 = \frac{k_f^2-k_i^2}{1-V_i/V_f} - k_f^2 = \frac{2M(\omega-\omega_o)}{\hbar}\left[\frac{1}{1-V_i/V_f} - \left(1+E_i/\hbar(\omega-\omega_o)\right)\right]$$

$$= \frac{2M(\omega-\omega_o)}{\hbar}\left[1/\xi - E_i/\hbar(\omega-\omega_o) + \frac{1}{2}\right], \tag{1.87}$$

with ξ being given by (1.80), i.e.,

$$\xi = \frac{\alpha^2\lambda^2\hbar}{2\mu_v\omega_o};$$

as pointed out in the text subsequent to Eq. (1.80), its numerical value may generally be expected to be small compared to unity.

Upon substituting (1.86) into (1.38), one has

$$P_{10} \cong \left[\frac{\mathcal{E}\mu_o}{\hbar(\omega-\omega_o)}\right]^2 \frac{\pi}{\alpha}\left[\frac{2M(\omega-\omega_o)}{\hbar\eta}\right]^{-1/2} \exp(-[8M(\omega-\omega_o)/\alpha^2\hbar]^{1/2}g), \tag{1.88}$$

where the wiggle above the equality sign denotes an approximation wherein a factor equal to the curly bracket of (1.71) has (in accordance with the text subsequent to that equation) been replaced by unity,

$$\eta \equiv 1/\xi - E_i/\hbar(\omega-\omega_o) + 1/2, \tag{1.89}$$

[with ξ being given by (1.80) and (1.81)], and

$$g \equiv \left[\left(E_i/\hbar(\omega-\omega_o)\right)^{1/2} + \left(1+E_i/\hbar(\omega-\omega_o)\right)^{1/2}\right]f. \tag{1.90}$$

It is now of interest to "normalize" the r.h.s. of (1.88) with respect to the standard Lorentz-type absorption profile. To this end, let us briefly sketch a derivation of the phenomenological impact-theory formula for P_{10}.

One considers the diatomic molecular oscillator (initially in its ground state) in the presence of the electromagnetic field of the light wave and subject to certain collisional events which have the following two properties:

1) They are random in time; that is to say, a collision occurs in a differential interval, dt, at a time t after the preceding collision with the probability

$$dW_{coll} = e^{-t/\tau} dt/\tau \ . \qquad (1.91)$$

2) Their effect is to randomize the phase relationships between the ground and excited states of the vibrator. As is known, such phase relationships occur as a result of the perturbative action of the electromagnetic field; in particular, at a time, t, after the electromagnetic field is "turned on" (i.e., after a previous randomizing collision), the coherent part of the vibrational wave function is[15]

$$\phi = \phi_o + \left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)} \left(e^{-i\omega t} - e^{-i\omega_o t} \right) + \frac{\mu_{10}}{\hbar(\omega+\omega_o)} \left(e^{+i\omega t} - e^{-i\omega_o t} \right) \right] \phi_1 . \qquad (1.92)$$

The significance of property (2) is that, immediately after a collision the coefficient of ϕ in (1.92) gets multiplied by an arbitrary phase factor. It then follows that the state of the system is specified entirely by the occupation probability of the individual eigenstates, in particular, if the collision occurs at time t (subsequent to the previous one), the occupation probability of the first vibrational level is augmented by an amount equal to the absolute square of the coefficient of ϕ_1 in (1.92). If this quantity be averaged over the time, t, between collisions, with a weight factor given by the r.h.s. of (1.91), one obtains the average probability per collision that, as a result of the simultaneous action of collisions and the electromagnetic field, a (0 → 1) vibrational transition occurs. Carrying out the indicated operation, one obtains for this probability a sum of three contributions, two of which are proportional to the absolute squares of the first and second term of the square bracket of (1.92), respectively, the third being the interference term. In what follows, let us restrict the discussion to the "resonance" region defined by the condition[16]

$$|\omega-\omega_o| \ll \omega_o . \tag{1.93}$$

In this case, the first contribution dominates, thereby permitting us to consider the transition as being associated with electromagnetic absorption. In conformance with this feature, let us denote it as $P_{10}^{(im)}$ (the superscript "(im)" referring to the impact-theory basis of its derivation).

In carrying out the average over t, let us introduce the further condition

$$|\omega-\omega_o| \gg 1/\tau ,$$

(which is appropriate for the discussion of the wings of a Lorentzian line, and which, moreover, is quite well obeyed in atmospheric environments for the spectral shifts of relevance to the present paper). One then obtains

$$P_{10}^{(im)} = 2\left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)}\right]^2 . \tag{1.94}$$

It is now necessary to recognize that the quantity of ultimate interest is not the absorption probability per collision, but rather the absorptive probability <u>per unit time</u> (which will here be denoted as W_{10}). Generally, the relation between the two quantities is of the form

$$W_{10} = P_{10}\,\nu_{eff} , \tag{1.95}$$

where ν_{eff} is a suitably defined "effective" collision rate. In the case of the phenomenological impact treatment sketched above, ν_{eff} is simply the reciprocal of τ, so that

$$W_{10}^{(im)} = P_{10}^{(im)}/\tau = \left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)}\right]^2 \frac{2}{\tau} . \tag{1.96}$$

From (1.96), it is now apparent how to rewrite the basic result, (1.88), of the present calculation in a form suitable for comparison with the impact theory; namely,

$$P_{10} = \left[\frac{\mathcal{E}\mu_{10}}{\hbar(\omega-\omega_o)}\right]^2 \frac{2}{\tau} , \tag{1.97}$$

$$\frac{1}{\tau} = \frac{\pi}{2\alpha}\left[\frac{2M(\omega-\omega_o)}{\hbar\eta}\right]^{1/2} e^{-[8M(\omega-\omega_o)/\alpha^2\hbar]^{1/2}g} \nu_{eff} , \tag{1.98}$$

where ν_{eff} is the effective number of collisions per second.

In a one-dimensional model of relative translational motion — which, in effect, has been imposed on us by the collinear collision restriction — ν_{eff} would be something like the relative velocity of molecule and perturbing atom times a suitably defined linear density of perturbing atoms. In order to go behond a phenomenological prescription of this type, it is necessary to generalize the treatment to include collisions other than collinear. A crude preliminary treatment, which should (in the opinion of the present author) nevertheless yield results of semiquantitative significance, will now be given.

Specifically, it will still be assumed that the trajectory of the colliding atom, relative to the center-of-gravity of the diatomic molecule is parallel to the diatomic axis — the direction of said axis being taken as fixed, in accordance with the neglect of rotational motion (which was introduced at the beginning of the treatment). However, the distance between the trajectory and the center-of-gravity (that is, the classical impact parameter) is now permitted to take on a nonvanishing value.

A simple procedure for the treatment of these "off-center" collisions is afforded by an approximation — here designated as the <u>Takayanagi approximation</u>, in view of its prior use by that author in a paper on vibrational deactivation[17] — which is nevertheless (in the opinion of the present author) quite suitable for obtaining results of semiquantitative accuracy. In describing the approximation, let us first note that, for impact parameters $\lesssim$ atomic radii, (~3Å), the incoming particle finds itself in a spherical potential (centered, of course, around atom B of the molecule). It is to be noted that the scale of variation of the potential is $\sim 1/\alpha \approx .25$Å. This dimension is substantially smaller than the distance of closest approach, (~3Å). In other words, the radius of curvature of the equipotential surfaces is large compared to the distance ($\sim 1/\alpha$) in which the colliding particle experiences its principal interaction with the molecule. In the Takayanagi approximation the curvature of these surfaces is neglected. Specifically, the potential is taken as one-dimensional with the equipotential planes oriented perpendicular to that radius which intersects the trajectory at its distance of closest (classical) approach. The potential on each plane is taken to be that of the (actually) equipotential sphere which is tangent to the plane in question. With this approximation, one writes the wave function as a product of two factors, describing motion parallel and perpendicular to the (fictitiously) equipotential planes, respectively. The parallel motion is described by a plane wave whose wave vector lies in the "plane of incidence" (i.e., the one containing the classical trajectory and the center of atom B) and has a magnitude

$$k_{\parallel} = k \sin \theta = k\rho/r_c , \qquad (1.99)$$

(where θ is the angle between the trajectory direction and the radius which contacts it at the distance of closest approach, r_c, and ρ is the distance from the trajectory to the center of atom B). (For the particular collisions under consideration, ρ is also the distance from the trajectory to the molecular center of gravity).

For the perpendicular motion, one is then left with a Schrödinger equation which is identical to (1.31) except that k is to be replaced by its "perpendicular" component[18]

$$k_{\perp} = k \cos \theta = k\left(1-\rho^2/r_c^2\right)^{1/2} . \qquad (1.100)$$

Equivalently, the incident energy E_i undergoes the replacement[19]

$$E_i \rightarrow E_i \cos^2 \theta = E_i\left(1-\rho^2/r_c^2\right) . \qquad (1.101)$$

From the above results [in particular, from (1.01) and preceding text], it follows that the transition probability at an impact parameter ρ obeys the equation[20]

$$P_{10}(\rho,E_i) = P_{10}\left[0,E_i(1-\rho^2/r_c^2)\right] . \qquad (1.102)$$

With the aid of (1.102), the approximate first-principles replacement of the phenomenological equation (1.98) reads

$$\frac{1}{\tau} = \frac{N_p\pi v_i}{2\alpha}\int_0^\infty\left[\frac{2M(\omega-\omega_o)}{\hbar\eta(\rho)}\right]^{1/2} e^{-[8M(\omega-\omega_o)/\alpha^2\hbar]^{1/2}g(\rho)}\,2\pi\rho d\rho , \qquad (1.103)$$

where N_p is the density of perturbing atoms, $v_i \equiv (2E_i/M)^{1/2}$ is the initial relative velocity and where $\eta(\rho)$ and $g(\rho)$ are gotten by using the replacement (1.101) in (1.89) and (1.90) respectively.

A quantitatively accurate evaluation of (1.103) for all cases of interest remains to be carried out in the future. Preliminary studies indicate that, if (1.103) be expressed in the form

$$\frac{1}{\tau} = \frac{\pi v_i N_p}{2\alpha}\left[\frac{2M(\omega-\omega_o)}{\hbar\eta}\right]^{1/2} e^{-[8M(\omega-\omega_o)/\alpha^2\hbar]^{1/2}g}\,\pi\rho_{opt}^2 , \qquad (1.104)$$

[where η and g are, as before, the values of $\eta(\rho)$ and $g(\rho)$ for $\rho = 0$, and where ρ_{opt}, the "optical" collision radius, is of course to be determined by integrating (1.103)], then

$$\rho_{opt} \lesssim r_{co} \approx 3\text{Å} . \qquad (1.105)$$

That is, the upper limit of the optical collision radius is of the order of a gas-kinetic value. It will now be shown that, even with this upper limit, the far wing broadening, given by (1.104) is numerically far below the impact-theory result.

In carrying out the numerical comparison, let us approximate η by its first term, which is, cf.(1.81), large compared to unity (the other terms being numerically $\lesssim 1$); in particular, let us fix η at the value suggested by (1.81), i.e.,

$$\eta = 10 . \tag{1.106}$$

Then, upon using the estimate

$$\alpha = 4 \times 10^8 \text{cm}^{-1} , \tag{1.107}$$

and the relationship

$$v_i = \left(\frac{2E_i}{M}\right)^{1/2} \approx \left(\frac{2kT}{M}\right)^{1/2} = 2.2 \times 10^5 \mathfrak{M}^{-1/2} , \tag{1.108}$$

(where $\mathfrak{M} \equiv \frac{M}{M_{\text{proton}}}$ and where T has been set equal to 300°K), as well as

$$N_p = 2.7 \times 10^{19} \mathcal{N} \text{ cm}^{-3} , \tag{1.109}$$

(where $\mathcal{N}$ is the perturbing gas density in atmospheres), one has

$$\frac{1}{\tau} \cong \left(\frac{\Delta\bar{\nu}}{10^3}\right)^{1/2} (1.8) \times 10^9 \rho_{\text{opt}}^2 \; e^{-4\mathfrak{M}^{1/2}(\Delta\bar{\nu}/10^3)^{1/2} g} \text{ sec}^{-1} , \tag{1.110}$$

where $\Delta\bar{\nu}$ is the frequency shift, $\omega - \omega_o$, expressed in wave-numbers, and where ρ_{opt} is given in angstroms; in what follows ρ_{opt} is set equal to three.

Turning to the evaluation of g, as given by (1.90) and (1.85b), one easily verifies that, with the quantity $c = V_i/V_f = \xi$ set at a fixed value, (1/10), g is only a function of the dimensionless parameter, $\hbar(\omega-\omega_o)/E_i$. For a representative value of this parameter, say 3, (corresponding to $\Delta\bar{\nu} \approx 900 \text{ cm}^{-1}$), a numerical calculation gives $g = 1.1$. One then has, even for the extreme case of $M = 1$ (mass of relative motion = hydrogen mass)

$$e^{-4\mathfrak{M}^{1/2}(\Delta\bar{\nu}/10^3)^{1/2} g} \approx e^{-4} = .018 .$$

The corresponding value of $1/\tau$ is found to be

$$\frac{1}{\tau} = (.9)^{1/2}(1.8) \times 10^{9}(9)(.018) = 2.8 \times 10^{8}\,\mathrm{sec}^{-1}\ .$$

Expressed in wave-number units, this is $2.8 \times 10^{8}/2\pi c \cong 1.4 \times 10^{-3}\,\mathrm{cm}^{-1}$, a value substantially below the corresponding quantity used in Penner's article,[3] namely, $4 \times 10^{-2}\,\mathrm{cm}^{-1}$/atmosphere.

Another representative calculation: for $\hbar(\omega-\omega_o)/E_i = 2(\Delta\bar{\nu} \approx 600\ \mathrm{cm}^{-1})$ one has $g = .88$; $\exp\left[-4\mathfrak{M}^{1/2}(\Delta\bar{\nu}/10^{3})^{1/2}g\right] = \exp\left[-4(.6)^{1/2}(.88)\right] = e^{-2.72} = .066.$

The corresponding value of $1/\tau$ is

$$\frac{1}{\tau} = (.6)^{1/2}(1.8) \times 10^{9}(9)(.066) = 8 \times 10^{8}\,\mathrm{sec}^{-1} = 4 \times 10^{-3}\,\mathrm{cm}^{-1}$$

— a factor of ten less than the Penner value.[21]

SUMMARY AND FUTURE PROSPECTS

In this paper a model-type treatment of the far wing broadening of the vibrational lines of a diatomic molecule by a monatomic perturber has been given. The model is one in which interatomic forces are assumed to be of the exponential type, $e^{-\alpha r}$, and in which rotational motion is ignored. Specific results are derived for collinear collisions; these are generalized somewhat by the use of an approximation due to Takayanagi.

It is found that the so-called statistical theory is valid only out to distances of the order of 30 cm^{-1} from the line center. Beyond this point the line profile falls exponentially with increasing frequency shift. Numerical estimates at distances ~600 cm^{-1} and 900 cm^{-1} from the line center indicate that the actual absorption falls substantially below the impact-theory estimates of Penner.[3]

With regard to future work in this area, the following items may be listed:

1) First of all, a systematic numerical analysis of the final formulae of the present paper is required, in order to present a proper picture — in particular the overall frequency variation of the line profile, and a comparison with the impact-theory predictions of the model (exponential interatomic forces).

2) The role of attractive forces should be considered; it may be possible to do this rather straightforwardly, using Morse-type potentials.[22] Quantitatively, attractive forces, by speeding up the particles, increase the effective incident energy; this increase is preliminarily expected to lead to an enhancement in the absorption probability.

3) By an extension of the Takayanagi approximation, it appears possible to generalize the treatment further, to include collisions where trajectories are inclined at an arbitrary angle to the molecular axis.

4) It would, of course, be eminently desirable to take account of rotational motion. This, however, promises to be a tricky business.

REFERENCES

1. T. Holstein, Phys. Rev., 79, 744 (1950) The present discussion follows closely the results of this reference.

2. A discussion of this last possibility is given in an augmented version of Reference (1) unpublished, but available on request.

3. These magnitudes are suggested in the article of S. Penner, Laser Summer Study, (1965), The Institute for Radiation Physics and Aerodynamics, Univ. of Calif. at San Diego, in connection with the absorption of 1 micron due to H_2O lines situated in the spectral region.

4. It may at this point be mentioned that realistic value for α lie in the range $4 - 5 \times 10^8$ cm^{-1}. Such values begin to approach the requirements of condition (a).

5. cf. e.g. G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, 1950), pp. 125-127, especially the quoted values of the frequency separations of the maxima of the two rotational branches (P and R) for HCl (124 cm^{-1}) and CO (55 cm^{-1}) at room temperature. These values, of course, characterize the rotational states of the molecule before collision; after collision, the "effective" rotational temperature will in general be augmented by the conversion of the energy $\hbar(\omega-\omega_o)$ into rotational plus translational energy. However, since room temperature corresponds to $\sim$300 cm^{-1}, the values quoted here will not be augmented by more than a factor of

$$\left(\frac{(\omega-\omega_o) + kT}{kT}\right)^{1/2} \lesssim 2 \; .$$

6. Alternatively stated, the conversion of an appreciable fraction of the energy $(\omega-\omega_o)$ into energy of rotation would require $\Delta J >> 1$.

7. It may be remarked here that in line with this similarity, the thermal wavelengths of rotational wave functions are easily shown to be comparable to those of translational wave functions, both in magnitude and energy variation.

8. cf. N.F. Mott and H.W. Massey, Theory of Atomic Collisions, 3rd Ed. (Oxford 1965) pp. 686-690.

9. It may parenthetically be remarked that the approximation represented by Eqs. (1.8 - 1.10) - the so-called distorted-wave approximation - should give good results since (a) in practice, by virtue of the repulsive character of the interaction, V(R,X) will generally be of the order of the incident energy $E_i \sim kT << \hbar\omega_o$ (larger values of the repulsive potential being, in essence, dynamically inaccessible). As will later be seen, the intervibrational matrix elements of V(R,X) are even smaller. It is the neglect of these matrix elements which constitute the distorted wave approximation.

10. Here, it is necessary to introduce the full time dependence of the unperturbed wave function.

11. It will generally be the case that the product of the range parameter, α, and the vibration-amplitude scale-factor, $(\hbar/\mu_v\omega_o)^{1/2}$, is small. One may then expand the exponential factor, $\ell^{\alpha\lambda\lambda}$, in the integrals, obtaining

$$V_i = V_o \exp(\alpha\lambda\gamma_e)\left[1+\alpha^2\lambda^2\hbar/4\mu_v\omega_o\right],\quad V_f = V_o \exp(\alpha\lambda\gamma_e)\left[1+3\alpha^2\lambda^2\hbar/4\mu_v\omega_o\right].$$

12. Not surprisingly, the r.h.s. of (1.76) is identical with the R for which the above discussed modification of the Franck-Condon Principle [cf. Eqs. (1.67a,b) and (1.68)] is satisfied (as may be easily verified by the reader).

13. G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand), 2nd Ed. (1950), p. 534.

14. The details will have to be relegated to a future report.

15. The initial time dependence, $e^{-iE_i t/\hbar}$, occurs as a common factor, and will hence be discarded.

16. It may be remarked in passing that, if this condition is not fulfilled, the randomization recipe of (2) is not correct. Namely, as shown by Van Vleck and Weisskopf [Rev. Mod. Phys. 17, 227 (1945)], the total vibrational state immediately after collision is to be considered as an incoherent aggregate, not of the eigenstate of the field-free vibrator, but rather of the vibrational eigenstates in the presence of a static electric field, equal to the momentary value of the oscillating electromagnetic field at the impact-time, t. A detailed analysis shows that this recipe becomes equivalent to the one used above when (1.93) is fulfilled.

17. K. Takayanagi, Prog. Theoret. Phys. 8, 497 (1952).

18. There is, of course, a further correction because of the fact that the direction of molecular vibration no longer coincides with that of the line-of-centers of the colliding atoms (B and C). This involves alterations in the formulae of Ref. 11, for the constants V_i and V_f. These alterations turn out to be of secondary importance and will be ignored in this report.

19. It may here be remarked that Takayanagi's formulation is somewhat different than the foregoing. He separates the Schrödinger equation of relative motion in spherical coordinates, obtaining a radial equation which differs from (1.31) in the presence of the usual centrifugal term, $\ell(\ell+1)/r^2$. Takayanagi's approximation is the replacement of this term by $\ell(\ell+1)/r_c^2 \approx \ell^2/r_c^2$, which, with the introduction of the impact parameter, $\rho = \hbar\ell/mv$, is easily seen to be equivalent to (1.100).

20. It is incidentally to be noted that r_c is itself a function of ρ, to be determined by solution of the equation [cf. (1.31), (1.30c), and (1.1)]

$$0 = k^2\left(1-\rho^2/r_c^2\right) - \left(2M/\hbar^2\right)V_o\, e^{-\alpha r_c} .$$

However, for the case in which $\rho \ll r_{co}$ (where r_{co} is the value of r_c for $\rho = 0$), one may clearly approximate r_c by r_{co}. As will shortly be seen below, only this case is treated explicitly in the present paper.

21. It should be kept in mind that the choice $\mathfrak{n} = 1$ yields an extreme upper limit for $1/\tau$. E.g., for H_2O, it would seem that even with the rotational motion taken into account, a minimum value of $\mathfrak{n} = 2$ would seem to be more appropriate. For this choice, the value for $1/\tau$ is reduced by a factor $e^{-2.72(.41)} = .33$. The resultant width is 30 times smaller than the Penner value.

22. Cf. Devonshire, Proc. Roy. Soc. A158, 269 (1937).

Chapter 2.

ABSORPTION STUDIES OF THE $(O_2)_2$ COMPLEX

This chapter describes studies of various physical processes involved in the heating of the atmosphere in the vicinity of a high-powered laser pulse. The starting point of these studies is to be found in Appendices E and G of the Laser Summer Study Report (K.A. Brueckner, Institute for Radiation Physics and Aerodynamics, UCSD, La Jolla, California, Aug. 9-20, 1965). The analyses reported in the latter assume as an engineering requirement that the effective[1] absorption coefficient be less than or of the order of $10^{-11}\mathrm{cm}^{-1}$ (at pressures of the order of one atmosphere). Specifically, Penner and Olfe (Appendix E, loc. cit.) arrived at the conclusion that in the vicinity of the wavelength 10,468 Å the absorption coefficient[2] $k(\nu)$ is $\sim 1.5 \times 10^{-11}\mathrm{cm}^{-1}$. With this result the engineering problem would appear to have been solved, were it not for the fact that, as pointed out by Kolb and Ory (cf. Appendix G, loc. cit.), atmospheric absorption in the spectral neighborhood of 10,468 Å is actually dominated by a continuous absorption band, due to the existence (momentary or otherwise) of $(O_2)_2$ complexes. From the data of Dianov-Klokov,[3] Kolb and Ory conclude that at 10,468 Å the absorption coefficient is $1.5 \times 10^{-9}\mathrm{cm}^{-1}$ (down by a factor of ten from the peak at 10,600 Å).

It is clear that, if the energy absorbed from the laser beam is immediately converted into heat, one is reduced to the investigation of (a) the possibilities of an atmospheric window in the further wings of the $(O_2)_2$ band (e.g., in the neighborhood of say 10,300 Å or 10,800 Å), or (b) looking for a window in an entirely different spectral region (such as the 10 micron window mentioned by Kolb and Ory). Deferring these approaches for the time being, let us consider in some detail the physical processes responsible for the conversion (wholly or in part) of the absorbed laser energy into heat.

To begin with one may note from the results of Badger et al[4] (as well as from the earlier references quoted therein) that the 10,600 Å band is associated with the transitions

$$\left[{}^3\Sigma_g(0),\ {}^3\Sigma_g(0)\right] \rightarrow \left[{}^3\Sigma_g(0),\ {}^1\Delta_g(1)\right]$$
$$\rightarrow \left[{}^3\Sigma_g(1),\ {}^1\Delta_g(0)\right] ,$$

in which the resulting complex may be regarded as consisting of a pair of loosely bound (or momentarily colliding) diatomic oxygen molecules. One of these molecules ends up in the first excited electronic state $^1\Delta_g$, the other in the electronic ground state $^3\Sigma_g$; in addition, one of the molecules acquires a single quantum of vibrational excitation. As will be seen shortly, there is good evidence that under atmospheric conditions the lifetime of the electronic state is considerably in excess of one millisecond; on the other hand, there is equally good evidence that (under typical mid-latitude atmospheric conditions) vibrational de-excitation of O_2 takes place in a time substantially less than one millisecond.

Before getting into the detailed estimation of relaxation times, let us briefly note some interesting (and perhaps eventually pertinent) facts concerning the structure of the $(O_2)_2$ dimers. According to Ref. 4 [cf. their Eq. (6)] the radiative decay rate of $^1\Delta_g$ states is given by the formula

$$\frac{1}{\tau} (\mathrm{sec}^{-1}) = 2.6 \times 10^{-4} \left[1 + 3.8 P_{O_2} + 3.0 P_{CO_2} + .7 P_{N_2}\right],$$

where the P's are partial pressures in atmospheres. Of interest here is the term proportional to P_{O_2}; it gives the strength of the radiative transition associated with the $(O_2)_2$ complex (either a stabilized dimer, or a momentary O_4 complex formed by two colliding O_2 molecules). Now, the likelihood of an O_2 molecule being in the atomic vicinity $R_{O_2-O_2} \sim 2 \times 10^{-8}$ cm is $\sim \frac{4\pi}{3} N_{O_2} R^3_{O_2-O_2}$. Introducing the symbol $1/\tau_{O_4}$ to denote an effective radiation rate for the O_4 complex, we then have

$$(2.6 \times 10^{-4})(3.8) P_{O_2} = \left[1/\tau_{O_4}\right] \frac{4\pi}{3} N_{O_2} R^3_{O_2-O_2}.$$

With N_{O_2} $3 \times 10^{19} P_{O_2}$, and with the above estimate for $R_{O_2-O_2}$ one then has

$$1/\tau_{O_4} \sim 1 \ \mathrm{sec}^{-1},$$

which is extremely small compared to the rate of allowed electric dipole transitions. This result suggests an <u>extremely</u> loose coupling of the two O_2 molecules, such that the spins, parities, and/or axial angular momenta of the individual diatomic constituents remain good quantum numbers.[5]

This conclusion is supported by the very low quoted estimates of the dissociation energies of $(O_2)_2$ dimer states. According to Bader and Ogryzlo[6] these range from 200-600 cal/mole, which is equivalent to .009-.025 ev. Such small dissociation energies are indicative of long range, extremely weak, attractive interactions (probably of van der Waals origin) in which the individual O_2 molecules are kept well apart by the usual shorter range but relatively strong repulsive interaction.

It may be remarked here that Bader and Ogryzlo emphasize that their results lead to the conclusion that the radiating complexes are true dimers. However, in our opinion, the low dimer-dissociation energies quoted by them strongly suggest that such dimer states exist for at most a few collision times $\sim 10^{-9}$ sec. For the overwhelming fraction of time, electronic and vibrational excitations reside in individual O_2 molecules.

With these preliminary observations out of the way, let us proceed to a discussion of the lifetime of the electronic state $^1\Delta_g$ under atmospheric conditions. Here, very fortunately, relatively strong experimental evidence for a lifetime far in excess of one millisecond is provided by the previously quoted[6] work of Bader and Ogryzlo. These authors, using calorimetric techniques, find (cf. curve (b) of Figure 1) that in a fast-flow system in which gas flows from a discharge at a drift speed $v_d \sim 200$ cm/sec,[7] the concentration of excited O_2 molecules (which they identify as $^1\Delta_g$ molecules) does not exhibit perceptible diminution in a flow-distance of 45 cm; moreover, said persistence of excitation is unaffected by the presence of small amounts ($\sim$1 percent) of H_2O, NO_2, N_2O (as well as some non-atmospheric constituents). One may immediately infer that under these experimental conditions

$$\tau_{^1\Delta_g} \gg \frac{45}{200} = .23 \text{ sec}^{-1}.$$

Postulating a hypothetical volume-destruction process involving the binary collision of excited O_2 molecules with other atmospheric constituents (O_2 or N_2)

one may then infer a lifetime

$$\tau_{^1\Delta_g} \gg .23(4.4)/760 = 1.3 \text{ millisecond.}$$

Two possible loopholes in the above chain of reasoning may be pointed out here. One is the tacit assumption that $O_2^* - N_2$ collisions will not be more effective than $O_2^* - O_2$ collisions for electronic de-excitation. In our opinion this assumption appears [in the light of preliminary study of the theory of such quenching reactions, as presented, e.g., in the paper by K. Laidler, J. Chem. Phys. 10, 34 (1942(] to be eminently reasonable. Similarly, it appears quite reasonable to assume that minor atmospheric constituents, such as carbon dioxide, will not be more effective than H_2O in excitation-quenching.

The other loophole is the assumption that the volume-destruction process is two-body. If, on the contrary, it were a three-body process, one would have to multiply the above estimate of 1.3 milliseconds by another factor of 4.4/760, thereby obtaining $\tau_{^1\Delta_g} \gg .077$ millisecond — a result which tells us essentially nothing. However, without further experimental or theoretical evidence it would be unduly pessimistic to be concerned about this possibility.[8]

Proceeding then from the above-deduced conclusion that, under atmospheric conditions

$$\tau_{^1\Delta_g} \gg 1.3 \text{ millisecond,}$$

let us discard the electronic excitation energy of $^1\Delta_g - O_2$ states as a source of atmospheric heating. The fate of the vibrational excitation remains to be considered. Here, the engineering situation is not favorable. Specifically, as will now be shown, it turns out that the presence of water vapor in concentrations encountered under typical mid-latitude conditions leads to vibrational de-excitation of O_2 in times substantially less than one millisecond.

The required information concerning collisional quenching of vibrational excitation in O_2 is obtained from experiments on absorption and dispersion of ultra-sound in gases. These experiments yield the so-called "Napier" relaxation frequency $f_N = 1/2\,\pi\,\tau_N$, where τ_N, the "Napier" time, is the time required for thermal equilibration between vibrational and translational degrees of freedom of a gas; τ_N may be identified as the lifetime of vibrational excitation, and is hence of direct interest to us.

The results of Henderson, Clark, and Lintz[9] will form the basis of the present discussion. According to these authors, τ_N in O_2-H_2O mixtures is given by the expression

$$\frac{1}{2\pi\tau_N} = (7 + 183h + 132h^2)p$$

(with $1/\tau_N$ in $\sec^{-1}$), where p is the pressure of the main constituent, O_2, in atmospheres, and where $h \equiv 10^3 N_{H_2O}/N_{O_2}$. One notes that when h exceeds unity ($N_{H_2O}/N_{O_2} > .1\%$), the term quadratic in the water vapor concentration becomes dominant.

Before going on to evaluate the engineering situation, let us digress briefly to discuss the mechanism of the quadratic term. The currently believed mechanism (first proposed by Tuesday and Boudart[10]) consists of a two-step process. The first step is the transfer of vibrational energy from O_2 to H_2O in a binary collision; this transfer, by virtue of the close energetic proximity of the lowest vibrational level of O_2(1556 cm^{-1}) to the lowest bending-mode excitation of H_2O (1595 cm^{-1}), is quasi-resonant, and hence assumed to be rapid enough to establish a common vibrational temperature for the two species, i.e.,

$$\frac{N^*_{H_2O}}{N^*_{O_2}} = \frac{N_{H_2O}}{N_{O_2}},$$

where $N^*_{O_2}$ and $N^*_{H_2O}$ denote the concentrations of vibrationally excited molecules of O_2 and H_2O. The second step consists of the conversion of H_2O-vibrational excitation into translatory (or rotatory) energy via H_2O - H_2O collisions. This reaction, although quite rapid compared to other bimolecular vibrational de-excitation processes (e.g., O_2 with itself) is still taken to be slow compared to the reverse of the first step (i.e., $H_2O^* + O_2 \rightarrow H_2O + O_2^*$). It is then readily seen that the quadratic term in the above expression for τ_N is given by the formula

$$\frac{1}{\tau} = \frac{N_{H_2O}}{N_{O_2}} N_{H_2O} \langle v_{H_2O} \rangle Q_q,$$

where N_{H_2O} is the concentration of normal H_2O molecules, $\langle v_{H_2O} \rangle$ is some average relative velocity of two colliding H_2O molecules, and Q_q is the cross section for vibrational quenching of H_2O^* in such a collision. Inserting into this relation the experimental value for $1/\tau_2$, namely $2\pi(132)h^2$ sec^{-1}, and using the formula $h = 10^3\ N_{H_2O}/N_{O_2}$, one finds $N_{H_2O} \langle v_{H_2O} \rangle Q_q = 8.3 \times 10^8$ sec^{-1}/atmosphere. With $N_{H_2O} = 2.7 \times 10^{19} cm^{-3}$ at one atmosphere, and with $\langle v_{H_2O} \rangle \sim 10^5 cm/sec^{-1}$, one has

$$Q_q \sim 3 \times 10^{-16} cm^2,$$

which is 1/10 a gas-kinetic cross section. This is perhaps one order of magnitude higher than the usual rate of vibrational deactivation in reactions involving polyatomic molecules.[11]

It should finally be stated that the basic reason for the credibility of the Tuesday-Boudart mechanism (as compared to, e.g., a three-body interaction between one oxygen and two water molecules) is that the quadratic term is unique to H_2O; D_2O and HDO give rise only to terms linear in their respective concentrations. Since the vibrational frequencies of these molecules are not close to that of O_2, the absence of the quadratic term finds a natural explanation in the Tuesday-Boudart theory.[12]

Having discussed the mechanism of the quadratic term (the linear term being presumably associated with the reaction $O_2^* + H_2O \rightarrow O_2 + H_2O$ + K.E., let us evaluate the engineering situation. For this evaluation it is useful to present a table of h as a function of altitude for an average mid-latitude location.[13]

Altitude (km)	Mixing Ratio($W \equiv M_{H_2O}/M_{atm}$)	$h = W(29/18) \times 10^3$
0	$.63 \times 10^{-2}$	10.2
2	$.38 \times 10^{-2}$	6.1
4	$.19 \times 10^{-2}$	3.1
6	$.09 \times 10^{-2}$	1.45
8	$.027 \times 10^{-2}$	.43

With h at sea level equal to 10.2, it is immediately apparent that the quadratic term $2\pi\ (132)h^2$ is dominant and yields a value

$$\frac{1}{\tau^*_{O_2}} \approx 8.5 \times 10^4\ \text{sec}^{-1} >> / \text{inverse millisecond}$$

for the deactivation rate. Furthermore, the corresponding lifetime $\tau^*_{O_2}$ remains less than a millisecond for altitudes below a value ~6.3 km. It is thus apparent that, for engineering purposes, one must consider the vibrational part of the absorbed laser energy as contributing its full quota to atmospheric heating.

The energy bookkeeping now proceeds as follows: if $\bar{\nu} = 1/\lambda$ is the wave-number of the laser beam, one observes (with $\bar{\nu}_{el} = 10^4/1.26 = .794 \times 10^4 \text{cm}^{-1}$) that the fraction of energy available for atmospheric heating[14] is

$$\frac{\bar{\nu} - \bar{\nu}_{el}}{\bar{\nu}} = \frac{\bar{\nu}-7940}{\bar{\nu}} .$$

Taking $\bar{\nu}$ equal to the Penner value (Appendix E of the above-quoted Summer Report), $10^4/1.047 = 9550\ \text{cm}^{-1}$, one has

$$\frac{\bar{\nu} - \bar{\nu}_{el}}{\bar{\nu}} = .17 .$$

Hence, for the effective absorption cross section (i.e., the cross section for effective conversion of laser energy into heat), one has

$$k_{eff}(\nu) = \frac{\bar{\nu} - \bar{\nu}_{el}}{\bar{\nu}} k(\nu) = .17\ k(\nu) ,$$

where $k(\nu)$ is the actual absorption cross section. Using the value mentioned at the beginning of this report, one has

$$k_{eff}(\nu) = 2.5 \times 10^{-10} \text{cm}^{-1}.$$

It is thus clear that if it is possible to reduce $k_{eff}(\nu)$ by another factor of ten, the engineering situation will begin to look optimistic. One possibility for such a reduction will now be discussed briefly.

Specifically, it appears that apart from the $(O_2)_2$ absorption, Penner's wavelength choice, 10,468 Å, is not uniquely indicated. Preliminary inspection of the Babcock and Moore solar atlas[15] as well as more recent data[16] from the Naval Research Laboratories, indicates the essential absence of atmospheric absorption lines down to about 10,300 Å. Moreover, Penner's calculation for 10,468 Å indicated that the dominant absorption (apart from the $(O_2)_2$ band is due to the relatively distant, strong H_2O lines between 11,103 Å and 11,601 Å. This contribution will certainly not increase with decreasing wavelength. On the other hand, according to Fig. 1 of Ref. 3, the contribution of $(O_2)_2$ absorption diminishes substantially with decreasing wavelength over the interval 10,468 Å → 10,300 Å. The possibility of obtaining the required factor of ten in the wavelength region 10,300 - 10,370 Å appears at the present time to merit further investigation.

REFERENCES

1. The word "effective" refers to those events which result in conversion of laser energy into heat (i.e., molecular translational energy) in a time of one millisecond, this interval constituting the duration of the laser pulse under consideration.

2. This absorption coefficient refers to all processes which remove energy from the laser pulse. According to Penner and Olfe essentially all of this energy is deposited as vibrational energy of H_2O molecules. The conversion of this vibrational energy into translational energy is assumed to take place in a time small compared to one millisecond (cf. discussion below on vibrational relaxation of H_2O in the atmosphere).

3. V.I. Dianov-Klokov, Opt. Spectry. 17, 76 (1964).

4. R.M. Badger, A.C. Wright, and R.F. Whitlock, J. Chem. Phys. 43, 4345 (1965).

5. If the coupling were substantial, the axial angular momenta, parities, and spins of the individual O_2 molecules would hardly continue to be good quantum numbers; the only reliable one would be the total spin S. In electronically excited $(O_2)_2$, S is unambiguously equal to unity; however, the ground state is spin-degenerate, with S taking on the values 0, 1, and 2. Under these conditions, no electric-dipole selection rules would be violated by the radiative transition.

6. W. Bader and E.A. Ogryzlo, Disc. Faraday Soc. 37, "Chemical Reactions in the Atmosphere," pp. 46-56 (1964).

7. This estimate for v_d is obtained from the data of Table I of Ref. 6 in which, at an O_2 pressure of 4.4 mm Hg, and temperature of 25°C, the O_2 flow-rate through a tube of radius 1 cm is (e.g.) 160 μ moles/sec = 1.6×10^{-4} moles/sec.

8. In this connection, one may note that the persistence of excitation in Bader and Ogryzlo's experiment permits one to conclude that wall-destruction processes are also extremely inefficient. Namely, for de-excitation probabilities of the order of one per collision — in fact, even for probabilities not much larger than the ratio of mean free path to the tube radius (which ratio << 1) — the wall-destruction rate is given by the standard diffusion formula

$$\frac{1}{\tau_W} \sim \frac{(2.4)^2}{R^2} \frac{\ell_D v_{th}}{3} \sim 2\ell_D v_{th},$$

where R = 1 cm is the tube radius, ℓ_D the "diffusion" mean free path, and v_{th}, a typical thermal velocity of 0_2 molecules. Taking for the diffusion cross section, $Q_D = 1/N\ell_D$, a characteristic gas-kinetic value of $3x10^{-15}cm^2$, one has $1/\ell_D \sim (4.4)(3x10^{16})(3x10^{-15}) = 400\ cm^{-1}$. With $v_{th} \sim 4x10^4 cm/sec$, one then has $\tau_W \sim .005$ sec, which is very much less than the observed lifetime (>> .23 sec). It is therefore immediately apparent that the quenching probability per wall collision ξ is very much less than unity. However, for $\xi <<<< 1$, it is known that the diffusion expression for τ_W should be replaced by $1/\tau_W \sim v_{th}/R\ \xi \sim (\xi)\ 4x10^4\ sec^{-1}$. It is thus apparent that, with $1/\tau_W$ experimentally found to be much less than $(1/.23)\ sec^{-1}$, $\xi << 10^{-4}$. Such extremely small quenching probabilities (involving surfaces undoubtedly well contaminated with adsorbed layers of 0_2 and other constituents) constitute strong evidence for the assumption that the quenching efficiencies of ternary, etc., collisions are generally extremely small. Since the relative rate of ternary to binary collisions is gas-kinetically small $[\sim 4\pi N/3\ (Q_D/\pi)^{3/2} \sim .004$ at one atmosphere], values of $\xi << 10^{-4}$ would then appear to rule out the above discussed possibility of three body collisions playing any significant engineering role in quenching $^1\Delta_g$ molecules.

9. J. Acoust. Soc. Am. <u>37</u>, 457 (1965).

10. C.S. Tuesday and M. Boudart, Princeton University Technical Note 7, Contract AF33(038)-23976 (Jan. 1955); a detailed account is more conveniently given in the book, <u>Absorption and Dispersion of Ultrasonic Waves</u>, by K.F. Herzfeld and T.A. Litovitz (Academic Press Inc., New York, 1959, p. 212).

11. This cross section, although large, can easily be shown to be compatible with the basic assumption of the Tuesday-Boudart mechanism; namely, the dominance of the vibrational-equilibration reaction $H_20 + 0_2^* \rightleftarrows H_20^* + 0_2$. If in fact one assumes that the cross section for $H_20^* + 0_2 \rightarrow H_20 + 0_2^*$ is not less than gas-kinetic (reasonable in view of the quasi-resonance of vibrational energies), one finds that vibrational transfer from H_20 to 0_2 is some three orders of magnitude more frequent than vibrational deactivation in $H_20 - H_20$ encounters.

12. This statement, while applying to D_20 with bending-mode frequency = 1178.7 cm^{-1}, becomes somewhat questionable in the case of HDO, for which this frequency is 1403 cm^{-1}. Here, it would appear possible that the

discrepancy between this and the 0_2 vibrational frequency (1556 cm^{-1}), namely 153 cm^{-1}, is small enough to allow an appreciable transfer between 0_2 and HDO. This detail requires further investigation.

13. Handbook of Geophysics and Space Environments, Air Force Cambridge Research Laboratories, McGraw-Hill, New York (1965), p. 3-37.

14. The quantity $\bar{\nu} - \bar{\nu}_{el}$ appearing in the numerator of this expression represents that part of the laser energy which appears not only as vibrational, but also as rotational and translational energy. (Note that the signs of the latter two may be negative, i.e., the rotational and translational energies of the absorbing molecules may be diminished in the act of absorption.) All these forms of energy contribute to atmospheric heating.

15. H.D. Babcock and C.S. Moore, The Solar Spectrum, λ6600 to λ13495, Carnegie Institute of Washington, Publication 579, Washington D.C., 1947.

16. An Atlas of the Absorption of the Atmosphere From 8512 to 11,600 Å, J.A. Curcio, R. Eckhardt, C.V. Acton, and T.H. Cosden, NRL Report 635L, U.S. Naval Research Laboratory, Washington, D.C. (1965).

Chapter 3.

COLLISION-INDUCED ABSORPTION

I. INTRODUCTION AND BACKGROUND

One of the processes by which light may be removed from a beam traversing the atmosphere, and converted directly to heat, is collision-induced absorption. During a collision between two molecules a transient dipole moment may be induced by the overlap of the electron clouds, and, in some cases by a permanent quadrupole moment on one of the molecules. Because of the induced dipole moment an absorptive transition can occur which is forbidden for the isolated molecule. The transition may be strictly translational, or it may have both a translational and an internal (rotational, vibrational or electronic) component. The former case corresponds to an instantaneous transformation of all the photon's energy into heat. In the latter case, if the photon's energy exceeds the energy needed for the internal transition, then the excess goes instantaneously into translational motion, and therefore into heat. Conversely, if the photon's energy is less than that needed for the internal transition, the difference is provided from the translational energy of the molecules; this process corresponds to instantaneous cooling. In either event the internal energy is, in general, eventually transformed into heat by collisional relaxation.

Collision-induced absorption is not to be confused with ordinary pressure-broadened absorption. Ordinary pressure broadening applies to internal transitions which are permitted for isolated molecules; the collisions result in a modification of the spectral shape of the line, but do not affect the magnitude of the frequency-integrated absorption coefficient, which is proportional only to the density of molecules of the species making the transition. The integrated absorption coefficient for collison-induced absorptions, however, is proportional to the product of densities of the two molecular species involved in the event (or to the square of the density, if only one species is involved). At standard pressure ordinary absorption usually dominates strongly over collision-induced absorption in the spectral vicinity of a permitted transition. However, in the neighborhood of a forbidden transition collision-induced absorption becomes the dominant process.

Collision-induced absorption is characterized spectrally by broad, continuous bands having widths (in reciprocal wavelengths) of the order of

100 cm^{-1} (about 10^{-2} ev in energy units). These widths may be regarded as following from the uncertainty principle because of the transient nature of the induced dipole moments, which exist only during the collision period of several times 10^{-14} seconds. The bands are centered at, and superposed on forbidden rotational bands, rotational-vibrational bands, etc. In addition there are bands corresponding to purely translational transitions, which peak at ~100 cm^{-1}. At their peaks the absorption coefficients range in magnitude from the order of* $10^{-6}\mathrm{cm}^{-1}$ amagat^{-2} to the order of $10^{-4}\mathrm{cm}^{-1}$ amagat^{-2}.

A number of collision-induced absorption bands have been observed experimentally,[1-15] and the corresponding absorption coefficients have been measured in the neighborhood of the peaks. The mean free paths are quite long at standard pressure, so the measurements must be made at pressures of about 100 atmospheres and higher. Most measurements are within about 400 cm^{-1} of the peak. In the far wings none have yet been achieved.

Our interest in atmospheric heating via collision-induced absorption stems from the possibility of its leading to a self-defocusing of a laser beam propagating through the atmosphere. The defocusing is brought about by a decrease in the local index of refraction as a result of laser heating; the net effect is an undesirable decrease in the transmitted power density. Given an upper limit on the acceptable decrease in transmitted power density one can determine a corresponding "critical" value of the reciprocal mean free path for heating, which will lead to the self-defocusing instability. This critical value has been estimated elsewhere for a contemplated choice of laser power, frequency, and pulse duration.[16]

The peak values of reciprocal mean free path for collision-induced absorption, which obtain at atmospheric pressure for the more abundant constituent gases like N_2 and O_2, range from ~$10^{-6}\mathrm{cm}^{-1}$ to ~$10^{-4}\mathrm{cm}^{-1}$, and are much greater than the particular critical value referred to above. It is only in the far wings of these bands that the absorption decreases to the critical value. Therefore, to determine whether or not a given collision-induced absorption band can cause a defocusing instability, one must know the far wing behavior of the band. However, the far wings have so far been too difficult to

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*An amagat is a partial pressure of one atmosphere.

study experimentally even at high pressure, so that it is desirable to attempt a theoretical prediction of their behavior.

Whether or not collision-induced absorption presents a potential limitation to laser beam transmission through the atmosphere depends upon the laser power being considered. The maximum absorption coefficient for heating which can be tolerated (insofar as beam self-defocusing is concerned) is smaller for larger laser power. For some beams which one might wish to use, such as the kilowatt c-w beam in the 10 micron wavelength range, obtainable with the CO_2 laser, collision-induced absorption is probably not a serious problem. For megawatt beams, however, the critical absorption coefficient is much less than the peak values of typical collision-induced absorption coefficients; in this case the relative spectral locations of the laser beam and the absorption bands are crucial. If for a given laser frequency and intensity the critical absorption coefficient proves to be exceeded, then collision-induced absorption has associated with it a difficulty not present for most other heating mechanisms. In other mechanisms the absorbed light energy is temporarily stored in some internal state of the absorbing molecule, and is released into heat energy over a period of some collisional relaxation time. Therefore, by making the laser pulse duration less than the collisional relaxation time one can, at least in principle, overcome the defocusing instability resulting from most heating mechanisms. However, in the case of collision-induced absorption, all or a large part of the photon energy may go instantaneously into heat, and the heating problem cannot be surmounted by using a short laser pulse.

The specific list of laser beams (with their powers, frequencies, and pulse lengths) for which we wish to evaluate the capability of atmospheric transmission has not yet been made final, and in fact cannot be predicted much better than the characteristics of lasers that will be developed in the next few years can be predicted. In view of this circumstance and the fact that atmospheric collision-induced absorption bands are scattered throughout the visible spectrum (they presumably occur everywhere that forbidden transition lines occur), we have concluded that, despite the current emphasis on the relatively low power CO_2 laser, collision-induced absorption bands require investigation.

Two of the atmospheric "windows," which are currently under consideration, are located in the wavelength vicinity of one micron and ten microns respectively.[17] The ten micron window (reciprocal wavelength $\sim 10^3 cm^{-1}$) appears to be threatened by a collision-induced absorption band resulting from a collision between two N_2 molecules.[12] This band is superposed on a rotational band of N_2; its peak, located at ~ 100 cm^{-1}, corresponds to an absorption coefficient of $\sim 2.5 \times 10^{-6} cm^{-1}$ amagat^{-2}. The estimation of the magnitude of this absorption coefficient at $10^3 cm^{-1}$ has been made a specific goal of our program.

The ten micron window is also endangered by a vibrational-rotational band of O_2, which results from $O_2 - O_2$ collisions[12] (and probably also from $O_2 - N_2$ collisions). This band has a peak absorption coefficient of $3.5 \times 10^{-6} cm^{-1}$ amagat^{-2}, with the peak located at 1550 cm^{-1}. It is considerably closer to the window than the $N_2 - N_2$ bands and therefore at first sight might be expected to dominate.* However, the reverse is probably the case because of the fact that collision-induced absorption bands characteristically decrease much more rapidly on the low frequency side of their peaks than on the high frequency side. Specifically, the frequency dependence of the absorption coefficient on both sides differs principally by an extra factor $\exp[-\hbar(\omega_o-\omega)/KT]$ on the low frequency side, where ω_o is the peak frequency and ω is the frequency in question.** The explanation of this behavior is straightforward. The peak frequency ω_o is essentially the frequency of the internal transition. If the photon energy $\hbar\omega$ is greater than $\hbar\omega_o$, the absorption is always energetically possible, since the excess can go into kinetic energy of the colliding molecules. However, if $\hbar\omega < \hbar\omega_o$, the absorption is not energetically

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* Since the excited vibrational-rotational level (which is located at about the same frequency as the peak of the absorption coefficient) is at a higher frequency than the window (1000 cm^{-1}) the initial effect is a cooling of the atmosphere by the energy equivalent of (1550-1000) cm^{-1} = 550 cm^{-1}. However, if the pulse length is greater than the collisional relaxation time of the excited level, the entire 1550 cm^{-1} of energy will be deposited in time for the pulse to experience a heating by a net energy equivalent of 1000 cm^{-1}.

**This statement and the explanation that follows apply only to transitions involving internal modes, and not to purely translational transitions.

possible unless the kinetic energy E of the molecules is great enough to make up the difference, i.e., unless $E \geq \hbar\omega_0 - \hbar\omega$. The extra Boltzmann factor on the low frequency side, then, is just the probability that the colliding molecules have sufficient kinetic energy.

The far wing behavior ($\sim 10^3 \mathrm{cm}^{-1}$) of the N_2 - N_2 rotational band is then a prime target of our program. However, as a first step we have chosen to study collision-induced absorption by rare gas molecules (specifically Ne-A, He-A, and He-Ne for which considerable data exists*[9,12]). The reason is that this process is much simpler; there are no internal states involved and the transition is purely translational. To describe a translational transition we need only know the induced dipole moment as a function of intermolecular separation. However, to describe a rotational-translational transition we must know, in addition, the dependence of the induced dipole moment on the orientations of the individual molecules. Therefore we shall first study the simpler absorption by rare gases, then use the rare gas absorption coefficients in the far wings to make a first, primitive estimate of the N_2 - N_2 absorption at 1000 cm^{-1}, before we go on to attack the latter more directly.

Considerable theoretical work has been done by Van Kranendonk and others on the frequency-integrated collision-induced absorption coefficient.[18-24] Satisfactory agreement with the data appears to be obtained by using a model in which the induced dipole moment consists of two terms. The first is a result of the overlap of the electron clouds of the two molecules during the collision and of their consequent distortion; it is very short range and has an exponential dependence $\sim e^{-R/\rho}$ on the intermolecular separation R, and is directed along the intermolecular axis. The second term describes a dipole moment induced on one molecule by a permanent quadrupole moment on the other;

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*There is no collision-induced absorption by rare gas molecules of the same species, because the spatial symmetry in the center of mass system precludes the existence of an asymmetric quantity like the induced dipole moment. In the case of diatomic molecules of the same species, like N_2 - N_2, the freedom of orientation of each molecule relative to the intermolecular axis destroys the symmetry, so that the dipole moment can be induced.

it is longer range than the overlap term and goes as R^{-4}. Since rare gas atoms do not possess permanent quadrupole moments, we shall be concerned only with the overlap moment.

The evidence for an exponential overlap moment also includes a direct quantum mechanical calculation by Van Kranendonk and Bird,[19] who find that their numerical results can be well represented by an $e^{-R/\rho}$ dependence.

We are aware of only three papers concerned with the frequency dependent collision-induced absorption coefficient.[25-27] All three are confined to rare gas molecules. Levine and Birnbaum[25] describe the molecular motion by a classical straight line trajectory and take for the induced dipole moment $\vec{\mu}(\vec{R}) = \mu_o \gamma R \, e^{-\gamma^2 R^2} \, (\vec{R}/R)$. The factor γR in front is used to simulate the behavior of the scattering wave functions: the molecules are actually scattered by a potential which has a steep, short range, repulsive part that causes the wave functions to decrease rapidly for small R. The exponent is chosen quadratic in R, instead of linear, because the former choice significantly simplifies the analysis and permits a closed form expression for the absorption coefficient. The parameter μ_o appears trivially in the result as a scale factor multiplying it; the spectral shape of the absorption coefficient depends only on γ. By choosing γ appropriately they are able to fit the data remarkably well for He-A. For Ne-A the fit is good at low frequencies, but their theoretical absorption coefficient begins to decrease more rapidly than the measured coefficient at higher frequencies. From their ability to fit the data with a classical straight line trajectory they conclude that the absorption coefficient is not sensitive to the potential.

Levine[26] has done a quantum mechanical calculation, replacing the true scattering wave functions by plane waves, and using the same dipole moment as above, with the factor γR again having the purpose of simulating the true behavior of the wave functions at small R. The results are again in closed form and differ little from those of the classical model at lower frequencies. At higher frequencies the two results begin to diverge.

Tanimoto[27] has done a strictly quantum mechanical calculation using a more realistic model. The scattering wave functions are solutions, albeit approximate, to the Schroedinger equation with an exponential repulsive potential of the form $V(R) = V_o e^{-2R/\lambda}$. The induced dipole moment is taken to be of the form recommended by the work of Van Kranendonk, etc., namely, $\vec{\mu}(\vec{R}) = \mu_o e^{-R/\rho} (\vec{R}/R)$. Tanimoto's results depend on three parameters, V_o, λ, and ρ, in addition to the trivial dependence on μ_o. He uses values of V_o and λ which have been inferred from scattering data,[28] and chooses ρ to fit the absorption coefficient measurements. Unlike the approaches of Levine and Birnbaum, Tanimoto's analysis requires extensive numerical computations. For some special values of ρ, viz., λ/ρ = integer, his expressions simplify and there is a radical decrease in the required computations. He considers only these cases and chooses the most satisfactory, viz., $\rho = \lambda$.

It is difficult to make a direct comparison between Tanimoto's results and those of Levine and Birnbaum for the following reason. There are two sets of measurements of absorption during rare gas collisions. The earlier measurements by Kiss and Welsh,[9] are in the near wings, covering the range from 350 cm^{-1} to 700 cm^{-1}. The later measurements, by Bosomworth and Gush,[12] cover the peaks of the bands, and run from 50 cm^{-1} to 400 cm^{-1}. Tanimoto's analysis was made before the results of Bosomworth and Gush were available, and his parameters were chosen to fit the data in the wings. In the vicinity of the peaks his absorption coefficients have reasonable shapes, but are incorrect quantitatively by as much as a factor of two. Levine and Birnbaum choose their parameters to match the data at the peaks. They have pointed out that the absorption curves measured in the two ranges do not join smoothly; in fact there is an overlap region in which they definitely disagree.*
Consequently, we cannot evaluate the accuracy of Tanimoto's results in the neighborhood of the peak, or compare them directly with those of Levine and Birnbaum.

The approach we have chosen is very nearly, but not quite identical to that of Tanimoto. Although the models used by Levine and Birnbaum are much more convenient, and actually describe the experimental observations quite

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*There is a puzzling feature of these measurements. Kiss and Welsh find an absorption coefficient in the wings for He-Ne which is roughly the same magnitude as those for He-A and Ne-A. Bosomworth and Gush, however, measure the absorption for He-A and Ne-A at their peaks but report finding no absorption there for He-Ne.

well up to about 400 cm^{-1}, we do not feel confident about extending their use to the far wings, i.e., to $\sim$1000 cm^{-1}. First, we must immediately eliminate the classical model from consideration, since we are concerned (at reciprocal wavelengths of 1000 cm^{-1}) with processes in which the energy of the absorbed light quantum is about five times as great as the initial (thermal) kinetic energy of the colliding molecules. Second, although Levine in his quantum mechanical model has demonstrated that the use of a presumably incorrect dipole moment ($\sim e^{-\gamma^2R^2}$) has no serious consequence at low frequencies, our goal is to extrapolate to higher frequencies, where we do not have observations as a check. Therefore, we cannot start with an a priori incorrect model and gamble that the predictions will again be insensitive to it.

Furthermore, we cannot expect the higher frequency behavior to be so insensitive to the potential. The latter behavior comes from the close collisions, and in these the details of the potential are more important.

Our analysis has been carried to the point where it is now being prepared for the final step: a numerical evaluation of integrals by computer. The differences between our work and Tanimoto's lie in the evaluation of the integrals. He has used an approximation (it will be discussed in Section VI). whose effect it is difficult to assess, so that we feel it should be avoided in spite of the additional computations required. In addition he has considered only special values of the scale size ρ of the dipole moment, so as to facilitate the computational procedure. We plan to use a quite accurate approximation which will permit us to perform the calculation for any value of ρ without seriously affecting the complexity of the numerical program.

II. GENERAL EXPRESSION FOR DIPOLE ABSORPTION

We begin by deriving a general expression for the rate of photon absorption by a dipole. The absorption and emission rates are given by the following two well known expressions,

$$R_{abs}(\omega) = \frac{2\pi}{\hbar} \sum_{i,f} P_i |T(f|\vec{\omega},\vec{\varepsilon};i)|^2 \delta(E_f-E_i-\hbar\omega), \tag{2.1}$$

$$R_{emm}(\omega) = \frac{2\pi}{\hbar} \sum_{i,f} P_i |T(\vec{\omega},\vec{\varepsilon};f|i)|^2 \delta(E_f+\hbar\omega-E_i), \tag{2.2}$$

where $T(f|\vec{\omega},\vec{\varepsilon};i)$ is the T-matrix element for a transition between an initial state i and a final state f of the colliding atoms accompanied by the absorption of a photon of wave vector $\vec{\omega}/c$ and polarization $\vec{\varepsilon}$, and P_i is the statistical weight factor for the initial states of energy E_i. By means of a time reversal argument it can be shown that $R_{emm}(\omega)$ can be expressed in terms of the T-matrix for absorption and that, as a result, the net absorption rate $R(\omega) = R_{abs} - R_{emm}$ may be written in the form

$$R(\omega) = \frac{2\pi}{\hbar} \sum_{i,f} (P_i-P_f) |T(f|\vec{\omega},\vec{\varepsilon};i)|^2 \delta(E_f-E_i-\hbar\omega). \tag{2.3}$$

To lowest order in the electronic charge the T-matrix element is

$$T(f|\vec{\omega},\vec{\varepsilon};i) = \left(\frac{2\pi\hbar I}{\omega c}\right)^{1/2} (\psi_f|\sum_j \frac{e_j}{m_j} \exp(i\vec{\omega}\cdot\vec{x}_j/c)\ \vec{p}_j\cdot\vec{\varepsilon}|\psi_i)\ , \tag{2.4}$$

where ψ_i and ψ_f are the initial and final state scattering wave functions of the colliding atom pair, e_j, m_j, p_j, and x_j are the charge, mass, momentum, and position of the j^{th} charged particle (electron or nucleus), and I is the photon flux. In the dipole approximation this expression reduces to

$$T(f|\vec{\omega},\vec{\varepsilon};i) = -i\left(\frac{2\pi\hbar\omega I}{c}\right)^{1/2} \vec{\mu}_{fi}\cdot\vec{\varepsilon}, \tag{2.5}$$

where

$$\vec{\mu}_{fi} = (\psi_f|\sum_j e_j\vec{x}_j|\psi_i) , \qquad (2.6)$$

and $\sum_j e_j\vec{x}_j$ is the total dipole operator of the system.

We assume that the statistical weight factors P_i and P_f are independent of direction. The angular integrations in the sum over final states and the average over initial states then have the effect of averaging over directions of the polarization vector $\vec{\varepsilon}$. Bearing this in mind, and substituting the expression (2.5) for $T(f|\vec{\omega},\vec{\varepsilon};i)$ into (2.3) for $R(\omega)$ we obtain

$$R(\omega) = \frac{4\pi^3}{3}\frac{\omega I}{c}\sum_{i,f}(P_i-P_f)|\vec{\mu}_{fi}|^2\delta(E_f-E_i-\hbar\omega) . \qquad (2.7)$$

Eq. (2.7) is the starting point for many of the theoretical papers on collision induced absorption. We shall be concerned with the absorption coefficient or reciprocal mean free path for photon absorption $A(\omega)$, which is related to the absorption rate by

$$A(\omega) = nn'VR(\omega)/I, \qquad (2.8)$$

where n,n' are the number densities of the two species of colliding atoms, and V is the quantization volume. The statistics are described by the Boltzmann distribution,

$$P_{i,f} = P(E_{i,f}) = \text{const.} \times \exp(-E_{i,f}/KT), \qquad (2.9)$$

and the delta function in (2.7) requires $E_f = E_i + \hbar\omega$, so that

$$P_f = P_i \exp(-\hbar\omega/KT) . \qquad (2.10)$$

Thus we find for $A(\omega)$,

$$A(\omega) = \frac{4\pi^3}{3} \frac{nn'V}{c} \omega\left[1 - \exp(-\hbar\omega/KT)\right] \sum_{i,f} P_i |\vec{\mu}_{fi}|^2 \delta(E_f - E_i - \hbar\omega) . \qquad (2.11)$$

For $h\omega << KT$ the dominant behavior of the purely translational bands is provided by the factor $\omega\left[1 - \exp(-\hbar\omega/KT)\right] \propto \omega^2$, and, although it is not obvious, the remaining factor in $A(\omega)$ approaches a nonzero value as $\omega \to 0$. Thus, although the purely translational bands may be thought of as centered about "the line at zero frequency," they actually have their peaks at some nonzero frequency because of this factor ω^2. The term $\exp(-\hbar\omega/KT)$ may be traced back to Eq. (2.2), where it is seen to be a reflection of the stimulated emission rate into the photon beam; the stimulated emission rate tends to cancel the absorption rate, and in fact does so identically at zero frequency. At photon energies much greater than KT, such as correspond, for example, to vibrational bands, the effect of stimulated emission is evidently negligible.

III. PARTIAL WAVE EXPANSION

In the Born-Oppenheimer approximation the total wave function $\psi(\vec{R},\vec{r})$ is written

$$\psi(\vec{R},\vec{r}) = \chi(\vec{R})\,\phi(\vec{R},\vec{r}), \tag{3.1}$$

where $\vec{R}$ is the internuclear coordinate and $\vec{r}$ represents all the electronic coordinates. $\chi(\vec{R})$ is assumed to satisfy a Schroedinger equation with an intermolecular potential $V(\vec{R})$, and $\phi(\vec{R},\vec{r})$ is assumed to have only a slowly varying dependence on $\vec{R}$. The dipole matrix element $\vec{\mu}_{fi}$ of (2.6) is then given by

$$\vec{\mu}_{fi} = \int \chi_f^*(\vec{R})\vec{\mu}(\vec{R})\chi_i(\vec{R})d^3R , \tag{3.2}$$

where

$$\vec{\mu}(\vec{R}) = \int (\Sigma_j e_j \vec{x}_j)\,|\phi(\vec{R},\vec{r})|^2\, d^3r \tag{3.3}$$

is the expectation value of the dipole moment operator for a fixed internuclear coordinate $\vec{R}$. It is understood here that the electronic state of the system (which is the only internal state for rare gas atoms) remains unchanged in the transition.

Since we are concerned only with rare gas atoms, whose properties are independent of orientation, we assume the dipole moment $\vec{\mu}$ to be dependent only on the magnitude of the interatomic distance R, and to be directed along the radius vector $\hat{R} = \vec{R}/R$,

$$\vec{\mu}(\vec{R}) = \mu(R)\hat{R} . \tag{3.4}$$

We shall use two center-of-mass coordinate systems*, one with its polar axis along the initial-state wave vector $\vec{k}_i$ of the colliding atoms, and the other with its polar axis along the final-state wave vector $\vec{k}_f$. Assuming that χ_i and χ_f are scattering states for a spherically symmetric interaction we may expand them in Legendre functions in the $\vec{k}_i$ and $\vec{k}_f$ coordinate systems, respectively

$$\begin{aligned} \chi_i &= \frac{1}{\sqrt{V}} \sum_\ell (2\ell+1)\, i^\ell \exp(i\delta_{i\ell}) \frac{u_{i\ell}(R)}{k_i R} P_\ell(\cos\theta_i) \;, \\ \chi_f &= \frac{1}{\sqrt{V}} \sum_\ell (2\ell+1)\, i^\ell \exp(i\delta_{f\ell}) \frac{u_{f\ell}(R)}{k_f R} P_\ell(\cos\theta_f) \;, \end{aligned} \tag{3.5}$$

where V is the quantization volume and $\delta_{i\ell}$ and $\delta_{f\ell}$ are the standard scattering phase shifts. The coefficients $\sqrt{1/V}\ (2\ell+1)\ i^\ell \exp(i\delta_\ell/k)$ have been chosen so that the wave functions have the correct asymptotic form,[29]

$$\chi(\vec{R}) \rightarrow \frac{1}{\sqrt{V}}\left[\exp(i\vec{k}\cdot\vec{R}) + f(\theta)\,\frac{\exp(ikR)}{R}\right], \text{ as } R \rightarrow \infty \;, \tag{3.6}$$

provided the radial wave functions $u_{i\ell}$ and $u_{f\ell}$ are normalized so that

$$u_\ell(R) \rightarrow \sin(kR + \ell\pi/2 + \delta_\ell), \text{ as } R \rightarrow \infty \;. \tag{3.7}$$

Inserting the partial wave expansions (3.5) into the expression (3.2) for $\vec{\mu}_{fi}$, and using (3.4) for $\vec{\mu}(\vec{R})$, we obtain

$$\vec{\mu}_{fi} = \frac{1}{Vk_f k_i} \sum_{\ell,\ell'} (2\ell+1)(2\ell'+1)(-i)^\ell i^{\ell'} \exp\left[i(\delta_{i\ell'} - \delta_{f\ell})\right] M(\ell,\ell')\, \vec{I}(\ell,\ell'), \tag{3.8}$$

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* The energy absorbed by the center of mass in the transition is $(\hbar\omega/Mc^2)(\hbar\omega/2) \sim 10^{-11}\ \hbar\omega$, which is so small compared to its initial energy ($\sim$KT) that its motion may be completely ignored.

where $M(\ell,\ell')$ is the matrix element

$$M(\ell,\ell') = \int u^{*}_{f\ell}(R)\mu(R)\; u_{i\ell'}(R)dR \;, \tag{3.9}$$

and $\vec{I}(\ell,\ell')$ is the integral over solid angle

$$\vec{I}(\ell,\ell') = \int P_{\ell}(\cos\theta_f)\; P_{\ell'}(\cos\theta_i)\hat{R}\; d\Omega_i \;. \tag{3.10}$$

The evaluation of $M(\ell,\ell')$ is reserved for the next section, in which we choose a specific model for $\mu(R)$, and a specific scattering potential (so that the radial wave functions may be obtained by solving the Schroedinger equation). $\vec{I}(\ell,\ell')$ may be evaluated straightforwardly using well known properties of Legendre functions. The procedure is outlined in the appendix; the result is

$$\frac{1}{4\pi}\,\vec{I}(\ell,\ell') = P^{1}_{\ell}(\cos\theta_{fi})(\cos\phi_{fi}\hat{x} + \sin\phi_{fi}\hat{y})\left[\frac{\delta(\ell-1,\ell')}{(2\ell-1)(2\ell+1)} - \frac{\delta(\ell+1,\ell')}{(2\ell+1)(2\ell+3)}\right]$$
$$+ P_{\ell}(\cos\theta_{fi})\;\hat{z}\left[\frac{\ell\delta(\ell-1,\ell')}{(2\ell-1)(2\ell+1)} + \frac{(\ell+1)\delta(\ell+1,\ell')}{(2\ell+1)(2\ell+3)}\right] , \tag{3.11}$$

where θ_{fi}, ϕ_{fi} are the polar and azimuthal angles of $\vec{k}_f$ in the $\vec{k}_i$ coordinate system, $\hat{x},\hat{y},\hat{z}$ are unit vectors in the same coordinate system, with $\hat{z}$ in the $\vec{k}_i$ direction, and $\delta(\ell,\ell')$ is a Kroneker delta.

Now, in the expression (2.11) for the absorption coefficient $A(\omega)$ the integration over final states contains an integration over the solid angle variable Ω_{fi}. Therefore, we shall ultimately need the integral $\int |\vec{\mu}_{fi}|^2\, d\Omega_{fi}$. If we use (3.8) for $\vec{\mu}_{fi}$, insert (3.11) for $\vec{I}(\ell,\ell')$, and utilize the well known orthogonality relations for Legendre functions, we obtain

$$\int |\vec{\mu}_{fi}|^2\, d\Omega_{fi} = \frac{(4\pi)^3}{V^2k_f^2k_i^2} \sum_{\ell} \left\{(\ell+1)\;|M(\ell+1,\ell)|^2 + \ell|M(\ell-1,\ell)|^2\right\} . \tag{3.12}$$

As the quantization volume is made arbitrarily large the summations over states become integrals according to

$$\sum_f \rightarrow \frac{V}{(2\pi)^3} \int d^3k_f , \text{ as } V \rightarrow \infty . \qquad (3.13)$$

Thus the summation over final states in (2.11) becomes

$$\sum_f |\vec{\mu}_{fi}|^2 \, \delta(E_f - E_i - \hbar\omega) \rightarrow \frac{V}{(2\pi)^3} \frac{mk_f}{\hbar^2} \int |\vec{\mu}_{fi}|^2 \, d\Omega_{fi} , \qquad (3.14)$$

where m is the reduced mass of the atom pair, and comes from the density of final states.

The normalized Boltzmann distribution is

$$P_i = \frac{(2\pi)^3}{V} \left(\frac{\hbar^2}{2\pi mKT}\right)^{3/2} \exp(-E_i/KT) . \qquad (3.15)$$

Combining this expression with (3.14) and (3.12) in Eq. (2.11) for $A(\omega)$ we finally find, in the limit of infinite quantization volume,

$$A(\omega) = \frac{(4\pi)^3}{3} \frac{nn'}{c} \left(\frac{\hbar^2}{2\pi mKT}\right)^{3/2} \omega \left[1 - \exp(-\hbar\omega/KT)\right]$$
$$\times \sum_{\ell=0}^{\infty} \sum_{\substack{\ell'=\ell\pm1 \\ \ell'\geq 0}} \left(\frac{\ell+\ell'+1}{2}\right) \int |M(\ell',\ell)|^2 \exp(-E/KT) \left(\frac{k^2}{Ek'}\right) dk , \qquad (3.16)$$

where

$$E = \hbar^2 k^2/2m, \quad E' = \hbar^2 (k')^2/2m , \qquad (3.17)$$

$$E' = E + \hbar\omega . \qquad (3.18)$$

IV. EVALUATION OF THE DIPOLE MATRIX ELEMENT

We wish to evaluate the matrix element

$$M(\ell,\ell') = \int u^*_{f\ell}(R)\mu(R)u_{i\ell'}(R)dR. \tag{3.9}$$

To do so we must specify the model to be used. First, in accordance with the discussion of Section I we take the dipole moment to be

$$\vec{\mu}(\vec{R}) = \mu_o \exp(-R/\rho)\ \hat{R}\ , \tag{4.1}$$

so that $\mu(R) = \mu_o \exp(-R/\rho)$. Second, we take for the potential

$$V(R) = V_o \exp(-2R/\lambda)\ . \tag{4.2}$$

Support for this model is cited by Mason[30] and by Abrahamson.[31] More precisely, the potential they discuss is of the form

$$V(R) = V_o \exp(-2R/\lambda) - V_1\left(\frac{R_1}{R}\right)^6 . \tag{4.3}$$

However, Mason gives as the value of the potential at its minimum 6.35×10^{-3}ev for Ne-A, and 2.88×10^{-3}ev for He-A. Since we shall be concerned with a gas having a thermal distribution of energies with an average of $\sim 2.5 \times 10^{-2}$ev, we may drop the attractive term and use the form (4.2). Therefore, the radial wave functions must satisfy the radial Schroedinger equation

$$\frac{d^2u_\ell}{dR^2} + \left[k^2 - \frac{\ell(\ell+1)}{R^2} - A^2 \exp(-2R/\lambda\right] u_\ell = 0\ , \tag{4.4}$$

where $k^2 = 2mE/\hbar^2$, and $A^2 = 2mV_o/\hbar^2$.

Now, this equation cannot be solved in closed form, but the equation

$$\frac{d^2u_\ell}{dR^2} + [q^2 - A^2 \exp(-2R/\lambda)]u_\ell = 0 \tag{4.5}$$

can be. We shall adopt the following approximation, which is used by Tanimoto,[27] and appears to be due originally to Takayanagi.[32] We substitute Eq. (4.5) for Eq. (4.4) with q^2 taken to be

$$q^2 = k^2 - \frac{\ell(\ell+1)}{R_o^2} , \tag{4.6}$$

where R_o is the classical turning point, defined as the solution to

$$k^2 - \frac{\ell(\ell+1)}{R_o^2} - A^2 \exp(-2R_o/\lambda) = 0 . \tag{4.7}$$

The idea of the approximation is as follows. We wish to evaluate the integral for $M(\ell,\ell')$ given by (3.9). The integrand decreases rapidly for large R because of the exponential decrease of $\mu(R)$, so that it is not important that the approximations to $u_{f\ell}$ and $u_{i\ell}$ be accurate at large R. Both the real and approximate wave functions are sinusoidal for large R (recall Eq. (3.7)), but the details of the oscillatory behavior do not have much effect on the integral (3.9). The integrand decreases rapidly for small R, because the wave functions must turn down sharply inside the classically forbidden region (i.e., for $R < R_o$). In this region ($R < R_o$), as well, the details of the wave functions are not too important, provided the approximations turn down sharply, as do the real wave functions. The principal contribution to the integral then comes from the vicinity of the larger of the two turning points, since the integrand is washed out by the corresponding wave function for smaller R, and by $\mu(R)$ for larger R.

Thus it is important that the wave functions turn down at the right place, i.e., that the turning points be correct. To this extent the approximation is accurate, since the turning points R_o of (4.4) and (4.5) have been arranged to be identical. It is, however, subject to the criticism that the true and approximate wave functions cannot be guaranteed to turn down at similar rates for $R < R_o$; since $\mu(R)$ rises rapidly as R decreases, it is conceivable that a wave function which decreases too slowly will lead to an appreciable overestimate of the integral, and vice versa.

By making the substitution $z = A\lambda e^{-R/\lambda}$ one may convert (4.5) into the canonical form of Bessel's equation.[33] The solution, having the required boundary condition $u_\ell(0) = 0$, is

$$u_\ell(R) = N' \left[\frac{I_{iq\lambda}(A\lambda e^{-R/\lambda})}{I_{iq\lambda}(A\lambda)} - \frac{I_{-iq\lambda}(A\lambda e^{-R/\lambda})}{I_{-iq\lambda}(A\lambda)} \right] , \tag{4.8}$$

where $I_{i\mu}(z)$ represents the Bessel function of imaginary argument (and imaginary index $i\mu$), and N' is a normalization constant. From the asymptotic form of the Bessel function,[34]

$$I_{\pm i\mu}(z) \sim \frac{e^z}{(2\pi z)^{1/2}} \left[1 + \frac{1+4\mu^2}{8z} + \ldots \right] , \tag{4.9}$$

and the values of $A\lambda$ and $q\lambda$ it may be seen that

$$I_{iq\lambda}(A\lambda) \cong I_{-iq\lambda}(A\lambda) , \tag{4.10}$$

so that we may write

$$u_\ell(R) = N \left[I_{iq\lambda}(A\lambda e^{-R/\lambda}) - I_{-iq\lambda}(A\lambda e^{-R/\lambda}) \right] . \tag{4.11}$$

Specifically, from Mason's conclusions[30] ($V_o = 1.07 \times 10^{-8}$ erg, $\lambda = 4.86 \times 10^{-9}$ cm for Ne-A, and $V_o = 2.09 \times 10^{-9}$ erg, $\lambda = 5.28 \times 10^{-9}$ cm for He-A) it follows that for Ne-A: $A\lambda = 3.16 \times 10^3$ and (recall Eq. (4.6)) $q\lambda \leqslant k\lambda = 7.6$ (at thermal energy); and for He-A: $A\lambda = 7.95 \times 10^2$ and $q\lambda \leqslant k\lambda = 4.3$ (at thermal energy). Therefore, the first term of the asymptotic expansion (4.9) is sufficient, and (4.11) follows.

From the series expansions of the Bessel functions[33] it can easily be seen that $u_\ell(R)$ has the asymptotic form

$$u_\ell(R) \to -2iN\left(\frac{\sinh\pi q\lambda}{\pi q\lambda}\right)^{1/2} \sin\left[qR-q\lambda\ln(A\lambda/2) + \phi(q\lambda)\right], \text{ as } R \to \infty , \tag{4.12}$$

where ϕ is the phase of the gamma function of complex argument,

$$\Gamma(1+i\mu) = |\Gamma(1+i\mu)|e^{i\phi(\mu)}. \tag{4.13}$$

By comparison with the required asymptotic form (3.7) it may then be seen that the normalization constant N must be chosen to be

$$N = \frac{i}{2}\left(\frac{\pi q\lambda}{\sinh\pi q\lambda}\right) . \tag{4.14}$$

Finally, noting that the modified Bessel function of imaginary argument (and imaginary index) is defined by[35]

$$K_{i\mu}(z) = \frac{-\pi}{2i\,\sinh\pi\mu}\left[I_{i\mu}(z) - I_{-i\mu}(z)\right] , \tag{4.15}$$

we may write u_ℓ in the form

$$u_\ell(R) = \frac{1}{\pi}(\pi q\lambda\,\sinh\pi q\lambda)^{1/2}\,K_{iq\lambda}(A\lambda e^{-R/\lambda}) . \tag{4.16}$$

Inserting wave functions of the form (4.16) into the integral (3.9) for $M(\ell,\ell')$, and making the substitution $z = A\lambda e^{-R/\lambda}$, we now obtain

$$M(\ell,\ell') = \frac{\mu_o}{\pi^2}(\pi q'\lambda\,\sinh\,\pi q'\lambda)^{1/2}\,(\pi q\lambda\,\sinh\,\pi q\lambda)^{1/2}\,\frac{\lambda}{(A\lambda)^{\lambda/\rho}}\,F(A\lambda), \tag{4.17}$$

$$F(A\lambda) = \int_o^{A\lambda} K_{iq'\lambda}(z)\,K_{iq\lambda}(z)\,z^{\lambda/\rho-1}\,dz , \tag{4.18}$$

where we have now modified the notation so that the unprimed variables refer to the initial state i and the primed variables refer to the final state f. For large argument the modified Bessel functions go as[36]

$$K_\nu(z) \sim (\pi/2z)^{1/2} e^{-z} , \qquad (4.19)$$

so that, since $A\lambda \sim 10^3$, we may extend the limits of the integral(4.18) to infinity with negligible error. The resulting integral can be evaluated in closed form,[37]

$$F(\infty) = \frac{2^{\lambda/\rho-3}}{\Gamma(\lambda/\rho)} \left|\Gamma[\lambda/2 + i(q'+q)\lambda/2]\right|^2 \left|\Gamma[\lambda/2\rho + i(q'-q)\lambda/2]\right|^2 . \qquad (4.20)$$

V. FINAL EXPRESSION FOR THE ABSORPTION COEFFICIENT

We now collect the results of the previous sections and write the final expression for the absorption coefficient $A(\omega)$. It is given as the following integral over the thermal energy distribution of the colliding molecules, and summation over their initial and final angular momenta,

$$A(\omega) = B\omega(1-e^{-\hbar\omega/KT}) \sum_{\ell=0}^{\infty} \sum_{\substack{\ell'=\ell\pm 1 \\ \ell' \geqslant 0}} \left(\frac{\ell+\ell'+1}{2}\right)$$

$$\times \int \left|\Gamma[\lambda/2\rho+i(q'+q)\lambda/2]\right|^4 \left|\Gamma[\lambda/2\rho+i(q'-q)\lambda/2]\right|^4$$

$$\times \exp(-\hbar^2k^2/2mKT) \sinh \pi q'\lambda \sinh \pi q\lambda \left(\frac{qq'}{k'}\right) dk, \qquad (5.1)$$

where the constant B is given by

$$B = \frac{2\pi}{3} \frac{\mu_o^2\lambda^7 nn'm}{\hbar^2 c} \left(\frac{\hbar^2}{2\pi mKT\lambda^2}\right)^{3/2} \left(\frac{2\hbar^2}{mV_o\lambda^2}\right)^{\lambda/\rho} \frac{1}{\Gamma^2(\lambda/\rho)}, \qquad (5.2)$$

the final state wave number k' is a function of the initial state wave number k,

$$k' = \left(k^2 + 2m\omega/\hbar\right)^{1/2}, \qquad (5.3)$$

the initial and final state turning points R_o and R_o' must be determined for all values of the pairs (k,ℓ) and (k',ℓ'), respectively, as the solutions to

$$\left.\begin{aligned} k^2 - \frac{2mV_o}{\hbar^2} \exp(-2R_o/\lambda) - \frac{\ell(\ell+1)}{R_o^2} &= 0 \\ k'^2 - \frac{2mV_o}{\hbar^2} \exp(-2R_o'/\lambda) - \frac{\ell'(\ell'+1)}{R_o'^2} &= 0 \end{aligned}\right\}, \qquad (5.4)$$

so that R_o and R'_o are ultimately functions of the integration variable k and the summation variables ℓ and ℓ', and finally q and q' are defined as functions of k, ℓ, ℓ' by

$$\left.\begin{aligned} q &= \left[k^2 - \frac{\ell(\ell+1)}{R_o^2}\right]^{1/2} \\ q' &= \left[k'^2 - \frac{\ell'(\ell'+1)}{R_o'^2}\right]^{1/2} \end{aligned}\right\} , \tag{5.5}$$

VI. REMARKS ON THE EVALUATION OF THE INTEGRAL

Eq. (5.1) for the absorption coefficient $A(\omega)$ is equivalent to Tanimoto's expression.[27] The differences lie in approximations used in numerically evaluating the integral. Tanimoto has done machine computations for reciprocal wavelengths up to $\omega/2\pi c = 500\ \mathrm{cm}^{-1}$, and has developed an analytical approximation which he asserts duplicates the machine results quite closely above $300\ \mathrm{cm}^{-1}$. Since we plan to do an independent computer evaluation of $A(\omega)$, which is likely to be nontrivial, we feel an obligation to indicate why we do not instead simply use Tanimoto's results to predict the absorption by rare gases.

In addition to the mathematical reasons, it would be desirable to re-do the calculations and choose the parameters to fit the more recent data[12] at the (presumably) more easily measurable peaks of the absorption coefficients; Tanimoto's parameters were chosen to fit the older data in the near wings.[9]*

Now let us return to the mathematics. For certain special cases the gamma functions of complex argument reduce to more elementary functions. In particular we have[38]

$$|\Gamma(1/2 + iy)|^2 = \pi/\cosh \pi y, \tag{6.1}$$

$$|\Gamma(1 + iy)|^2 = \pi y/\sinh \pi y, \tag{6.2}$$

By combining these with the general relation for gamma functions

$$\Gamma(z + 1) = z\Gamma(z) \tag{6.3}$$

one may significantly simplify the integrals in Eq. (5.1) provided λ/ρ has any integral value. For this reason Tanimoto has chosen to consider only integral

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* This statement contains the implicit assumption that the more recent data is also the more reliable (recall that, as mentioned in Section I, the two sets of measurements are not strictly consistent with one another), which in turn is based only on the assumption that the larger the absorption coefficient the more easily it can be measured. Unfortunately, we are aware of no solid basis for choosing either set.

values of λ/ρ and has found $\lambda/\rho = 1$ to provide the best fit. One might consider going a step further and calculating $A(\omega)$ only for integral values of λ/ρ, but interpolating to obtain $A(\omega)$ for nonintegral values. However, one is still left with no satisfactory evaluation of $A(\omega)$ for the range $\lambda/\rho < 1$.

We have chosen the following alternative. Stirling's asymptotic formula for the gamma function,[38]

$$\Gamma(z) \sim \sqrt{2\pi}\, z^{z-1/2}\, e^{-z}\left(1 + \frac{1}{12z} + \dots\right) , \tag{6.4}$$

is very accurate for $|z| \gtrsim 2$. Therefore, by using (6.3) we may write

$$\Gamma(z) = \frac{\Gamma(z+2)}{z(z+1)} , \tag{6.5}$$

and then use Stirling's formula in (6.5) for $\Gamma(z+2)$. The result is ($z = x+iy$)

$$|\Gamma(z)|^2 \sim \frac{2\pi\left[(x+2)^2 + y^2\right]^{x+3/2}}{(x^2+y^2)\left[(x+1)^2 + y^2\right]}\left[1 + \frac{x+2}{6\left[(x+2)^2 + y^2\right]}\right] \times \exp\left[-2\left\{x + 2 + y \arctan\frac{y}{x+2}\right\}\right] , \tag{6.6}$$

which is quite accurate for $x \geq 0$. Thus we can evaluate $A(\omega)$ for all positive values (and therefore all physical values) of λ/ρ.

The other approximation to be considered has to do with the turning points R_o and R_o', which are defined as the solutions of Eq. (5.4) and therefore are functions of k, ℓ, ℓ'. Tanimoto has chosen to ignore the k, ℓ, ℓ' dependence and use one fixed value of R_o (and the same value for R_o'), namely the turning point for thermal energy and zero angular momentum, i.e., the solution to

$$k^2_{\text{thermal}} = \frac{2mV_o}{\hbar^2}\exp(-2R_o/\lambda) . \tag{6.7}$$

If we assume that the principal contribution to the integral in (5.1) does in fact come at the thermal value of k, there appears to still be a serious problem from ignoring the angular momentum dependence of R_o, and R'_o. The turning point in the absence of the repulsive angular momentum potential is necessarily smaller than in its presence, so that when the smaller values of R_o and R'_o are used in (5.5) the repulsive effect of the angular momentum terms is magnified and the effective wave numbers q and q' are diminished. As a result the wave function does not penetrate as far in and does not "see" as much of the dipole moment. Thus it would appear that this approximation systematically underestimates the dipole matrix element $M(\ell,\ell')$ of (3.9), and therefore underestimates $A(\omega)$. It is true that for small values of ℓ the angular momentum potential is negligible at the turning point compared to the exponential potential. However, we have made some numerical estimates of the terms contributing to the summation over ℓ in (5.1) for the special case in which the Boltzmann distribution over energy is replaced by a delta function peaked at thermal energy; we found that the maximum contribution occurred for $\ell \sim 30$, and significant contributions still occurred for $\ell \sim 60$.

Thus we feel that the approximation of a constant turning point is unsatisfactory. The remainder of our program includes a solution of (5.4) to obtain R_o and R'_o as functions of k, ℓ, and ℓ'.

APPENDIX

In this appendix we outline the procedure for evaluating the integral

$$\vec{I}(\ell,\ell') = \int P_\ell(\cos\theta_f)\ P_{\ell'}(\cos\theta_i)\ \hat{R}\ d\Omega_i\ . \tag{A1}$$

First, in the coordinate system with polar axis along $\vec{k}_i$, $\hat{R}$ may be written

$$\hat{R} = \sin\theta_i\ \cos\phi_i\ \hat{x} + \sin\theta_i\ \sin\phi_i\ \hat{y} + \cos\theta_i\ \hat{z}\ . \tag{A2}$$

Next, $P_\ell(\cos\theta_f)$ may be written in terms of the variables of this same coordinate system by using the addition theorem for Legendre polynomials,[39]

$$P_\ell(\cos\theta_f) = P_\ell(\cos\theta_{fi})\ P_\ell(\cos\theta_i) + 2\sum_{m=1}^{\ell} \frac{(\ell-m)!}{(\ell+m)!}\ P_\ell^{\ m}(\cos\theta_{fi})\ P_\ell^{\ m}(\cos\theta_i)\ \cos m(\phi_i-\phi_{fi}), \tag{A3}$$

where θ_{fi} and ϕ_{fi} are the coordinates of $\vec{k}_f$ in the $\vec{k}_i$ system. Using the addition theorem in (A1) we obtain

$$I_x(\ell,\ell') = \frac{2\pi}{\ell(\ell+1)}\ P_\ell^{\ 1}(\cos\theta_{fi})\ \cos\phi_{fi} \int_0^\pi P_\ell^{\ 1}(\cos\theta)\ P_{\ell'}(\cos\theta)\ \sin^2\theta\ d\theta, \tag{A4}$$

$$I_y(\ell,\ell') = \frac{2\pi}{\ell(\ell+1)}\ P_\ell^{\ 1}(\cos\theta_{fi})\ \sin\phi_{fi} \int_0^\pi P_\ell^{\ 1}(\cos\theta)\ P_{\ell'}(\cos\theta)\ \sin^2\theta\ d\theta, \tag{A5}$$

$$I_z(\ell,\ell') = 2\pi\ P_\ell(\cos\theta_{fi}) \int_0^\pi P_\ell(\cos\theta)\ P_{\ell'}(\cos\theta)\ \cos\theta\ \sin\theta\ d\theta\ . \tag{A6}$$

The integrals in (A4, 5, 6) may now be evaluated using the identities[40]

$$(2n+1)\ (1-z^2)^{1/2}\ P_n^{\,m}(z) = P_{n+1}^{m+1}(z) - P_{n-1}^{m+1}(z)\ , \tag{A7}$$

$$(2n+1)\ z\ P_n^{\,m}(z) = (n-m+1)\ P_{n+1}^{m}(z) + (n+m)\ P_{n-1}^{m}(z)\ , \tag{A8}$$

and the orthogonality relation for Legendre functions,[40]

$$\int_{-1}^{1} P_\ell^{\,m}(z)\ P_{\ell'}^{m}(z)dz = \frac{2}{2\ell+1}\ \frac{(\ell+|m|)!}{(\ell-|m|)!}\ \delta(\ell,\ell')\ , \tag{A9}$$

where $\delta(\ell,\ell')$ is a Kroneker delta. The result is

$$\begin{aligned}\int_0^\pi P_\ell^{\,1}(\cos\theta)\ P_{\ell'}(\cos\theta)\ \sin^2\theta d\theta &= \frac{2\ell(\ell+1)}{(2\ell-1)(2\ell+1)}\ \delta(\ell-1,\ell') \\ &\quad - \frac{2\ell(\ell+1)}{(2\ell+3)(2\ell+1)}\ \delta(\ell+1,\ell')\ ,\end{aligned} \tag{A10}$$

$$\begin{aligned}\int_0^\pi P_\ell(\cos\theta)\ P_{\ell'}(\cos\theta)\ \cos\theta\ \sin\theta d\theta &= \frac{2\ell}{(2\ell-1)(2\ell+1)}\ \delta(\ell-1,\ell') \\ &\quad + \frac{2(\ell+1)}{(2\ell+3)(2\ell+1)}\ \delta(\ell+1,\ell')\ .\end{aligned} \tag{A11}$$

When these are substituted into (A4, 5, 6) we obtain Eq. (3.11) of the text.

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Chapter 4.

STIMULATED RAMAN EFFECT

I. INTRODUCTION

In this chapter we shall investigate the effects of Raman scattering on the propagation of high intensity laser light through the atmosphere. The general problem of laser light propagation is an extremely complex one which involves many different physical processes. In order to make any headway in understanding the effects of Raman scattering we shall consider a situation in which the effects of self-focusing, etc., have produced a stable beam (or filamentary "hot spot" within a beam) of uniform intensity and cross-section. Extending the work of Helwarth,[1,2] it is possible to derive a set of rate equations which relate the intensities of the various orders of forward amd back amplified Stokes waves to the laser-light intensity. This set of coupled, nonlinear, partial differential equations with varying coefficients appears, at first glance, to be quite intractable. However, by first examining a highly simplified version of these equations and then treating, in turn, each of the various complications of the simplified equations which comprise the original equations, it is possible to obtain a coherent description of the physical phenomena involved.

The rate of creation of Raman-scattered photons in a laser beam is composed of a term proportional to the laser beam intensity (spontaneous emission) and a term proportional to the product of the laser beam intensity and the intensity of the Raman photons already present (stimulated emission). If the rate of creation of Raman-scattered photons parallel to the beam (i.e., either forward or backscattered) is much larger than the rate of destruction of these photons due to Rayleigh scattering, then the intensity of these Raman photons will be amplified at the expense of the primary laser photons until the primary beam is totally depleted. The specific manner in which the primary beam is extinguished will be the subject of sections II through V. Section VI will relate the current status of the author's researches into certain transient phenomena.

II. NEGLIGIBLE BACKSCATTER

Let us consider the propagation of a beam of laser light through a gas in which the amplification of the backscattered Stokes waves may be neglected (the criteria for the existence of such a gas will be discussed in section V.). Assuming, to begin with, that only the first Stokes wave is of any consequence, the densities of the laser photons $\rho_\ell(x,t)$ and amplified forward scattered Raman photons $\rho_r(x,t)$ in the beam are related by the rate equations

$$\left(\frac{\partial}{\partial t} + c\,\frac{\partial}{\partial x}\right)\rho_\ell = -\,\rho_\ell(\alpha\rho_r+\beta_o) - \gamma\rho_\ell\ , \qquad (1)$$

$$\left(\frac{\partial}{\partial t} + c\,\frac{\partial}{\partial x}\right)\rho_r = +\,\rho_\ell(\alpha\rho_r+\beta) - \gamma\rho_r\ , \qquad (2)$$

where

$$\alpha = \frac{c^3}{2\nu^2\Delta\nu}\,c\rho_T\sigma(0),\quad \beta_o = c\rho_T\,\sigma_{\mathrm{Ram.}}\ ,\quad \gamma = c\rho_T\,\sigma_{\mathrm{Ray.}}\ .$$

The quantities $\sigma_{\mathrm{Ray.}}$ and $\sigma_{\mathrm{Ram.}}$ are the Rayleigh and Raman total scattering cross-sections respectively, ρ_T is the density of the gas, $\Delta\nu$ is the line width of the amplified wave, and $\sigma(0)$ is the Raman forward scattering cross-section. The quantity β is given by

$$\beta = c\rho_T\,\sigma(0)\,\frac{\Omega_o}{4\pi}\ , \qquad (3)$$

where Ω_o is the effective cone angle for Raman amplification — Ω_o' will be discussed in greater detail later in this section. The boundary value conditions for Eqs. (1) and (2) are

$$\rho_\ell(0,t) = \rho_o(t)\ ,\quad \rho_o(t) = 0 \text{ for } t < 0, \text{ and } \rho_r(0,t) = 0\ . \qquad (4)$$

We now make the substitutions:

$$s = t - \frac{x}{c} , \quad y = x , \quad \frac{\partial}{\partial t} + c \frac{\partial}{\partial x} = c \frac{\partial}{\partial y}$$

in Eqs. (1) and (2). Equation (1) may now be rewritten as

$$c \frac{\partial \rho_\ell}{\partial y} = -\rho_\ell(\alpha\rho_r + \beta) - (\gamma + \beta_o - \beta)\, \rho_\ell \tag{5}$$

For nitrogen^3

$$\sigma_{Ram.} \cong 10^{-28} cm^2 \quad \text{and} \quad \sigma_{Ray.} \cong 10^{-27} cm^2 .$$

and hence $\gamma >> \beta_o - \beta$, and we can neglect $\beta_o - \beta$ with respect to γ in Eq. (5) and make only a minimal error. The solution of Eqs. (1) and (2) with this approximation is

$$\left.\begin{aligned} \rho_\ell(x,t) &= \rho_o(s)\, \frac{e^{-\Gamma(x)}}{1+J(x)} , \\ \rho_r(x,t) &= \rho_o(s)\, e^{-\Gamma(x)} - \rho_\ell(x,t) \end{aligned}\right\} \tag{6}$$

where $\Gamma(x) = \frac{1}{c} \int_o^x dx' \, \gamma(x')$ and

$$J(x) = \int_o^x \frac{dx'}{c} \, \beta(x') \exp \left\{ \int_{x'}^x \frac{dx''}{c} \left[\beta(x'') + \rho_o(s)\alpha(x'') \, e^{-\Gamma(x'')} \right] \right\} \tag{7}$$

The x-dependance of α, β, and γ is due to the altitude dependance of ρ_T and $\Delta\nu$ for a laser beam which is aimed nonhorizontally in the atmosphere. From Eq. (2) we may note that no amplification of ρ_r can occur unless $\alpha\, \rho_o > \gamma$. For N_2 at atmospheric pressure this is equivalent to having the laser intensity at

$x = o$ (I_o) satisfy the inequality

$$I_o > 60 \text{ watts/cm}^2.$$

We shall therefore assume the above inequality to be valid for the remainder of this work.

Consider first a horizontally aimed laser beam. For distances of a few tens of kilometers $\Gamma(x)$ is completely negligible. Assuming that $\rho_o(t) = \rho_o$ is a constant for $t > o$ and defining the dimensionless quantities

$$\mu = \frac{\alpha}{\beta}\,\rho_o,\ z = \frac{\beta}{c}\,x,\ F_\ell = \frac{\alpha}{\beta}\,\rho_e,\ F_r = \frac{\alpha}{\beta}\,\rho_r\,.$$

Equation (6) may now be rewritten as

$$\left.\begin{aligned} F_\ell &= \frac{\mu(\mu+1)}{\mu + e^{(\mu+1)z}}\,, \\ F_r &= \mu\,\frac{e^{(\mu+1)z} - 1}{\mu + e^{(\mu+1)z}}\,. \end{aligned}\right\} \qquad (8)$$

These solutions indicate that for $\mu >> 1$ the laser light will penetrate the gas to a depth of the order of $z_c = \mu^{-1}\ell n(\mu)$ in such a manner as to be essentially undiminished in intensity (i.e., $F_\ell \doteq \mu$ for $z \lesssim z_c$). Beyond this depth the laser light intensity will rapidly decrease to zero and the intensity of the first Stokes wave will rapidly rise to the level of the original laser beam.

The effective cone angle for Raman amplification (Ω_o) is a vaguely defined quantity as it represents an attempt to solve a basically three-dimensional problem by geometrically correcting one of the coefficients in the solution of the corresponding one-dimensional problem. However, since - as we shall demonstrate below - the laser intensity drops from $I_o = \rho_o\ h\nu c$ to zero is a very small distance, and the initial intensity I_c which will cause the intensity to drop to zero at a distance $\ell = 8 \times 10^3$ km (the scale height of the atmosphere) is extremely insensitive to our choice of Ω_o, the results we obtain with the aid of this correction factor should be quite good.

For a beam diameter D and a z_c corresponding to ℓ, Ω_o is given by

$$\Omega_o = \frac{1}{\ell^2}\left(\frac{\pi}{4} D^2\right) = \frac{\pi D^2}{4\ell^2} \quad .$$

For N_2 at one atmosphere $\Delta\nu$ is the pressure broadened line width given by[4]

$$\frac{\Delta\nu}{c} = .09 \text{ cm}^{-1} \quad .$$

Using $\sigma(o) = (4\pi)^{-1}\ \sigma_{Ram}$, $\nu = 5 \times 10^{14}$ sec^{-1} and taking D = 10 cm we may define a quantity I_c which is that value of $I_\ell(o) \equiv I_o$ for which $I_\ell(\ell)$ is one half of I_o; i, e.,

$$I_\ell(o) \equiv I_o = I_c \quad \text{and} \quad I_\ell(\ell) = \frac{1}{2} I_c \quad . \tag{9}$$

This quantity may be obtained from

$$\xi_c = \mu_c z = \alpha\rho_o \frac{\ell}{c} \qquad \text{or} \qquad I_c = 3.90\ \xi_c \text{ kilowatts/cm}^2 \ ,$$

where ξ_c is the solution of the equation

$$\frac{e^{\xi_c}}{\xi_c} = \frac{1}{z} = \frac{1}{\ell\rho_T\sigma(o)}\left(\frac{1}{\Omega_o}\right) = 6.4 \times 10^{13} \quad . \tag{12}$$

The solution of this equation is $\xi_c = 35.4$ and hence

$$I_c = 140 \text{ kw/cm}^2 .$$

From Eq. (12) we obtain that

$$\frac{\delta\xi_c}{\xi_c} = \frac{\delta I_c}{I_c} = -\frac{1}{35}\frac{\delta\Omega o}{\Omega_o}$$

verifying our assertion that I_c is insensitive to our choice of Ω_o. Examining Eq. (8) we find that for $I_o = I_c$, I_ℓ drops from $(.75)I_c$ to $(.25)I_c$ in a distance Δx given by

$$\frac{\Delta x}{\ell} = .062 \quad \text{or} \quad \Delta x = 500 \text{ meters},$$

and hence the transition region is quite narrow and Ω_o may be defined in a reasonably unambiguous manner. In fact, $\delta\Omega_o/\Omega_o \doteq 2\ \Delta x/\ell$ and hence the ambiguity in Ω_o results in a fractional error

$$\frac{\delta I_c}{I_c} \doteq \frac{1}{35}\frac{2\Delta x}{\ell} \doteq 4 \times 10^{-3} .$$

A plot of the fractional transmission to a depth ℓ versus the initial intensity, or

$$\frac{1}{\mu} F_\ell = \frac{1+\mu}{\mu + e^{(\mu+1)z}}$$

versus μ for fixed z, would result in a curve much like that for $I_\ell(x)$ vs. x.

That is, $I_o^{-1} I_\ell(\ell)$ would be roughly constant and equal to one for $0 < I_o < I_c$, equal to 1/2 for $I_o = I_c$, and drop sharply to zero for $I_o > I_c$. A plot of the total transmission (I_ℓ) versus I_o would therefore yield a curve which would show a roughly linear rise from zero to some maximum value $I_m \approx I_c$, and then fall rapidly to zero. The maximum transmission to a depth ℓ is readily obtained from Eq. (8) by setting the derivative of F_ℓ with respect to μ equal to zero. The result is

$$I_m = \frac{I_o}{1 + (\xi_m - 2)^{-1}} \;, \quad I_o = 3.90\, \xi_m \text{ kw/cm}^2 \;, \tag{13}$$

where ξ_m is the solution of

$$(1 - \frac{2}{\xi_m}) e^{\xi_m} = \frac{1}{z} \;. \tag{14}$$

For the parameters of interest here

$$I_m = 120 \text{ kw/cm}^2 \text{ and } I_o = 124 \text{ kw/cm}^2 \;.$$

III. ALTITUDE DEPENDENCE

Let us now consider a vertically aimed beam in an exponential atmosphere with

$$\rho_T(x) = \rho_T(o)e^{-x/\ell} \quad . \tag{15}$$

Since we are mainly concerned with computing the maximum intensity which can be transmitted through the top of the atmosphere we may assume that the Raman line is virtually unchanged throughout almost the entire beam. We may therefore assume the line width of the amplified wave to be

$$\Delta\nu = \Delta\nu_p(o)\left[\eta + e^{-x/\ell}\right] \quad \text{and} \quad \eta = \frac{\Delta\nu_\ell}{\Delta\nu_p(o)} \quad , \tag{16}$$

where $\Delta\nu_p(o)$ is the pressure broadened Raman line width and $\Delta\nu_\ell$ is the line width of the original laser beam. Using Eqs. (15) and (16) to obtain α, β, and γ as a function of x and inserting the results in Eqs. (6) and (7) we find that $\Gamma(x)$ (the effects of Rayleigh scattering) is negligible. A good approximation to $J(y)$ may then be obtained for altitudes greater than one kilometer. The result is

$$J(y) = \frac{1}{\mu} e^{\mu z_o f(y)} \quad , \tag{17}$$

where $z_o = \beta\ell/c$ and

$$f(y) = -\ln\left\{\frac{\eta + e^{-y/\ell}}{\eta + 1}\right\} \quad . \tag{18}$$

Inserting Eq. (18) in Eq. (6) we obtain

$$F_\ell(y) = \frac{\mu^2}{\mu + e^{\mu z_o f(y)}} \quad . \tag{19}$$

Choosing $(\Delta\nu_\ell/c) = 1.2 \times 10^{-3}\ \mathrm{cm}^{-1}$ (which is typical for the line width for a Ruby Giant Pulse Laser[5]) we find that

$$\eta = \frac{1}{75} \ .$$

For $y << y_o = -\ell \ \ell n \ \eta = 35$ km, it follows that $z_o f \doteq z_o y/\ell = z$, and Eq. (19) agrees with Eq. (8) to within the approximations made here.

A calculation of the maximum transmission of laser light to an altitude y may be made in a manner similar to that used for the analogous quantity in the preceding section. The result is

$$I_m = \frac{I_o}{1 + (\xi_m - 2)^{-1}} \quad , \ I_o = 3.90 \ \frac{\xi_m}{f(y)} \ \mathrm{kw/cm}^2 \ , \tag{20}$$

where ξ_m is solution of

$$(1 - \frac{2}{\xi_m}) e^{\xi_m} = \frac{1}{zf(y)} = \frac{f(y)}{z_o} \ . \tag{21}$$

The last equality is valid since for $y > y_o$ the effective cone angle for Raman amplification (Ω_o) is proportional to y_o^2. For y >> 35 km (i.e., for above the atmosphere), the maximum laser intensity which can be transmitted, and the laser intensity necessary at the source to achieve that maximum are

$$I_m = 27 \ \mathrm{kw/cm}^2 \quad , \ I_o = 28 \ \mathrm{kw/cm}^2 \ .$$

It is of interest to note that the atmosphere will act as an amplifier for Raman waves up to an altitude of approximately y_o (about four scale heights). This fact is most easily understood if we note that the gain is proportional to $\rho_T/\Delta\nu$. It then becomes clear that the amplification of Raman waves up to y_o occurs because although the density of N_2 decreases with altitude, the width of the pressure broadened Raman line decreases in a proportionate manner. The net effect is to produce a constant gain for $y < y_o$ (i.e., as long as $\Delta\nu$ is dominated by $\Delta\nu_p$) and a consequent decrease in the maximum transmittable power. In order to minimize this effect the laser line should be made as broad as possible. If the laser line is significantly broader than the pressure broadened Raman line, then $\alpha(x)$ is proportional to the local density and the solution of Eqs. (1) and (2) may be obtained from Eqs. (8) by making the substitution

$$z \rightarrow \tau = z_o(1 - e^{-x/\ell}) \qquad (22)$$

where τ is the optical depth. Consequently, the intensity of laser light transmitted vertically to a point far above the atmosphere will be the same as that transmitted a distance of one scale height through air held at the constant pressure of one atmosphere throughout the beam.

Of further interest is the fact that Rayleigh scattering is virtually always inconsequential for the intensities of interest here. Its major effect is to provide us with a good reason for changing β_o to β in Eq. (1).

IV. MULTIPLE STOKES LINES

Let us now consider a case in which the laser beam intensity is much larger than that necessary to induce its conversion to the first Stokes wave within a certain prescribed distance. This first Stokes wave will then propagate a certain distance until it is converted into the second Stokes wave, etc. Assuming that the pressure is constant along the beam path and that the effects of back scattering may be neglected, there will, in general be N Stokes waves (of frequency $\nu_\ell - \nu_r$, $\nu_\ell - 2\nu_r$, ..., $\nu_\ell - N\nu_r$, for a laser frequency ν_ℓ and a Raman frequency shift ν_r) which will attain a significant intensity within a given depth in the gas. In the dimensionless units of Section II the photon densities of these Stokes waves are coupled by the set of equations:

$$\left.\begin{aligned}
\frac{d}{dz} F_\ell &= - F_\ell(F_1 + 1) \\
\frac{d}{dz} F_1 &= F_\ell(F_1 + 1) - F_1(F_2 + 1) \\
&\vdots \\
\frac{d}{dz} F_{N-1} &= F_{N-2} (F_{N-1} + 1) - F_{N-1}(F_N + 1) \\
\frac{d}{dz} F_N &= F_{N-1}(F_N + 1)
\end{aligned}\right\} \qquad (23)$$

These equations have been solved exactly for the case of $N = 2$. The solution is too complicated mathematically for the reader to obtain much use from its display here. Basically, it describes a situation in which the laser beam penetrates the gas to a depth $z_1 = \mu^{-1} \ln \mu$ in such a manner as to be essentially undiminished in intensity. Beyond this depth the laser light intensity will rapidly decrease to zero and the first Stokes wave will rapidly rise to the level of the original laser beam. Between z_1 and $z_2 = 2\mu^{-1} \ln \mu$, F_1 is roughly equal to the constant μ. At z_2 the first Stokes wave suddenly falls to zero and the second Stokes wave (F_2) rises to μ. A close examination of Eq. (22), taking due note of the fact that

$$F_\ell(z) + \sum_{m=1}^{N} F_m(z) = \mu$$

(obtained by adding Eq. (23) and integrating the result), indicates that this process will continue for a very large number of orders if $\mu >> N$. Hence, if we wish to transmit energy in a beam vertically through the atmosphere, it would be advisable to choose ν_ℓ as the highest frequency of a window in the atmospheric transmissivity. If the width of the window is $N\nu_r$, and if the intensity of the laser beam is the maximum permissible, then a light beam of frequency $\nu_\ell - N\nu_r$ will emerge from the top of the atmosphere. On the basis of Eq. (22) we may estimate this maximum intensity to be the critical intensity for a distance ℓ/N. That is

$$I_m = 3.90 \, (N\xi_c) \text{ kw/cm}^2 \tag{24}$$

where

$$\frac{e^{\xi_c}}{\xi_c} = \frac{1}{Nz_o} \; .$$

For a transmission window of 100 Å and a Raman wavelength shift[6] of 12 Å we have N = 8 and

$$I_m = 1.0 \text{ megawatt/cm}^2 \quad ,$$

if $\Delta\nu_\ell \lesssim \Delta\nu_p(o)$.

V. THE EFFECTS OF BACKSCATTERING

For the case of comparable Raman forward and back scattering cross sections in an infinite gas of uniform density along the ray path let us assume that only the first Stokes wave is of any consequence (this is true up to the second critical depth which is beyond the distances of interest in this section). The rate equations relating ρ_ℓ to the forward (ρ_f) and back scattered (ρ_b) photon densities are

$$\left(\frac{\partial}{\partial t} + c\frac{\partial}{\partial x}\right)\rho_\ell = -\rho_\ell\left[\alpha_f\rho_f + \alpha_b\rho_b + \beta_f + \beta_b\right] , \qquad (25)$$

$$\left(\frac{\partial}{\partial t} + c\frac{\partial}{\partial x}\right)\rho_f = \rho_\ell(\alpha_f\rho_f + \beta_f) , \qquad (26)$$

$$\left(\frac{\partial}{\partial t} - c\frac{\partial}{\partial x}\right)\rho_b = \rho_\ell(\alpha_b\rho_b + \beta_b) . \qquad (27)$$

The transient response of the above equations is extremely complex. Let us reserve our discussion of this response for Section VI and consider only the steady state solutions (i.e., where the time derivatives in the above equations vanish) here.

Adding Eqs. (25), (26), and (27), and integrating the result we obtain

$$\begin{aligned}\rho_\ell(x) + \rho_f(x) - \rho_b(x) &= \text{constant} \\ &= \rho_o - \rho_b(o) = \rho_f(L) \qquad (28)\end{aligned}$$

or,

$$\rho_b(o) + \rho_f(L) = \rho_o \quad . \tag{29}$$

In the above we have taken L to be a point just before the second Stokes wave becomes important. Dividing Eq. (26) by Eq. (27) we readily obtain

$$\left[1 + \frac{\alpha_f}{\beta_f}\rho_f(x)\right]\left[1 + \frac{\alpha_b}{\beta_b}\rho_b(x)\right]^{\alpha_f/\alpha_b} = \text{constant}$$

$$= 1 + \frac{\alpha_f}{\beta_f}\rho_f(L) = \left[1 + \frac{\alpha_b}{\beta_b}\rho_b(o)\right]^{\alpha_f/\alpha_b} \tag{30}$$

or,

$$1 + \frac{\alpha_f}{\beta_f}\rho_f(L) = \left[1 + \frac{\alpha_b}{\beta_b}\rho_b(o)\right]^{\alpha_f/\alpha_b} , \tag{31}$$

The substitution of Eq. (31) into Eq. (29) yields

$$\left[1 + \frac{\alpha_b}{\beta_b}\rho_b(o)\right]^{\alpha_f/\alpha_b} + \frac{\alpha_f}{\beta_f}\rho_b(o) = 1 + \frac{\alpha_f}{\beta_f}\rho_o \quad . \tag{32}$$

If $\Delta\nu_f = \Delta\nu_b$, then $(\alpha_f/\beta_f) = (\alpha_b/\beta_b)$, $(\alpha_f/\alpha_b) = \sigma(o)/\sigma(\pi)$ and we may define a quantity M such that

$$M = 1 + \frac{\alpha}{\beta}\rho_b(o) \quad .$$

M satisfies the equation

$$M^{\sigma(o)/\sigma(\pi)} + M = 2 + \mu \quad . \tag{33}$$

If $\sigma(o) = \sigma(\pi)$ then

$$\rho_b(o) = \rho_f(L) = \frac{1}{2}\rho_o$$

and the energy in the original laser beam is shared equally between the forward and back scattered waves. However, for $I_o = 100$ kw/cm^2 the solution of Eq. (33) indicates that for

$$\rho_b(o) = .05\ \rho_o \text{ and } \rho_f(L) = .95\ \rho_o ,$$

$$\frac{\sigma(o) - \sigma(\pi)}{\sigma(o)} = .08 .$$

That is, forward scattering will dominate back scattering as a mechanism for extinguishing the laser beam if the asymmetry in the cross-section is as small as 8%. Conversely, the back scattering will dominate the forward scattering if the cross section of the former exceeds that of the latter by as little as 8%. This second case is particularly distressing since the atmosphere will then essentially act as a mirror - reflecting all the energy back at the source - if the source intensity exceeds some critical value for a given path length.

If $\sigma(o) = \sigma(\pi)$ then Eqs. (25), (26) and (27) are easily solved. The results are

$$\left.\begin{aligned} F_\ell &= \frac{\mu(\mu+4)^2W}{[2(\mu+2)W-\mu][4W+\mu]} , \\ F_f &= 2\mu\ \frac{W-1}{4W+\mu} , \\ F_b &= \left(\frac{1}{2}\right)\frac{\mu(\mu+4)}{2(\mu+2)W-\mu} , \end{aligned}\right\} \tag{34}$$

where $W = e^{\frac{\mu+4}{2} z}$.

The critical intensity defined by Eq. (9) is 130 kw/cm^2 which is virtually unchanged from the case of pure forward scattering where $I_c = 140\ kw/cm^2$. However, the shape of the $I_\ell(x)$ vs. x and $I_\ell(\ell)$ vs. I_o curves are somewhat different for the two cases: The distance in which I (x) drops from .75 I_c to .25 I_c is $\Delta x = 850$ meters versus 500 meters for the case of no back scatter. Similarly, for $I_o = I_c$: $I_\ell(\ell) = 65\ kw/cm^2$, and $I_f(\ell) = I_b(\ell) = 2 \times 10^{-3}\ W/cm^2$; whereas for the case of negligible back scatter if $I_o = I_c$ then $I_\ell(\ell) = I_f(\ell) = 70\ kw/cm^2$. Consequently, the effect of backscatter is to soften the abrupt transitions in intensity which were characteristic of the I_ℓ curves.

It is of interest to note that if $\sigma(o) = \sigma(\pi)$ then the maximum achievable intensity at a depth ℓ, and the source intensity to achieve this intensity are

$$I_m = 118\ kw/cm^2 \text{ for } I_o = 243\ kw/cm^2$$

versus 120 and 124 kw/cm^2 for the case of negligible back scatter. Hence, I_m is essentially insensitive to the asymmetry in the cross section but, since $(.5)I_o$ is reflected back into the source for $\sigma(o) = \sigma(\pi)$, I_o must be roughly twice as large to achieve the same I_m in the symmetric case.

VI. TIME DEPENDANCE OF BACKSCATTERED WAVES

We were able to obtain ρ_ℓ and $\rho_f = \rho_r$ as a function of space and time for the case of inconsequential backscatter [see Eqs. (6) and (7)]. Unfortunately, we are unable to repeat this feat by solving Eqs. (25), (26), and (27). It is possible, however, to solve these equations for the case of inconsequential forward scattering and draw some inferences about the general case as well as obtain some results which are not directly related to the problem of atmospheric propagating but are nonetheless of physical interest.

Neglecting β_f in Eqs. (26) and (27), we find that $\rho_f = 0$. The change of variable

$$s = t - \frac{x}{c} \quad , \quad \tau = t + \frac{x}{c} \quad ,$$

$$R_\ell(s,\tau) = \rho_\ell(x,t) \quad , \quad R_b(s,\tau) = \rho_b(x,t)$$

enables us to write Eqs. (25) and (27) as

$$2 \frac{\partial R_\ell}{\partial \tau} = - R_\ell(\alpha R_b + \beta) \quad , \tag{35}$$

$$2 \frac{\partial R_b}{\partial s} = R_\ell(\alpha R_b + \beta) \; . \tag{36}$$

The general solution of these equations is given by

$$R_\ell(s,\tau) = \frac{\dot{F}(s)}{G(\tau) - \frac{\alpha}{2} F(s)} \quad , \tag{37}$$

$$R_b(s,\tau) = - \frac{\beta}{\alpha} + \frac{2}{\alpha} \frac{\dot{G}(\tau)}{G(\tau) - \frac{\alpha}{2} F(s)} \quad , \tag{38}$$

where F and G are arbitrary functions and $\dot{F}$ and $\dot{G}$ are the derivatives of these functions with respect to their arguments.

Let us now consider the solution of Eqs. (35) and (36) subject to the boundary value conditions

$$\rho_\ell(o,t) = \rho_o(t) \quad , \quad \rho_\ell = \rho_b = o \text{ for } t < o \quad . \tag{39}$$

Equation (36) indicates that R_b is a continuous function of s and hence, since $\rho_b = o$ for $t < 0$ we have

$$R_b(o,\tau) = o \quad . \tag{40}$$

Using Eqs. (39) and (40) in Eqs. (37) and (38) we obtain

$$R_\ell(s,\tau) = \rho_o(s) \frac{e^{-\beta \frac{x}{c}} - M(s,\tau)}{1 - M(s,\tau)} \tag{41}$$

$$R_b(s,\tau) = \frac{\beta}{\alpha} \frac{M(s,\tau)}{1 - M(s,\tau)} \quad , \tag{42}$$

where $2x = c(\tau-s)$ and

$$M(s,\tau) = \frac{\alpha}{2} \int_o^s d\xi \, \rho_o(\xi) \exp\left\{\frac{\beta}{2}(\xi-\tau) - \frac{\alpha}{2} \int_\xi^s d\xi' \, \rho_o(\xi')\right\} \quad . \tag{43}$$

If $\rho_o(t) = \text{constant} = \rho_o$ then for $s > o$

$$R_b = \rho_o \frac{1 - e^{-gs}}{[(\mu+1)e^z - \mu] + \mu e^{-gs}} \quad , \tag{44}$$

$$R_\ell = \rho_o \frac{1 + e^{-gs}}{[(\mu+1)e^z - \mu] + e^{-gs}} \tag{45}$$

where $2g = \beta + \alpha\rho_o$. Equation (45) indicates that

$$R_\ell(o, 2\frac{x}{c}) = \rho_\ell(x,ct) = \rho_o e^{-z} \tag{46}$$

and hence, since $z << 1$ for any distance of interest, the wave front propagates is such a manner as to be essentially unattenuated with distance. This is in contrast to the case where forward scattering dominates and ρ_ℓ drops sharply to zero for $x > x_c$. The reason for this difference is that: a spontaneously emitted photon which is created near the wave front and travels in the forward direction will maintain a constant distance with respect to the front and hence - upon being amplified - will exhaust the laser photon intensity at that point relative to the wave front; whereas, a similarly emitted photon which travels in the backward direction will rapidly leave the region of the wave front and hence cannot deplete the front by stimulating emission. Defining a quantity

$$t_o = \frac{1}{g} \ln(\frac{1}{z}) \doteq \frac{2}{\alpha\rho_o} \ln(\frac{c}{\beta x}) , \tag{47}$$

we find that for a time s - the time elapsed subsequent to the wave front passing a given point x - for $s > t_o$

$$R_\ell \rightarrow \frac{\rho_o}{(\mu+1)e^z - \mu} \doteq \frac{\rho_o}{1 + \mu z} . \tag{48}$$

That is, t_o is the time required for R_ℓ to come to a steady state.

Using $x = \ell$ and taking I_o to be the maximum intensity which can be transmitted through the atmosphere under the assumption of negligible back-scatter and $\eta \doteq 1$ (i.e., $I_o = 124$ kw/cm^2), we find that for $s > t_o$

$$I_\ell(\ell) \to 4 \text{ kw/cm}^2 \quad .$$

For this same choice of parameters

$$t_o = 5 \times 10^{-5} \text{ sec} \quad .$$

Hence, the steady state solutions of the preceding section are achieved in a time of the order of $t_o = 5 \times 10^{-5}$ sec. If we wish to circumvent the various limitations and difficulties imposed on us by backscatter, we must restrict ourselves to the transmission of pulses of laser light with durations less than 5×10^{-5} sec.

It is of interest to examine the interaction of a laser beam with a wave packet of photons at the first Stokes frequency which is traveling in the beam but antiparallel to it. For this problem it is most convenient to solve the initial value problem

$$\rho_\ell(x,o) = L(x) \quad , \quad \rho_b(x,o) = B(x) \; . \tag{49}$$

Using Eq. (49) in Eqs. (37) and (38), we readily obtain

$$R_\ell(s,\tau) = \frac{L(-cs)}{1 + \frac{\alpha}{2}\int_{-s}^{\tau} d\xi \; [B(c\xi) + \frac{\beta}{\alpha}] e^{\Gamma(\xi,-s)}} \; , \tag{50}$$

$$R_b(s\tau) = -\frac{\beta}{\alpha} + \frac{B(c\tau) + \frac{\beta}{\alpha}}{1 - \frac{\alpha}{2}\int_{-s}^{\tau} d\xi \; L(c\xi) e^{-\Gamma(\tau,\xi)}} \quad , \tag{51}$$

where

$$\Gamma(x,y) = \frac{\beta}{2}(x-y) + \frac{\alpha}{2}\int_x^y d\xi\,[L(c\xi) + B(c\xi)] \quad .$$

Let us examine the results of a wave packet of Stokes waves of spatial width W and photon density ρ_1 colliding with a laser beam of photon density ρ_o at $t = o$. That is, let

$$\left.\begin{aligned} L(x) &= \begin{cases} \rho_o & \text{for} \quad x \leq 0 \\ 0 & \text{for} \quad x > 0 \end{cases} \\ B(x) &= \begin{cases} \rho_1 & \text{for} \quad o < x < W \\ 0 & \text{Otherwise} \end{cases} \end{aligned}\right\} \quad . \qquad (52)$$

The R_b - wave which is generated by B(x) lies in the domain $o < \tau < W$ in the $s - \tau$ plane. The region $\tau < o$ is completely unaffected by B(x). If we define the gain and initial value parameters

$$g_i = \frac{1}{2}(\beta + \alpha\rho_i) \quad , \qquad \mu_i = \frac{\alpha}{\beta}\rho_i \quad ,$$

the photon densities for $\tau < o$ are

$$\rho_\ell(x,t) = \rho_o \frac{1 + \mu_o}{e^{2g_o t} + \mu_o} \quad . \qquad (53)$$

$$\rho_b(x,t) = \rho_o \frac{e^{2g_o t} - 1}{e^{2g_o t} + \mu_o} \quad . \qquad (54)$$

Therefore, in the absence of an initiating pulse: the back scattered wave is monotonically increasing in time and ρ_b approaches the value ρ_o as $t \to \infty$. The laser beam intensity is monotonically decreasing and eventually decays to zero.

The pulse shape is described by

$$R_b(s,\tau) = \frac{\rho_1(\mu_o+1) + \rho_o\, e^{-g_1\tau\left(1-e^{-g_o s}\right)}}{\mu_o + 1 - \mu_o\, e^{-g_1\tau\left(1 - e^{-g_o s}\right)}} \quad . \tag{55}$$

The wave front of the pulse is given by $\tau = o$. At a time which is long compared to $(2g_o)^{-1} \ln \mu_o$ the pulse height approaches

$$R_b(\infty,o) = \rho_1(\mu_o+1) + \rho_o = \rho_o(\mu_1+1) + \rho_1 . \tag{56}$$

The laser beam is therefore capable of amplifying the photon density to a level which is far in excess of ρ_o. This amplification however, is limited by the spontaneous depletion of the laser beam dictated by Eq. (53). If we wish to amplify a pulse by passing it through a cell of Raman-active material of length d we will generally find that for a reasonable set of assumptions about the parameters available in the laboratory

$$\mu_o\, e^{-\alpha\rho_o \frac{d}{c}} >> 1 \quad , \tag{57}$$

and hence, the maximum pulse height is limited by the length of the cell rather than the spontaneous creation rate β. In that case, the height of the emerging pulse is given by

$$R_b(2\,\tfrac{d}{c}\,,\, o) \cong \rho_1\, e^{\alpha\rho_o \frac{d}{c}} \quad . \tag{58}$$

The half width of this pulse is given by

$$\tau_o = \frac{2}{\alpha\rho_1} e^{-\alpha\rho_o \frac{d}{c}} \tag{59}$$

which will generally be an extremely short time. The ratio of the emerging pulse energy to the energy stored in that part of the beam which is present in the cell at t = o is approximately

$$U = 2 + \frac{\rho_1}{\rho_o} \frac{W}{d} - \frac{2c}{\alpha\rho_o d} e^{-\alpha\rho_1 \frac{W}{c}} . \tag{60}$$

On the basis of Eqs. (58), (59), and (60), it would seem to be feasible to concentrate virtually the entire energy in a laser beam into a pulse with an intensity of the order of 10^{13} watts/cm^2 and width of the order of 10^{-12} sec. Experiments have been performed[7] in which the initiating pulse appeared to be generated by Townes Self Focusing at the end of the cell. The emerging pulse had $U \doteq 1/5$ and $\tau_o \doteq 3 \times 10^{-11}$ sec.

VII. CONCLUSIONS

We have found that Raman backscattering is inconsequential as a loss mechanism in the propagation of a beam of laser light vertically through the atmosphere if the laser light is composed of pulses of duration no greater than 5×10^{-5} sec, or if $\sigma(o)$ exceeds $\sigma(\pi)$ by eight percent or more. If neither of these requirements are met then the source intensity necessary to transmit the maximum amount of energy through the atmosphere would be increased by a factor of two. In that case, the intensity of the back scattered wave at the source will be one-half the source intensity and considerable damage to the source and its environs may result. It is therefore recommended that experiments to determine the asymmetry of the Raman cross section be performed if pulse durations in excess of 5×10^{-5} sec are desired.

The maximum intensity of laser light which can be transmitted vertically through the atmosphere without frequency change due to Raman scattering is critically sensitive to the laser line width $(\Delta\nu_\ell/c)$. If $(\Delta\nu_\ell/c) = 1.2 \times 10^{-3}$ cm^{-1}, and if back scatter is inconsequential then for a beam with a 10 cm diameter, this maximum intensity is 27 kw/cm^2, whereas, if $\Delta\nu_\ell/c$ is of the order of the pressure broadened line width (9×10^{-2} cm^{-1}) the maximum intensity is 120 kw/cm^2. It was suggested that intensities far in excess of this figure may be transmitted in the form of a higher order Stokes wave. If we wish to transmit energy through a window in the atmospheric transmissivity of width $N\nu_r$ (ν_r being the frequency shift due to Raman scattering), then the maximum emergent N-th order Stokes wave will be approximately N times the figure cited above. However, this suggestion did not take the probably deleterious effects of defocusing on each successively higher order Stokes wave into account. A theoretical investigation of this three-dimensional effect as well as a more precise evaluation of the parameter Ω_o should be performed.

Finally, the technique for producing high intensity pulses of extremely short duration discussed at the end of Section VI, appears to be potentially quite promising. Further investigations along these lines may prove to be rather fruitful.

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13. ABSTRACT

The phenomena which constitute ultimate limitations to the transmission of intense laser radiation through the atmosphere are investigated, namely, self-defocusing due to atmospheric heating and the stimulated Raman effect. The heating studies are concerned with processes contributing to residual absorption in atmospheric transmission windows. A quantum mechanical study of the far-wing pressure broadening of molecular vibrational lines is carried out. The spectral distance beyond which the Lorentz-type behavior fails is found as a function of temperature and range of the interaction potential. It is shown that far wing fall-off is exponential. A study of the diffuse band of the $(O_2)_2$ complex spanning the window at 1.0468 microns indicates that it contributes about one order of magnitude less heating than anticipated originally by other workers. An analysis is made of collision induced absorption with emphasis on the far-wing behavior. A calculation is performed specifically for absorption during collisions between rare gas atoms; a numerical computation phase remains. Laser beam depletion by stimulated Raman scattering is investigated using a rate equation description. The particular effects are the interaction of competing Raman lines, multiple order Stokes wave generation, the amplification of Raman backscattered light, and the effect of pressure dependence on the propagation of a beam vertically through the atmosphere. The maximum intensity which can be transmitted through the atmosphere without frequency change due to Raman scattering is calculated.

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