ARPA ORDER NO. 189-61

AD620169

MEMORANDUM
RM-4664-ARPA
AUGUST 1965

RAYLEIGH AND RAMAN SCATTERING IN MOLECULAR NITROGEN

Horace A. Ory and Harold T. Yura

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This research is supported by the Advanced Research Projects Agency under Contract No. SD-79. Any views or conclusions contained in this Memorandum should not be interpreted as representing the official opinion or policy of ARPA.

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PREFACE

This Memorandum is a part of RAND's study of the various physical processes that attend the transmission of laser beams through air. It establishes a theoretical estimate of the Rayleigh and forward Raman scattering cross sections in N_2, useful to the understanding of the propagation of laser radiation through the atmosphere.

The study should be of general interest to those concerned with molecular structure and of specific interest in the area of laser light propagation through the atmosphere.

SUMMARY

The static polarizability and the cross sections for Rayleigh and rotational Raman scattering in molecular nitrogen are calculated by a direct perturbation technique. This approach is based on an effective intermediate state energy that is approximated closely through knowledge of potential energy curves for the nitrogen electronic states. Results obtained for the static polarizability agree with experimental values within about 20 per cent and represent considerable improvement over earlier calculations. The cross section for Rayleigh scattering is given for various polarizations and scattering angles, and is found to agree with experiment within about 30 per cent. The rotational Raman forward scattering cross section is obtained as a function of rotational level, and Stokes scattering from the $J = 6$ level is shown to be most easily stimulated in Raman lasers at room temperature, for illumination by ruby laser light.

ACKNOWLEDGMENTS

The assistance of Mrs. M. Lakatos in the computations, and helpful discussions with Dr. S.P. Cunningham, are gratefully acknowledged.

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I. INTRODUCTION

The ability to calculate theoretically fundamental molecular properties such as the polarizability is a good test of theoretical knowledge of molecular structure. The variational method has been applied in several such calculations, but accurate results have been obtained only for the case of the hydrogen molecule.(1) The nitrogen molecule is of interest as representative of molecules with more complex electronic structure and because it is a major atmospheric constituent; however, calculations for nitrogen(2,3) have given less accurate results, especially calculations of the anisotropy, for which the theoretical and experimental(4) results differ by a factor of about 3. This is significant because, for example, the rotational Raman cross section depends on the square of the anisotropy (which at optical frequencies differs little from the static value for nitrogen), as does the Rayleigh depolarization.

The closely related polarizability components for second-order scattering processes in nitrogen are relevant to the propagation of light in the atmosphere. These processes, like the static polarization, involve an array of intermediate states that, for most molecules, cannot be specified well enough to permit a direct perturbation calculation of the polarizability components. For nitrogen, however, a large energy separation exists between the ground electronic state and the lowest excited state for which a first-order radiative transition is allowed, and the important intermediate states converge on ionized states at only slightly greater energy. On the basis of known potential energy curves for the nitrogen electronic states,(5) a narrow range of energies can be specified for the important intermediate states, and this permits a direct perturbation treatment of the second-order processes in reasonably good approximation.

Results obtained for the static polarizability, Rayleigh scattering, and rotational Raman effect in nitrogen are presented here. The static polarizability, which in this approach is obtained in the zero frequency limit of the frequency-dependent polarizability, is compared with experiment as a check on the method of calculation, and found to agree more closely than the earlier variational calculations, especially with respect to the anisotropy.

II. THEORETICAL BASIS

METHOD OF APPROACH

Consider a gas of nitrogen molecules illuminated by a light beam of photon density n_b and photon energy ω_b (natural units, $\hbar = c = 1$ are used here). The scattering process transforms the incident photon energy to ω_s and the energy of the scattering molecule to $\omega_f = \omega_b - \omega_s$. For Rayleigh scattering $\omega_s = \omega_b$ and $\omega_f = \omega_i$ which is taken as zero for the initial state. For rotational Raman scattering ω_f is the change in rotational energy, $4B(J + 3/2)$, where B is the rotational constant (2.001 cm^{-1} for N_2(6)) and J is the rotational quantum number; for visible light $\omega_f \ll \omega_b \approx \omega_s$.

The differential transition rate per unit volume, Γ_s, for molecular scattering is given by(7)

$$\Gamma_s = 2\pi |M_s|^2 \rho \tag{1}$$

where the matrix element, M_s, for the second-order process involving intermediate states, ℓ, can be written in dipole approximation as

$$|M_s|^2 = \frac{Ne^4}{m^2} \left(\frac{2\pi n_b}{\omega_b}\right)\left(\frac{2\pi(n_s+1)}{\omega_s}\right) \left\{ \frac{1}{m} \sum_{\ell} \left[\frac{\left(\sum_k \vec{p}_k'\right)_{f\ell}\left(\sum_j \vec{p}_j'\right)_{\ell i}}{\omega_b - E_\ell} - \frac{\left(\sum_k \vec{p}_k\right)_{f\ell}\left(\sum_j \vec{p}_j'\right)_{\ell i}}{\omega_s + E_\ell} \right] + \delta_{fi} \cos \xi \right\}^2 \tag{2}$$

in terms of the molecular number density, N; the electronic charge, e, and mass, m; the intermediate state energies. E_ℓ; the angle, ξ, between the directions of polarization of the incident and scattered photons; and the sums over all electrons of the momentum matrix elements between the initial and intermediate states, $(\sum_k \vec{p}_k)_{\ell i}$, and between the intermediate and final states $(\sum_k \vec{p}_k)_{f\ell}$, where p and p$'$ denote components of the momentum in the direction of polarization of the incident and scattered photons, respectively. The density of states, ρ, is given by

$$\rho = \frac{\omega_s^2 \, d\Omega}{(2\pi)^3} \tag{3}$$

where $d\Omega$ is an element of solid angle. The equations apply to Rayleigh scattering for $f = i$, and to Raman scattering for $f \neq i$.

In terms of the matrix elements of the components of the polarizability tensor, with the μ component of $\vec{p}_k$ denoted as $p_{\mu k}$, etc.

$$(\alpha_{\mu\nu})_{fi} = \frac{e^2}{m^2 \omega_b \omega_s} \left\{ \sum_\ell \left[\frac{\left(\sum_k p_{\mu k}\right)_{f\ell} \left(\sum_j p_{\nu j}\right)_{\ell i}}{E_\ell - \omega_b} + \frac{\left(\sum_k p_{\nu k}\right)_{f\ell} \left(\sum_j p_{\mu j}\right)_{\ell i}}{\omega_s + E_\ell} \right] - m\delta_{fi} \cos \xi \right\} \tag{4}$$

Equation (1) can be expressed as

$$\Gamma_s = 2\pi N \, \omega_b \omega_s^3 \, n_b (n_s + 1) (\alpha_{\mu\nu})_{fi}^2 \, d\Omega \tag{5}$$

This is convenient in that the polarizability includes all of the dependence on intermediate state properties, which is the core of the problem because the intermediate states in general are not well known. For the case of N_2, however, the next section describes close limits that can be placed on the important $E_{\ell j}$ for each electron, so that effective $E^*_{\ell j}$ can be specified. Then for each electron a factor can be removed from the sum over intermediate states, and matrix multiplication can be performed, yielding

$$(\alpha_{\mu\nu})_{fi} = \frac{e^2}{m^2 \omega_b \omega_s} \left[\sum_j \left\{ \frac{\left[\left(\sum_k p_{\mu k}\right) p_{\nu j}\right]_{fi}}{E^*_{\ell j} - \omega_b} + \frac{\left[\left(\sum_k p_{\nu k}\right) p_{\mu j}\right]_{fi}}{\omega_s + E^*_{\ell j}} \right\} - m\delta_{fi} \cos \xi \right] \quad (6)$$

where the j refers to the different electrons. Actual evaluation of the matrix elements is facilitated by substitution in the matrix elements of $\vec{p}_{ab} = m\omega_{ab}\vec{r}_{ab}$, and application of the oscillator sum rule, $2m \sum\limits_b \omega_{ab} r^2_{ab} = 1$, to Eq. (4), leading to simplified expressions for computation(8)

$$(\alpha_{\mu\nu})_{fi} = e^2 \sum_j \left\{ \frac{\left[\left(\sum_k r_{\mu k}\right) r_{\nu j}\right]_{fi}}{E^*_{\ell j} - \omega_b} + \frac{\left[\left(\sum_k r_{\nu k}\right) r_{\mu j}\right]_{fi}}{\omega_s + E^*_{\ell j}} \right\} \quad (7)$$

INTERMEDIATE STATES

That the use of effective intermediate state energies is appropriate can be seen from a consideration of the N_2 electronic states. The intermediate states involved in the scattering process are described in terms of the N_2 stationary states, which have recently been reviewed by Gilmore.(5) An examination of the bound states discloses that radiative transitions between the ground state and the excited states below $b^1\Pi_u$ are forbidden by one or more of the following selection rules:(6)

$$\Delta S = 0$$

$$\Delta\Lambda = 0, \pm 1$$

$$g \leftrightarrow u, \quad g \not\leftrightarrow g, \quad u \not\leftrightarrow u$$

$$\Sigma^+ \not\leftrightarrow \Sigma^-$$

The next higher energy electronic states include the $b\,^1\Pi_u$ and $b'\,^1\Sigma_u^+$ states with minima between 12 and 13 ev, and with Franck-Condon transition energies from the ground state of between 12 and 14 ev. Not only are these transitions allowed, but also they are charge transfer transitions and should be among the strongest transitions from the ground state, in agreement with experimental observations.(9) A number of strong Rydberg transitions involving excitation of outer orbital electrons, $2\sigma_u$, $3\sigma_g$, and $1\pi_u$, to higher energy orbitals are known, converging on the N_2^+ states: X $^2\Sigma_g^+$ at 15.6 ev, A $^2\Pi_u$ at 16.7 ev, and B $^2\Sigma_u^+$ at 18.7 ev. The energies of these transitions differ from those to the $b\,^1\Pi_u$ and $b'\,^1\Sigma_u^+$ states by an amount that is small compared with the state energies, and setting them all equal to a single effective intermediate state energy is a good approximation. Transitions involving inner orbital electrons, $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$, necessarily correspond to much higher energy states, and as will be seen, the contributions of these electrons to the momentum matrix elements are sufficiently small that the use of a large lower bound on the corresponding intermediate state energies leads to negligible error. Finally, transitions to dissociated and ionized states of N_2 are ignored because the oscillatory nature of the dissociated and ionized wave functions leads to very small matrix elements, as confirmed by approximate calculations based on simplified wave functions.

For the outer electrons an effective intermediate state energy, E_ℓ^*, as large as 17 ev would be unreasonable on the basis of the potential curves of N_2, since only the $2\sigma_u$ electrons can give states so energetic. The value of 14 ev for E_ℓ^* is chosen to lend weight to the $b\ ^1\Pi_u$ and $b'\,^1\Sigma_u^+$ states, which are known to be important,(9) and to the fact that the $3\sigma_g$ excitation states are bounded by $N_2^+\ X\ ^2\Sigma_g^+$ at 15.6 ev and the $1\pi_u$ excitation states are bounded by $N_2^+\ A\ ^2\Pi_u$ at 16.7 ev. The degree of uncertainty in E_ℓ^* is then approximately 15 per cent, and it is likely that the error is less.

WAVE FUNCTIONS

For the evaluation of the static polarizability and the Rayleigh scattering probability, explicit expressions for only the ground state electronic wave functions are required, while for the evaluation of the rotational Raman transition probability, the rotational part of the wave functions can be treated separately. The present calculations are based on the self-consistent field wave functions for the N_2 ground state as derived by Richardson(10) through a variational method, taking electron-electron interactions into account. They are constructed from linear combinations of an expanded (double - ζ) basis set of Slater-type atomic orbitals, and lead to reasonably accurate computed energies. The total wave function, Φ_o, is an antisymmetrized product of molecular spin orbitals, φ_j, which, however, are not all orthogonal. Therefore, the integrals

$$\sum_j \int \Phi_o^*(r_j \sum_k r_k) \Phi_o \, d\tau$$

when expressed in terms of individual electrons, take the form

$$\frac{2}{N} \sum_{j=1}^{N} \left\{ \int \varphi_j^* r_j^2 \varphi_j \, d\tau - \sum_{k \neq j} \left[\int \varphi_j^* r_j \varphi_k d\tau^{\;2} + \int \varphi_j^* \varphi_k d\tau \int \varphi_j^* r_j^2 \varphi_k d\tau \right] \right\}$$

where N is the number of orbitals. The last two terms result from electron exchange, and the last term is non-zero because of the non-orthogonality of the φ_j of like spin. The integrals were evaluated for both the longitudinal and transverse components using an IBM 7044 computer and a Newton-Cotes type integrating procedure.

It can be noted that the wave functions for the equilibrium internuclear separation are used here. Actually, they should be expressed as functions of the internuclear separation and included in the integration over vibrational wave functions. An error ensues that depends on the anharmonicity of vibration and on the nonlinearity of the dependency of the polarizability on internuclear separation. The magnitude of the error can be estimated by comparison with more detailed calculations(1) on H_2, for which the error amounts to several per cent. The error is expected to be smaller for N_2 because, although no information is currently available on the nonlinearity of the polarizability, the anharmonicity of N_2 is known to be about five times less than that of H_2. A better knowledge of the nonlinearity effect is expected from further calculations now being performed on the variation of the polarizability with internuclear separation to determine the vibrational Raman scattering cross section; preliminary calculations indicate that the vibrational cross section is considerably smaller than the rotational cross section.

III. RESULTS AND DISCUSSION

STATIC POLARIZABILITY

In the limit of zero frequency, Eq. (7) reduces to the static polarizability, $\alpha^o_{\mu\nu}$

$$\alpha^o_{\mu\nu} = 2e^2 \sum_j \frac{\left[\left(\sum_k r_{\mu k}\right) r_{\nu j}\right]_{ii}}{E^*_{\ell j}} \qquad (8)$$

The z-axis is taken along the molecular axis, so that the longitudinal component is α^o_{zz}, and the transverse components, α^o_{xx} and α^o_{yy}, are equal for nitrogen by molecular symmetry.

$$\alpha^o_{zz} = 2e^2 \sum_j \frac{\left(z_i \sum_k z_k\right)_{ii}}{E^*_{\ell j}} \qquad (9)$$

$$\alpha^o_{xx} = 2e^2 \sum_j \frac{\left(x_j \sum_k x_k\right)_{ii}}{E^*_{\ell j}} \qquad (10)$$

Other quantities of interest are the rotational average

$$\alpha^o_{avg} = \frac{1}{3} (\alpha^o_{zz} + \alpha^o_{xx} + \alpha^o_{yy}) \qquad (11)$$

and the anisotropy, which for nitrogen is simply

$$\Delta^o = \alpha^o_{zz} - \alpha^o_{xx} \qquad (12)$$

Both experimental and other theoretical values for these quantities are available for comparison as a test of the method of calculation.

The contributions of the various doubly occupied molecular orbitals to the static polarizability are shown in Table 1, where the longitudinal component is denoted as α^o_{zz} and the transverse component as α^o_{xx}; the contributions to α^o_{yy} are the same as to α^o_{xx}, except that the contributions of $(1\pi_u)^2_x$ and $(1\pi_u)^2_y$, are interchanged.

A comparison of these results with experimental values and with the results of other theoretical calculations(2,3) is presented in Table 2. It shows that the present calculations represent considerable improvement over earlier attempts by variational methods, and confirms the validity of the approach used here. The discrepancies in the calculations for α^o_{zz} (and hence α^o_{avg} and $\alpha^o_{zz} - \alpha^o_{xx}$) are largely removed, although the value for α^o_{xx} is somewhat less accurate than the earlier results. It should be noted that this comparison excludes results obtained by Abbott and Bolton(2) through arbitrary variation of the pi orbital separation; such variation brings the results into excellent agreement with experiment, but it depends on prior knowledge of the polarizability and is not consistent with the use of realistic wave functions.

The comparison suggests that probably two factors are primarily responsible for the inaccuracy of the variational calculations.(2,3) The wave functions used for the unperturbed state are themselves derived by a variational method, and the resulting energy for the unperturbed state is thus larger than the true value. When the total energy is again minimized using the perturbed wave functions (corresponding to maximization of the polarizability), the additional parameters permit a closer approach to the true total energy, so that part of the error in the unperturbed wave functions is compensated, but at the same time an excessive value is obtained for the polarizability. The second

Table 1

MOLECULAR ORBITAL CONTRIBUTIONS TO STATIC POLARIZABILITY[a]

Orbital	α^o_{zz}	α^o_{xx}	α^o_{avg}	$(\alpha^o_{zz} - \alpha^o_{xx})$
$1\sigma_g$	.0051	.0001	.0018	.0050
$1\sigma_u$	.0057	.0002	.0020	.0055
$2\sigma_g$	.0285	.0223	.0244	.0062
$2\sigma_u$	.4588	.1151	.2297	.3437
$3\sigma_g$	.4976	.0847	.2223	.4129
$(1\pi_u)_x$	.5428	.6315	.6019	-.0887
$(1\pi_u)_y$	.5428	.2213	.3285	.3215
Total	2.081	1.075	1.410	1.006

[a] in units of 10^{-24} cm^3

Table 2

COMPARISON OF STATIC POLARIZABILITY RESULTS[a]

Source	α^{o}_{zz}	α^{o}_{xx}	α^{o}_{avg}	$\alpha^{o}_{zz} - \alpha^{o}_{xx}$
Experimental[b]	2.33	1.45	1.76	0.93
This work (% deviation)	2.081 (13)	1.075 (26)	1.410 (20)	1.006 (8)
Kolker and Karplus[c] (% deviation)	4.67 (96)	1.27 (12)	2.40 (36)	3.40 (266)
Abbott and Bolton[d] (% deviation)	4.77 (100)	1.35 (7)	2.49 (42)	3.42 (268)

[a] in units of $10^{-24} cm^3$.

[b] Reference 4.

[c] Reference 3.

[d] Reference 2. However, agreement was obtained within several per cent upon arbitrary adjustment of pi orbital separation.

factor is related to the excessive variational result for the anisotropy, which can be attributed to the inaccuracy of the wave functions used, which represent inadequately the contributions from atomic 2p and higher orbitals, so that there is a deficiency in electron density in the outer regions. This deficiency leads to a diminshed α^{o}_{zz} and a diminished α^{o}_{xx}, but because of the geometry of the 2p orbitals, α^{o}_{xx} is diminished much more than α^{o}_{zz}, so that, in effect, an excessive anisotropy results. It would be interesting to compare the results of the calculations reported here with those of a variational treatment using the same wave functions.

Richardson's(10) wave functions, used in the calculations reported here, also omit contributions from atomic orbitals higher than 2p. However, this is largely compensated by the use of an expanded basis set of atomic orbitals, which includes two different effective nuclear charges for each of the 2s and 2p orbitals. This effectively shifts electron density from the highest density region toward both inner and outer regions. The shift toward the outer regions, resulting from the use of a relatively small effective nuclear charge, appears to be responsible for the relative accuracy of the present calculation, compared with those based on simpler wave functions. Nevertheless, the present results for α^{o}_{zz} and α^{o}_{xx} are both lower than the experimental values, which suggests that some improvement could be obtained through the inclusion of contributions from higher orbitals.

RAYLEIGH SCATTERING

In the case of $f = i$, the polarizability matrix elements for Rayleigh scattering are obtained from Eq. (7) as

$$\alpha_{\mu\nu} = 2e^2 \sum_j \frac{E_\ell^* \, r_{\mu j} \sum_k r_{\nu k} \quad {}_{\ell\ell}}{E_\ell^{*2} - \omega_b^2} \tag{13}$$

Consider a fixed coordinate system such that the incident beam propagates along the positive X-axis, and the electric vector of the incident beam is in the Z-direction. The scattering angle is denoted by θ; the angle between the Z-axis and the propagation vector of the scattered beam is denoted by ψ; and the angle between the X-axis and the projection of the propagation vector of the scattered beam in the X-Y-plane is denoted by φ. The Rayleigh scattering differential cross section is given in terms of the polarizability as

$$\frac{d\sigma}{d\Omega} = \omega^4 \alpha_{\mu\nu}^2 \tag{14}$$

The polarization of the scattered beam can be specified in terms of two unit vectors mutually perpendicular and perpendicular to the scattered light propagation vector. It is convenient to define these such that one (Case 1) points toward (or parallels) the Z-axis. The two combinations of polarizations of the incident and scattered light can then be specified in terms of unit vectors in the directions of polarization of the incident beam (ϵ_b) and scattered beam (ϵ_s).

Case 1: $\epsilon_b = \epsilon_Z$, $\epsilon_s = \epsilon_Z \sin\psi - \epsilon_X \cos\psi \cos\varphi - \epsilon_Y \cos\psi \sin\varphi$,

$$\text{so that } \frac{d\sigma_1}{d\Omega} = \omega^4 (\alpha_{ZZ} \sin\psi - \alpha_{XZ} \cos\psi \cos\varphi - \alpha_{YZ} \cos\psi \sin\varphi)^2$$

Case 2: $\epsilon_b = \epsilon_Z$, $\epsilon_s = \epsilon_Y \cos\varphi - \epsilon_X \sin\varphi$

$$\text{so that } \frac{d\sigma_2}{d\Omega} = \omega^4 (\alpha_{XZ} \sin\varphi + \alpha_{YZ} \cos\varphi)^2$$

These expressions must be averaged over all orientations of the molecules with respect to the fixed coordinate system; that is, averages of the form $\overline{\alpha_{ik}\alpha_{jm}}$ are required, where the bar denotes an average over all orientations. Since the polarizability tensor is symmetric

$$\overline{\alpha_{ik}\alpha_{jm}} = A\,\delta_{ik}\delta_{jm} + B(\delta_{ij}\delta_{km} + \delta_{im}\delta_{jk}) \qquad (15)$$

where A and B are scalars. This is the most general tensor of rank four that is symmetric in i and k, and in j and m. By contraction of Eq. (15), first with respect to i, k and j, m; and second with respect to i, j and k, m; A and B are determined as

$$A = \frac{45\alpha_{avg}^2 - 2\Delta^2}{45} \qquad (16a)$$

$$B = \frac{\Delta^2}{15} \qquad (16b)$$

where α_{avg} is the average value of the polarizability

$$\alpha_{avg} = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \qquad (17)$$

and Δ is the anisotropy

$$\Delta^2 = \frac{1}{2}\left[(\alpha_1-\alpha_2)^2 + (\alpha_2-\alpha_3)^2 + (\alpha_1-\alpha_3)^2\right] \qquad (18)$$

Here α_1, α_2, and α_3 are the principal values of the polarizability tensor. After averaging, from Eqs. (15) and (16), the differential cross sections are determined as

$$\frac{d\sigma_1}{d\Omega} = \omega^4 \left[\left(\frac{45\alpha_{avg}^2 + \Delta^2}{45} \right) \sin^2\psi + \frac{\Delta^2}{15} \right] \tag{19}$$

$$\frac{d\sigma_2}{d\Omega} = \omega^4 \left(\frac{\Delta^2}{15}\right) \tag{20}$$

The sum of these describes the Rayleigh differential scattering cross section for an incident beam linearly polarized in the Z-direction

$$\frac{d\sigma(\text{Z-polarization})}{d\Omega} = \omega^4 \left[\left(\frac{45\alpha_{avg}^2 + \Delta^2}{45} \right) \sin^2\psi + \frac{2\Delta^2}{15} \right] \tag{21a}$$

A similar equation results for a Y-polarized incident beam, except that ψ is replaced by η, the angle between the scattered light propagation vector and the Y-axis.

$$\frac{d\sigma(\text{Y-polarization})}{d\Omega} = \omega^4 \left[\left(\frac{45\alpha_{avg}^2 + \Delta^2}{45} \right) \sin^2\eta + \frac{2\Delta^2}{15} \right] \tag{21b}$$

The Rayleigh differential scattering cross section for unpolarized incident light is given by half the sum of Eqs. (21a) and (21b), substituting $(1 + \cos^2\theta) = \sin^2\psi + \sin^2\eta$.

$$\frac{d\sigma(\text{unpolarized})}{d\Omega} = \frac{\omega^4}{90} \left[\left(45\alpha_{avg}^2 + \Delta^2\right)\left(1 + \cos^2\theta\right) + 12\Delta^2 \right] \tag{22}$$

These equations reduce to the appropriate expressions for the isotropic case.

The energy of visible light is sufficiently small compared with possible values of E_{ℓ}^{*} that the numerical values of the above matrix elements of the polarizability differ from the static polarizability by a negligible amount. Using values calculated here for α_{avg} and Δ, the total Rayleigh scattering cross section at the wavelength of ruby laser light is found to be

$$\sigma_{Rayleigh} = 1.18 \times 10^{-27}\ \mathrm{cm}^2$$

The corresponding value derived from experimental measurements(4) of the refractive index and the depolarization is $1.82 \times 10^{-27}\ \mathrm{cm}^2$, so that the disagreement is about 35 per cent. The calculated cross section corresponds to a photon scattering probability per unit path length of $2.9 \times 10^{-8}\ \mathrm{cm}^{-1}$ for nitrogen gas at 300° K and one atmosphere of pressure.

The depolarization factor for linearly polarized incident light scattered normal to the incident beam is calculated as

$$\rho_{\ell} = \frac{3\Delta^2}{45\alpha_{avg}^2 + 4\Delta^2} = 0.032 \qquad (23)$$

and that for unpolarized incident light as

$$\rho_u = \frac{6\Delta^2}{45\alpha_{avg}^2 + 7\Delta^2} = 0.063 \qquad (24)$$

The experimental value for unpolarized light is$^{(4)}$ 0.036, and the deviation of our calculation from that value, 75 per cent, is sensitive to the combination of an excessive Δ and a deficient α_{avg}, because the deviation arises approximately from the product of the squares of the ratios, $\Delta^{calc.}/\Delta^{exp.}$ and $\alpha_{avg}^{exp.}/\alpha_{avg}^{calc.}$. Even so, the deviation found here for ρ_u is almost an order of magnitude smaller than that found from previous calculations.

ROTATIONAL RAMAN SCATTERING

The evaluation of matrix elements for rotational Raman scattering requires essentially that the polarizability components be transformed from the rotating-molecule coordinate system to the fixed laboratory system before taking rotational matrix elements. For convenience in illustrating the direction and polarization of scattered light, the incident light is taken as polarized in the Z direction and propagating in the X direction (the capital denotes fixed laboratory coordinates). The components of polarizability are then expressed in terms of spherical harmonics, which are convenient for taking the matrix elements,$^{(11)}$ as

$$\left.\begin{aligned}
\alpha_{ZZ} &= \alpha_{xx}\sqrt{4\pi}\, Y_{0,0} + (\alpha_{zz}-\alpha_{xx})\left(\sqrt{\frac{4\pi}{9}}\; Y_{0,0} + \sqrt{\frac{16\pi}{45}}\; Y_{2,0}\right) \\
\alpha_{XZ} &= (\alpha_{zz}-\alpha_{xx})\sqrt{\frac{2\pi}{15}}\; i(Y_{2,-1} - Y_{2,1}) \\
\alpha_{YZ} &= (\alpha_{zz}-\alpha_{xx})\sqrt{\frac{2\pi}{15}}\; (Y_{2,-1} + Y_{2,1})
\end{aligned}\right\} \qquad (25)$$

The $Y_{0,0}$ terms correspond to scattering without change in frequency, and only the terms in $Y_{2,0}$ and $Y_{2,\pm 1}$ contribute to rotational transitions, and yield non-vanishing matrix elements only for $\Delta J = \pm 2$. The contributions of these terms are obtained, after averaging over the initial values of the angular momentum components and summing over the final values, as

$$\left(\alpha_{ZZ}\right)^2_{\Delta J=\pm 2} = \frac{2(J+2)(J+1)}{15(2J+3)(2J+1)}\left(\alpha_{zz}-\alpha_{xx}\right)^2 \tag{26}$$

$$\left(\alpha_{YZ}\right)^2_{\Delta J=\pm 2} = \left(\alpha_{XZ}\right)^2_{\Delta J=\pm 2} = \frac{(J+2)(J+1)}{10(2J+3)(2J+1)}\left(\alpha_{zz}-\alpha_{xx}\right)^2 \tag{27}$$

where J refers to the lower state. (For a more general treatment see Placzek and Teller.(12)) The depolarization factor for light scattered at right angles to the incident beam is

$$\rho = \frac{I_\perp}{I_\parallel} = \frac{\left(\alpha_{YZ}\right)^2_{\Delta J=\pm 2}}{\left(\alpha_{ZZ}\right)^2_{\Delta J=\pm 2}} = \frac{3}{4} \tag{28}$$

where $I_\perp$ refers to light polarized perpendicular to the incident light and $I_\parallel$ refers to light polarized parallel to the incident light. This is expected because only the anisotropic part of the polarizability gives rise to rotational Raman scattering.

The differential cross section for forward rotational Raman scattering, without change in polarization, $\sigma_{\text{Raman}}(0)$, which is pertinent to stimulated Raman scattering, is given by

$$\sigma_{\text{Raman}}(0) = \frac{d\sigma_{\text{Raman}}}{d(\cos\theta)}\bigg|_{\theta=0} = \frac{1}{Nn_b(n_s+1)}\,\frac{d\Gamma}{d(\cos\theta)}\bigg|_{\theta=0} = 2\pi\omega_b\omega_s^3\left(\alpha_{z_f z_f}\right)^2_{\Delta J=\pm 2} \qquad (29)$$

An illustration of the magnitude of the cross section is obtained by considering the case of nitrogen gas at 300°K. The cross sections for Stokes and anti-Stokes scattering of ruby laser light are listed in Table 3 as a function of J. The alternation of intensity between even and odd J arises from the nuclear-spin statistical factor. The relative accuracy of the entries of Table 3 is very good, because it depends essentially on the population factor $(2J+1)\exp[-BJ(J+1)/kT]$ and involves only well-known quantities. The absolute accuracy is determined by the square of $(\alpha_{zz} - \alpha_{xx})$, which is discussed further in the next paragraph. According to the table, Stokes scattering from $J = 6$ is most easily stimulated initially, as determined primarily by the initial level population. If the incident beam is sufficiently intense that the $J = 8$ level population is sufficiently increased at the expense of the $J = 6$ level population, stimulation of Stokes scattering from $J = 8$ then assumes greater importance. The total Raman scattering cross section for ruby laser light, including both Srokes and anti-Stokes scattering is

$$\sigma_{\text{Raman}} = 1.08 \times 10^{-28}\ \text{cm}^2$$

for nitrogen gas at 300° K. At one atmosphere of pressure, this corresponds to a photon scattering probability per unit length of $2.6 \times 10^{-9}\ \text{cm}^{-1}$.

It is difficult to assess the accuracy of the calculated value, 1.02 Å^3, of $(\alpha_{zz}-\alpha_{xx})$, on the square of which the value of the Raman cross section depends. The experimental value(4) compared earlier, 0.93 Å^3, differs from values derived from later measurements. Bridge and Buckingham(12)

Table 3

ROTATIONAL RAMAN FORWARD SCATTERING CROSS SECTION[a]

J	Stokes	anti-Stokes
0	4.5	---
1	4.2	---
2	11.5	4.5
3	7.1	3.8
4	16.1	10.1
5	8.7	6.0
6	17.9	13.0
7	8.9	6.8
8	17.1	13.5
9	8.0	6.5
10	14.5	12.0
11	6.4	5.4
12	11.0	9.4
13	4.6	4.0
14	7.6	6.6
15	3.1	2.7
16	4.8	4.3
17	1.9	1.7
18	2.8	2.5
19	1.0	0.9
20	1.5	1.3
Total	165.3	116.7

[a] in units of $10^{-31} cm^2$

report the value of 0.706 $\overset{\circ}{A}{}^3$, and the value of 1.025 $\overset{\circ}{A}{}^3$ can be derived from the measurements of Dintzis and Stein;(14) the difference between these values corresponds to a factor of two uncertainty in the rotational Raman cross section. (A collection of earlier determinations is listed by Cabannes.(15)) The value calculated here, 1.02 $\overset{\circ}{A}{}^3$ at the ruby laser frequency, falls within the spread of experimental values, which are obtained through measurements of the depolarization of polarized incident light. The measurements are difficult because the relatively low intensity of the scattered light requires the use of a very intense incident beam, and a decrease in the uncertainty of the experimental values can probably be expected through the utilization of more powerful lasers to provide a sufficiently intense incident beam.

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