Theory of stimulated Raman scattering by rotational transitions

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The theory of SRS by purely rotational transitions is considered by taking intermediate vibrational and purely rotational transitions into account. It is shown that the contribution to the amplification from these transitions may be the main one if a carbon dioxide laser is used for pumping.

The development of high-power pulsed lasers operating in the medium and far IR bands raises new problems in nonlinear optics. One of the principal problems is the study of stimulated scattering in these bands. Stimulated scattering exhibits in this case a number of distinguishing features due to the more complete manifestation of the atomic and molecular motions.

The present article is devoted to a theoretical investigation of stimulated Raman scattering (SRS) on rotational transitions. This scattering has already been observed in the visible band in[1–3], where some theoretical estimates are also given. However, there is, insofar as we know, no consistent theory of SRS on rotational transitions. We first describe an approach, based on classical premises, to the description of SRS on rotational transitions, and then present a consistent quantum theory in which account is taken of intermediate purely-rotational levels and the possibilities of resonance with the vibrational-rotational transitions. These cases can be realized by exciting SRS with radiation in the medium and far IR bands.

1. CLASSICAL THEORY

The classical approach is useful in qualitative consideration of the phenomenon. We therefore confine ourselves only to the simplest case of a rigid molecule, when the contribution of the nuclear vibrations to the polarizability can be negelcted. We consider only the rotation of the molecules in the (x, y) plane, which also contains the pump and Stokes-wave polarization vectors. In this approximation, the Hamiltonian of an individual molecule, without allowance for the interaction of the molecules, can be expressed in the form

$$\mathscr{H}_0=\frac{M^2}{2I}-\frac{1}{2}\mathbf{E}\varkappa\mathbf{E}, \tag{1}$$

where M is the angular momentum, I is the moment of inertia, κ is the electronic polarizability tensor, and

$$\mathbf{E}={}^1/_2\,\mathbf{E}^l\exp(-i\omega_lt)+{}^1/_2\,\mathbf{E}^s\exp(-i\omega_st)+\text{c.c.}$$

is the electric field of the pump and of the Stokes wave with their respective frequencies ω_l and ω_s.

For the distribution function $\rho(\varphi, M)$ in phase space, where φ is the angle between the molecule axis and the x axis, we can write down the Liouville equation

$$\frac{\partial\rho}{\partial t}+\frac{\partial\mathscr{H}_0}{\partial M}\frac{\partial\rho}{\partial\varphi}-\frac{\partial\mathscr{H}_0}{\partial\varphi}\frac{\partial\rho}{\partial M}=0, \tag{2}$$

which is equivalent to the classical equations of motion. By adding to this equation the relaxation terms that take into account the interaction between molecules, we get

$$\frac{\partial\rho}{\partial t}+\frac{M}{I}\frac{\partial\rho}{\partial\varphi}-\frac{\rho-\rho_0}{\tau'}-D\frac{\partial^2\rho}{\partial\varphi^2} \tag{3}$$

$$=\frac{1}{4}\frac{\partial\rho}{\partial M}(\varkappa_\parallel-\varkappa_\perp)\left[ie^{2i\varphi}(E_+{}^lE_-{}^{s*}e^{-i\Omega_0t}-E_-{}^{l*}E_+{}^se^{i\Omega_0t})+\text{c.c.}\right]$$

We have left out from the right-hand side the terms with frequencies different from Ω_0, since they have no bearing on our problem. Here $\Omega_0=\omega_l-\omega_s$, $\kappa_\parallel$ and $\kappa_\perp$ are the polarizabilities of the molecule parallel and perpendicular to the axis, $\mathrm{E}_\pm^{l,s}$ are the circular complex amplitudes of the fields (the plus sign corresponds to right-hand circular polarization and the minus sign to left-hand). The relaxation constant τ' determines the relaxation of the distribution function to the equilibrium function $\rho_0(m)$, and the term with the constant D describes the diffusion of the rotation phase. The relaxation terms introduced in this manner ensure preservation of the normalization

$$\int\rho\,d\varphi\,dM=\int\rho_0\,d\varphi\,dM=1.$$

Equation (3) can be solved by successive approximations: $\rho=\rho_0+\rho_1+\ldots$. The equation for ρ_1 is obtained by substituting the quantity $\partial\rho_0/\partial M$ for $\partial\rho/\partial M$ in the right-hand side of (3). The solution of the obtained equation is $\rho_1=\rho_1^{(+)}e^{-2i\varphi}+\rho_1^{(-)}e^{-2i\varphi}$, where $[\rho_1^{(+)}]^*=\rho_2^{(-)}$, while $\rho_1^{(+)}$ is obtained by solving the equation

$$\frac{\partial\rho_1^{(+)}}{\partial t}-\frac{2iM}{I}\rho_1^{(+)}+\left(\frac{1}{\tau'}+4D\right)\rho_1^{(+)}=-\frac{i}{4}(\varkappa_\parallel-\varkappa_\perp)\frac{\partial\rho_0}{\partial M}\times\left[E_+{}^{l*}E_-{}^se^{i\Omega_0t}+E_-{}^lE_+{}^{s*}e^{-i\Omega_0t}\right]. \tag{4}$$

The dipole moment produced by the molecules (per molecule) is equal to

$$\mathbf{P}=\int\mathbf{p}(\varphi)\rho(M,\varphi)\,dM\,d\varphi=\int\mathbf{P}(M)\,dM, \tag{5}$$

where

$$\mathbf{P}(M)=\int\mathbf{p}(\varphi)\rho(M,\varphi)\,d\varphi,\ \text{and}\ \mathbf{p}(\varphi)=\varkappa_\perp\mathbf{E}+(\varkappa_\parallel-\varkappa_\perp)\mathbf{n}(\mathbf{nE})$$

is the dipole moment of a molecule whose axis is directed along a unit vector **n** making an angle φ with the x axis.

With the aid of (4) and (5) we can investigate the onset of polarization at the Stokes frequency, including the nonstationary case for slowly varying amplitudes $\mathrm{E}_\pm^{l,s}$. We confine ourselves to the stationary case, when $\mathrm{E}_\pm^{l,s}$ do not depend on the time. In this case, using (4) and (5) we obtain the amplitudes of the polarization at the Stokes frequency

$$P_\mp{}^s(M)=\frac{\pi(\varkappa_\parallel-\varkappa_\perp)}{4(\Delta_\mp-i/\tau)}\frac{\partial\rho_0}{\partial M}|E_\pm{}^l|^2E_\mp{}^s, \tag{6}$$

where $\Delta_\mp=\Omega_0\pm2\Omega\equiv\Omega_0\pm2M/I$, and $1/\tau=1/\tau'+4D$, with τ playing the role of the "transverse" relaxation time. If we now integrate (6) with respect to M, assuming that $\partial\rho_0/\partial M$ varies little in the interval I/τ, then we obtain

$$P_\mp{}^s=\frac{i\pi^2I}{8}(\varkappa_\parallel-\varkappa_\perp)^2\frac{\partial\rho_0}{\partial M}|E_\pm{}^l|^2E_\mp{}^s. \tag{7}$$

According to (7), the total value of the polarization $P_{\mp}^{s}$, and consequently the gain at the Stokes frequency does not depend on the relaxation constant τ. A discussion of this feature will be carried out in the second part, in the comparison with the results of the quantum calculations.

As seen from (6), contributions to P_{+}^{s} are made by molecules having an angular velocity Ω approximately equal to $\Omega_0/2$. This agrees with the analysis of the interaction of one molecule with the field. The torque acting on the molecule

$$T=-\frac{\partial\mathcal{H}_0}{\partial\varphi}=\frac{\partial}{\partial\varphi}\left(\frac{1}{2}\mathrm{E}\varkappa\mathrm{E}\right),$$

averaged over the time, is in this case different from zero, and the polarizability of the molecule varies at double the rotation frequency 2Ω, thus ensuring the appearance of polarization at the frequency $\omega_l - 2\Omega = \omega_s$.

Amplification of the Stokes frequency, as seen from (6) and (7), occurs if $\partial\rho_0/\partial M < 0$; this is always the case at thermal equilibrium. The amplification of the radiation at the Stokes frequency is a consequence of ordering of the molecules over the rotation phases, and the degrees of phasing, i.e., the amplitudes $\rho_l^{(\pm)}$, as seen from (4), are proportional to the product $E^{l*}E^{s}$. In addition, it is seen from (6) and (7) that the pump component with right-hand polarization gives rise to amplification for the left-hand polarization of the Stokes wave, and vice versa.

In the next higher approximation, we obtain from (3) $\rho_2 = \rho_2^{(0)} + \rho_2^{(+)}e^{-4i\varphi} + \rho_2^{(-)}e^{4i\varphi}$, with $\rho_2^{(0)}$ describing the change in the populations and the saturation effect, while $\rho_2^{(\pm)}$ leads to the appearance of the combination frequencies $\omega_l \pm 2\Omega_0$. The equation for $\rho_2^{(0)}$ contains only the relaxation constant τ' (since $\rho_2^{(0)}$ does not depend on φ). Thus, τ' has the meaning of the time of the "longitudinal" relaxation.

2. QUANTUM THEORY

If we disregard the field at the antistokes frequency (as was done above), then in the lowest order of perturbation theory, in the quantum (more accurately, semiclassical) analysis, without allowance for the change of the populations or for the Stark shifts, we have the following expression for the polarization at the Stokes frequency (per molecule):

$$P_\alpha{}^s=\chi_{\alpha\beta\gamma\delta}E_\beta{}^sE_\gamma{}^lE_\delta{}^{l*}=-\frac{\rho_1-\rho_2}{4\hbar(\Delta-i/\tau)}\sum_{m_1m_2}(\varkappa_{\alpha\gamma}^{m_2m_1}E_\gamma{}^l)(E_\beta{}^{s*}\varkappa_{\beta\gamma}^{m_2m_1}E_\delta{}^{l*}).\qquad(8)$$

Here E_β^S and E_γ^l are the circular complex amplitudes of the Stokes wave and of the pump field $[E_0 = E_Z,\ E_{\pm1} = (\pm E_x + iE_y)/\sqrt{2}]$, ρ_2 and ρ_1 are the populations of the upper- and lower-level states (they do not depend on m_1 or m_2), $\Delta = \omega_l - \omega_s - \omega_0$ (where ω_0 is the frequency of the rotational transition), τ is the relaxation time, m_1 and m_2 are the quantum numbers of the projection of the angular momentum on the z axis for the lower and upper states, respectively, and

$$\varkappa_{\alpha\gamma}^{m_2m_1}=\frac{1}{\hbar}\left[\frac{\langle m_2|\mu_\gamma{}^*|r\rangle\langle r|\mu_\alpha|m_1\rangle}{\omega_l+\omega_{r,m_2}}-\frac{\langle m_2|\mu_\alpha|r\rangle\langle r|\mu_\gamma{}^*|m_1\rangle}{\omega_l-\omega_{r,m_1}}\right]\qquad(9)$$

is the scattering tensor. Summation over the repeated indices β, γ, and δ, as well as over the intermediate-state index r, is implied throughout. By μ_α we denote the circular components of the operator of the total dipole moment.

The quantum numbers for the angular momenta of the initial and final states will be designated J_1 and J_2. It follows directly from (9) (since μ_α is a vector operator) that J_2 is equal to J_1 or to $J_1 + 1$ or else to $J_1 + 2$. The first possibility is of no interest for a pure rotational transition. We consider first the case $J_2 = J_1 + 2$ for molecules of the symmetrical-top type, particularly for linear molecules. The tensor $\kappa_{\alpha\gamma}^{m_2m_1}$ can be represented in the form

$$\varkappa_{\alpha\gamma}^{m_2m_1}=\varkappa_{\alpha\gamma(e)}^{m_2m_1}+\varkappa_{\alpha\gamma(v)}^{m_2m_1}+\varkappa_{\alpha\gamma(r)}^{m_2m_1},$$

where the contributions from the electronic, vibrational, and rotational intermediate states are separated. Usually (in the Placzek approximation) one takes into account only the electronic part. In the case of pumping from an infrared laser, nuclear contributions can also play a role. It is assumed that the principal electronic term of the molecule is not degenerate and has no fine structure, since for most molecules in the ground state it is possible to separate in (9) intermediate states $|r\rangle$ that correspond to the electronic ground state. Then the remaining part of the tensor $\kappa_{\alpha\gamma}$ is transformed by Placzek's method and can be expressed in the form

$$\varkappa_{\alpha\gamma(e)}^{m_2m_1}=\langle J_2k_2m_2|\varkappa_{\alpha\gamma(e)}|J_1k_1m_1\rangle,\qquad(10)$$

where $\kappa_{\alpha\gamma(e)}$ is the electron-polarizability tensor averaged over the ground vibrational state and $|J_ik_im_i\rangle$ is a rotational eigenfunction, with k_i the quantum number of the angular-momentum projection on the molecule axis. Owing to the axial symmetry, $\kappa_{\alpha\gamma(e)}^{m_2m_1} \neq 0$ only at $k_1 = k_2 = k$. The eigenfunctions $|J_ik_im_i\rangle$, as is well known, coincide with the normalized Wigner functions for the representations J_i of the rotation group[4]. The nuclear part of the scattering tensor corresponds to transitions within the electronic ground state. An appreciable contribution to the tensor $\kappa_{\alpha\gamma(v)}$ is made only by those intermediate vibrational-rotational states for which the pump frequency ω_l approaches the transition frequency ω_v (the molecule is assumed to be active in the absorption spectrum). We need therefore retain only the intermediate states with vibrational quantum number v = 1 for that mode of oscillations for which this is satisfied. It is assumed that this is a nondegenerate oscillation mode.

Then the vibrational part of the scattering tensor takes the form

$$\gamma_{\alpha\gamma(v)}^{m_2m_1}=-\frac{1}{\hbar(\omega_l-\omega_v)}\sum_m\langle J_2m_2|\mu_\alpha|Jm\rangle\langle Jm|\mu_\gamma{}^*|J_1m_1\rangle.\qquad(11)$$

Since μ_α is a vector operator, we can write

$$\langle J_im_i|\boldsymbol{\mu}|Jm\rangle=\langle J_ikm_i|\mathbf{d}_i|Jkm\rangle,$$

where $\mathbf{d}_i$ is a certain vector directed along the molecule axis, and in the approximation in which no account is taken of the interaction between the vibrations and rotations we have $\mathbf{d}_1 = \mathbf{d}_2 = \mathbf{d}$, where $\mathbf{d}$ is the dipole moment of the vibrational transition.

At $J_2 = J_1 + 2$ we can sum in (11) also over J, since the tensor $\kappa_{\alpha\gamma(v)}$ differs from zero only at $J = J_1 + 1$. Taking this into account, we can write

$$\varkappa_{\alpha\gamma(v)}^{m_2m_1}=-\frac{d_1{}^*d_2}{\hbar(\omega_l-\omega_v)}\langle J_2km_2|n_\alpha n_\gamma{}^*|J_1km_1\rangle,\qquad(12)$$

where n_α is a unit vector directed along the molecule axis.

If the molecule has a constant dipole moment d_0 directed along its axis, then a noticeable contribution can be made by the intermediate rotational states. The corresponding contribution $\kappa^{m_2m_1}_{\alpha\gamma(r)}$ can be written, in analogy with (12), in the form

$$\varkappa^{m_2m_1}_{\alpha\gamma(r)} = \frac{d_0^2}{\hbar}\left(\frac{1}{\omega_l-\omega_{J_2,J}} - \frac{1}{\omega_l-\omega_{J,J_1}}\right)\langle J_2km_2|n_\alpha n_\gamma^*|J_1km_1\rangle \approx \frac{2d_0^2B}{\hbar\omega_l^2}\langle J_2km_2|n_\alpha n_\gamma^*|J_1km_1\rangle, \tag{13}$$

where $2B = \omega_{J_2,J} - \omega_{J,J_1}$.

Using (8)—(13), we can express $\chi_{\alpha\beta\gamma\delta}$ in terms of 3j-symbols in the form

$$\chi_{\alpha\beta\gamma\delta} = -\frac{\rho_1-\rho_2}{4\hbar(\Delta-i/\tau)}|\varkappa_0|^2(-1)^{\gamma+\delta}(2J_1+1)(2J_2+1) \times\begin{pmatrix}2 & J_2 & J_1\\ 0 & -k & k\end{pmatrix}^2\begin{pmatrix}1 & 1 & 2\\ \alpha & -\gamma & (\gamma-\alpha)\end{pmatrix}\begin{pmatrix}1 & 1 & 2\\ \beta & -\delta & (\delta-\beta)\end{pmatrix} \tag{14}$$

or

$$\mathbf{P}^s = -\frac{\rho_1-\rho_2}{4\hbar(\Delta-i/\tau)}|\varkappa_0|^2 g(J_1)\,[3\mathbf{E}^s(\mathbf{E}^{l*}\mathbf{E}^l) - 2\mathbf{E}^l(\mathbf{E}^{l*}\mathbf{E}^s) + 3\mathbf{E}^{l*}(\mathbf{E}^l\mathbf{E}^s)] \tag{15}$$

Here

$$\varkappa_0 = \varkappa_\parallel - \varkappa_\perp - \frac{d^2}{\hbar(\omega_l-\omega_v)} + \frac{2Bd_0^2}{\hbar\omega_l^2};$$

$\kappa_\parallel$ and $\kappa_\perp$ are the electronic polarizabilities of the molecules parallel and perpendicular to the axis, and

$$g(J_1) = \frac{1}{30}\,\frac{[(J_1+1)^2-k^2][(J_1+2)^2-k^2]}{(J_1+1)(J_1+2)(2J_1+3)}. \tag{16}$$

The factor $g(J_1)$ is known from the theory of spontaneous Raman scattering. For linear molecules we have $k = 0$.

Expressions (14) and (15) make it possible to obtain the Stokes-wave gain and its dependence on the polarizations. As seen from (15), this dependence is the same as proposed in[1]. The gain G is connected with χ by the relation

$$G = -4\pi N\frac{\omega_s}{c}\,\mathrm{Im}\,\chi|E^l|^2; \tag{17}$$

where N is the number of molecules per unit volume.

The gain for the electronic part of the tensor $\kappa_{\alpha\gamma}$ was estimated in[2] from data on the cross section of spontaneous scattering. It is meaningful to estimate the contribution of the nuclear part. The contributions of the vibrational and rotational parts referred to the contribution from the electronic polarizabilities are respectively equal to

$$\varepsilon_v = \frac{d^2}{\hbar|\varkappa_\parallel-\varkappa_\perp|\,|\omega_l-\omega_v|}, \qquad \varepsilon_r = \frac{2d_0^2B}{\hbar\omega_l^2|\varkappa_\parallel-\varkappa_\perp|}. \tag{18}$$

The quantities $\kappa_\parallel$ and $\kappa_\perp$ are well known for many molecules from measurements of the depolarization of Rayleigh scattering of light. When

$$|\varkappa_\parallel-\varkappa_\perp| \sim 10^{-24}\ \mathrm{cm}^3,\quad d\sim 10^{-19}\ \text{cgs esu}\quad d_0\sim 10^{-18}\ \text{cgs esu}$$
$$2B\sim 30\ \mathrm{cm}^{-1}\ \text{and}\ \omega_l\sim 10^3\ \mathrm{cm}^{-1}\ \text{we have}\ \varepsilon_v\sim 50\ \mathrm{cm}^{-1}/\Delta\nu,$$

where $\Delta\nu$ is the detuning $|\omega_l - \omega_v|$ in cm^{-1}, and $\epsilon_r \sim 0.15$.

Thus, at $\Delta\nu < 50\ \mathrm{cm}^{-1}$, the vibrational part can become comparable with the electronic part. As seen from (14) and (15), interference of these contributions takes place, and they can either reinforce or cancel each other, depending on the sign of $\omega_l - \omega_v$. At detunings of the order of $50\ \mathrm{cm}^{-1}$, it can be verified that the linear damping at the Stokes frequency will be smaller than the gain due to the Raman process over a considerable range of pump powers.

The rotational part can also make a noticeable contribution to the gain, and under certain conditions one can have $\epsilon_r > 1$ and $\epsilon_r > \epsilon_v$, i.e., this effect becomes the principal one. At $J_2 = J_1 + 1$ the contribution of the electronic part to χ is determined by expression (14) with $d = d_0 = 0$. The nuclear part leads to the appearance of an antisymmetrical component of the tensor $\kappa_{\alpha\gamma}$, so that the dependence on the polarizations turns out to be different from that given by expression (15) with $d \neq 0$.

The expressions presented above for χ and $\mathbf{P}^S$ are valid if only one transition does indeed play the principal role. Otherwise it is necessary to sum over the transitions, and then if the line width greatly exceeds the difference between the frequencies of two neighboring transitions, the gain ceases to depend on τ. This corresponds to the classical analysis; the then-obtained condition $\Omega_0 \approx 2\Omega$ corresponds to the selection rule $J_2 = J_1 + 2$.

Thus, we have considered the theory of stimulated Raman scattering on purely rotational transitions with allowance for the intermediate vibrational and purely rotational transitions. We have shown that the contribution of these transitions to the gain can be the principal one if pumping is with a carbon dioxide laser of wavelength 10.6 μ. Under these conditions, the dependence on the polarization is different (for the transition $J_2 = J_1 + 1$) than in the case of pure electronic polarizability.

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