

Polarization effects in stimulated Raman scattering and related phenomena

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1970 J. Phys. B: At. Mol. Phys. 3 1558

(<http://iopscience.iop.org/0022-3700/3/11/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 222.197.180.195

The article was downloaded on 01/07/2011 at 14:52

Please note that [terms and conditions apply](#).

Polarization effects in stimulated Raman scattering and related phenomena

L. D. BARRON

Department of Theoretical Chemistry, University Chemical Laboratory,
Lensfield Road, Cambridge

MS. received 4th February 1970

Abstract. Polarization effects in stimulated Raman and stimulated Rayleigh scattering and self focusing are investigated from the viewpoint of the scattering of polarized photons by molecules. Both stimulated vibrational Raman scattering in liquids and stimulated rotational Raman scattering in gases are considered, and it is demonstrated that the polarization changes and relative power thresholds for different laser polarizations should be somewhat different to those predicted in other theories. For example, the ellipticity η^0 of the stimulated rotational Raman photons in the forward direction from $\Delta J = \pm 2$ transitions in gaseous symmetric top molecules is given in terms of the initial ellipticity η^i by $\sin 2\eta^0 = -\frac{5}{7} \sin 2\eta^i$, whereas conventional theories predict that η^0 and η^i are equal in magnitude and opposite in sign. Furthermore it is shown that deviations from this relation could provide a measure of the degree of optical orientation of the molecules.

1. Introduction

Interesting polarization effects have been observed recently in connection with stimulated Rayleigh, Raman and self focused light. These observations include certain correlations between the polarization of the incident and scattered light beams, as well as a polarization dependence of the power thresholds for the onset of the particular scattering processes (Maker and Terhune 1965, Close *et al.* 1966, Minck *et al.* 1966, Foltz *et al.* 1968). For a general review of the stimulated Raman effect and related phenomena we refer to Bloembergen (1967).

All the theories put forward so far to explain the polarization effects are based on the conventional treatment involving the response of bulk media, characterized by appropriate non-linear susceptibility tensors, to a laser beam. An alternative approach involving photon scattering from individual molecules is presented here, and this is shown to provide an explanation of most of the polarization observations in more precise terms than the previous theories. For example, in the conventional treatments the polarization of the stimulated Raman light is obtained implicitly by comparing the magnitudes of the relevant non-linear bulk polarizations, which are assumed to be proportional to the scattering cross sections and hence the power thresholds for various input and output laser polarizations, and choosing the largest. But here the polarizations are calculated directly from the nature of the molecular scattering process; consequently the present treatment should be viewed in the context of the discussions of the molecular mechanisms responsible for stimulated Raman scattering (Buckingham 1965, Freedhoff 1967, Wallace 1967, Philpott 1968).

The theory is based on the simple model of stimulated Raman scattering in which the appropriate spontaneous Raman photons stimulate further emission of like photons, and if the incident light is sufficiently intense an exponential gain of the Raman wave results (Bloembergen 1967). Thus our basic assumption is that the stimulated Raman photons have the same polarization as their spontaneous precursors. Indeed the

conventional treatments (Minck *et al.* 1966, Chiao and Godine 1969) obtain ratios of polarization dependences for the power thresholds that are consistent with this assumption. In any event the two-step molecular mechanism of stimulated Raman scattering suggested by Wallace (1967) would provide stimulated Raman photons with the same polarization as spontaneous Raman photons. A calculation of the polarization resulting from a one-step mechanism (Buckingham 1965, Freedhoff 1967, Philpott 1968) would involve a molecular hyperpolarizability contribution to the scattering, and will not be considered here. A further point is that if more precise measurements of the polarizations were made and compared with the predictions below, their agreement or otherwise would provide additional insight into the mechanism of stimulated Raman scattering.

Consequently we require the polarization of Raman photons scattered spontaneously into the forward direction. This process must be carefully distinguished from refringent scattering, which is associated with completely different polarization changes. Refringent scattering refers to the fundamental process responsible for refraction and birefringence, namely interference between the transmitted and the forward scattered photons (Atkins and Barron 1970 a,b). This interference cannot occur with forward scattered Raman photons since they have a different frequency to the transmitted photons. A similar situation arises with self focusing, where the scattering is now slightly off-axis so the interference with transmitted photons is reduced. For simplicity we shall ignore polarization changes arising from optically induced birefringence effects such as the autorotation of the polarization ellipse.

In a recent paper (Atkins and Barron 1969, to be referred to as I) general equations were obtained for the polarization of photons scattered by molecules at any angle and for any incident polarization. The polarization of the scattered photons in the effects mentioned above ought to be given by equations (4.35) and (4.36) of I pertaining to nonrefringent forward scattering. Thus the ellipticity η and azimuth θ are given by

$$\sin 2\eta^0 = i \left(\frac{\langle 2(3) \| 1(3) \rangle - \langle 1(3) \| 2(3) \rangle}{\langle 1(3) \| 1(3) \rangle + \langle 2(3) \| 2(3) \rangle} \right) \quad (1.1)$$

$$\tan 2\theta^0 = \frac{\langle 2(3) \| 1(3) \rangle + \langle 1(3) \| 2(3) \rangle}{\langle 1(3) \| 1(3) \rangle - \langle 2(3) \| 2(3) \rangle} \quad (1.2)$$

where, if R is Hermitian,

$$\begin{aligned} \langle 2(3) \| 1(3) \rangle - \langle 1(3) \| 2(3) \rangle &= i \operatorname{Im} \{ R_{21} R_{11}^* (1 + \cos 2\eta^1 \cos 2\theta^1) \\ &\quad + R_{22} R_{12}^* (1 - \cos 2\eta^1 \cos 2\theta^1) \\ &\quad + R_{21} R_{12}^* (\cos 2\eta^1 \sin 2\theta^1 + i \sin 2\eta^1) \\ &\quad + R_{22} R_{11}^* (\cos 2\eta^1 \sin 2\theta^1 - i \sin 2\eta^1) \} \end{aligned} \quad (1.3)$$

$$\begin{aligned} \langle 2(3) \| 1(3) \rangle + \langle 1(3) \| 2(3) \rangle &= \operatorname{Re} \{ R_{21} R_{11}^* (1 + \cos 2\eta^1 \cos 2\theta^1) \\ &\quad + R_{22} R_{12}^* (1 - \cos 2\eta^1 \cos 2\theta^1) \\ &\quad + R_{21} R_{12}^* (\cos 2\eta^1 \sin 2\theta^1 + i \sin 2\eta^1) \\ &\quad + R_{22} R_{11}^* (\cos 2\eta^1 \sin 2\theta^1 - i \sin 2\eta^1) \} \end{aligned} \quad (1.4)$$

$$\begin{aligned} \langle 1(3) \| 1(3) \rangle \pm \langle 2(3) \| 2(3) \rangle &= \frac{1}{2} (R_{11} R_{11}^* \pm R_{21} R_{21}^*) (1 + \cos 2\theta^1 \cos 2\eta^1) \\ &\quad + \frac{1}{2} (R_{12} R_{12}^* \pm R_{22} R_{22}^*) (1 - \cos 2\theta^1 \cos 2\eta^1) \\ &\quad + \frac{1}{2} (R_{11} R_{12}^* \pm R_{21} R_{22}^*) (\cos 2\eta^1 \sin 2\theta^1 + i \sin 2\eta^1) \\ &\quad + \frac{1}{2} (R_{12} R_{11}^* \pm R_{22} R_{21}^*) (\cos 2\eta^1 \sin 2\theta^1 - i \sin 2\eta^1). \end{aligned} \quad (1.5)$$

All the quantities here are defined in I; however we are now using a different set of space-fixed axes ($\epsilon_1 \times \epsilon_2 = \epsilon_3$ rather than $\epsilon_1 \times \epsilon_2 = -\epsilon_3$).

If attention is restricted to non-absorptive scattering through electric dipole interactions only, the R -matrix elements may be written

$$R_{FG} = \frac{2\pi\hbar\omega}{V} \sum_{m'} \left(\frac{\langle m' | d_F | m'' \rangle \langle m'' | d_G | m \rangle}{E_m - E_{m''} + \hbar\omega} + \frac{\langle m' | d_G | m'' \rangle \langle m'' | d_F | m \rangle}{E_m - E_{m''} - \hbar\omega} \right) \quad (1.6)$$

where F, G are the space-fixed coordinates 1,2,3; $|m\rangle$ is the molecular state, being specified in the Born-Oppenheimer approximation by electronic, vibrational, and rotational quantum numbers n, ν, R , respectively; and d is the electric dipole moment operator. Equation (1.6) may be written to a good approximation as (Bridge and Buckingham 1966)

$$R_{FG} = \frac{2\pi\hbar\omega}{V} \langle R' | l_{F\alpha} l_{G\beta} | R \rangle \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle \quad (1.7)$$

where $l_{F\alpha}$ are direction cosines; α, β are molecule-fixed coordinates x, y, z ; and $\alpha_{\alpha\beta}$ is the electronic polarizability tensor:

$$\alpha_{\alpha\beta} = \sum_{n'', \nu''} \left(\frac{\langle g | d_\alpha | n'' \nu'' \rangle \langle n'' \nu'' | d_\beta | g \rangle}{E_{g\nu} - E_{n''\nu''} + \hbar\omega} + \frac{\langle g | d_\beta | n'' \nu'' \rangle \langle n'' \nu'' | d_\alpha | g \rangle}{E_{g\nu} - E_{n''\nu''} - \hbar\omega} \right) \quad (1.8)$$

where g is the ground electronic state. The initial and final vibrational and rotational states are specified so as to provide forward scattered photons at the frequency of interest.

2. Stimulated Raman scattering in liquids

We consider first stimulated vibrational Raman scattering in liquids, where free rotation is quenched. A classical Boltzmann average is then appropriate, so that the ellipticity and azimuth for a particular fundamental vibrational transition are obtained from (1.1) and (1.2) as

$$\sin 2\eta^0 = \left(\frac{5(\langle \nu' | \alpha_{\alpha\alpha} | 0 \rangle \langle \nu' | \alpha_{\beta\beta} | 0 \rangle - \langle \nu' | \alpha_{\alpha\beta} | 0 \rangle \langle \nu' | \alpha_{\beta\alpha} | 0 \rangle)}{\langle \nu' | \alpha_{\alpha\alpha} | 0 \rangle \langle \nu' | \alpha_{\beta\beta} | 0 \rangle + 7\langle \nu' | \alpha_{\alpha\beta} | 0 \rangle \langle \nu' | \alpha_{\beta\alpha} | 0 \rangle} \right) \sin 2\eta^i \quad (2.1)$$

$$\tan 2\theta^0 = \tan 2\theta^i. \quad (2.2)$$

For a symmetric top molecule with polarizability components α_{\parallel} and α_{\perp} parallel and perpendicular, respectively, to the symmetry axis, (2.1) becomes

$$\begin{aligned} \sin 2\eta^0 &= \left(\frac{5(\langle \nu' | \alpha_{\perp} | 0 \rangle^2 + 2\langle \nu' | \alpha_{\parallel} | 0 \rangle \langle \nu' | \alpha_{\perp} | 0 \rangle)}{4\langle \nu' | \alpha_{\parallel} | 0 \rangle^2 + 9\langle \nu' | \alpha_{\perp} | 0 \rangle^2 + 2\langle \nu' | \alpha_{\parallel} | 0 \rangle \langle \nu' | \alpha_{\perp} | 0 \rangle} \right) \sin 2\eta^i \\ &= \frac{5(1 - \kappa^2) \sin 2\eta^i}{5 + 7\kappa^2} \end{aligned} \quad (2.3)$$

with the 'transition anisotropy' κ defined as

$$\kappa = \frac{\langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle}{3\langle \nu' | \alpha | 0 \rangle}$$

where α is the mean polarizability $\frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$.

It is convenient to rewrite (2.3) as

$$\sin 2\eta^0 = \left(\frac{5(9 \langle \nu' | \alpha | 0 \rangle^2 - \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle^2)}{45 \langle \nu' | \alpha | 0 \rangle^2 + 7 \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle^2} \right) \sin 2\eta^{\dagger} \quad (2.4)$$

for then it can be seen that the decrease in ellipticity is a function of the asymmetry of the normal mode, since α can only span a totally symmetric mode. Also $\alpha_{\parallel} - \alpha_{\perp}$ vanishes if the molecule is isotropic, and the Raman photons will have the same ellipticity as the incident beam.

3. Stimulated Raman scattering in gases

The case of stimulated Raman scattering in gases is rather more subtle. In most gases the rotational fine structure is not resolved, and one observes the average polarization of photons arising from all the allowed rotational transitions for the vibrational transition of interest. A weighted sum over all the relevant initial and final rotational states is required; and if the populated rotational levels are close compared to kT , the sum may be replaced by an integral and a classical Boltzmann average suffices.

With molecular hydrogen at not too high a temperature, individual rotational levels are well separated and the classical Boltzmann average is not applicable. There have been several reports on the polarization of stimulated vibrational and rotational Raman light from molecular hydrogen (Maker and Terhune 1965, Minck *et al.* 1966), so an explicit calculation for hydrogen gas is appropriate.

From (1.1) and (1.2) together with

$$R_{FG}R_{HI}^* = \text{Re } R_{FG} \text{Re } R_{HI} + \text{Im } R_{FG} \text{Im } R_{HI} + i(\text{Im } R_{FG} \text{Re } R_{HI} - \text{Re } R_{FG} \text{Im } R_{HI})$$

and by anticipating the calculation of rotational matrix elements in the appendix and the summations over M, M' , we can write

$$\sin 2\eta^0 = \left(\frac{\text{Re } R_{22} \text{Re } R_{11} - \text{Im } R_{21} \text{Im } R_{21}}{\text{Re } R_{11} \text{Re } R_{11} + \text{Im } R_{21} \text{Im } R_{21}} \right) \sin 2\eta^{\dagger} \quad (3.1)$$

$$\tan 2\theta^0 = \left(\frac{\text{Im } R_{21} \text{Im } R_{21} + \text{Re } R_{22} \text{Re } R_{11}}{\text{Re } R_{11} \text{Re } R_{11} - \text{Im } R_{21} \text{Im } R_{21}} \right) \tan 2\theta^{\dagger}. \quad (3.2)$$

The following average must be used in these equations:

$$\langle R_{FG}R_{HI} \rangle = \sum_{\substack{J, M, \\ J', M'}} N_J \langle J'M' | l_{Fa} l_{G\beta} | JM \rangle \langle J'M' | l_{Hy} l_{I\delta} | JM \rangle \langle \nu' | \alpha_{\alpha\beta} | 0 \rangle \langle \nu' | \alpha_{\gamma\delta} | 0 \rangle \quad (3.3)$$

where $N_i = \exp(-E_i/kT) / \sum_j \exp(-E_j/kT)$ is the probability that a molecule is in the quantum state $|i\rangle$ with energy E_i . The sum over all J' is appropriate if the final rotational levels are not differentiated; otherwise a particular J' is specified corresponding to the ΔJ transition of interest. But one sums over all M' for the particular J' since the M levels are degenerate in the absence of external fields (we assume that the second order dynamic Stark splitting due to the optical field is negligible).

The polarizability tensor may be written in a principal axes system as

$$\alpha_{FG} = l_{Fx} l_{Gx} \alpha_{xx} + l_{Fy} l_{Gy} \alpha_{yy} + l_{Fz} l_{Gz} \alpha_{zz}.$$

Since $l_{F\alpha}l_{G\alpha} = \delta_{FG}$, this becomes for a symmetric top molecule

$$\alpha_{FG} = \alpha_{\perp}\delta_{FG} + (\alpha_{\parallel} - \alpha_{\perp})l_{Fz}l_{Gz} \quad (3.4)$$

where z is the symmetry axis. The required R -matrix elements can now be written

$$R_{11} = \frac{2\pi\hbar\omega}{V} \{ \langle \nu' | \alpha_{\perp} | 0 \rangle \delta_{R'R} + \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle \langle R' | l_{1z}^2 | R \rangle \} \quad (3.5)$$

$$R_{21} = \frac{2\pi\hbar\omega}{V} \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle \langle R' | l_{2z}l_{1z} | R \rangle \quad (3.6)$$

$$R_{22} = \frac{2\pi\hbar\omega}{V} \{ \langle \nu' | \alpha_{\perp} | 0 \rangle \delta_{R'R} + \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle \langle R' | l_{2z}^2 | R \rangle \}. \quad (3.7)$$

The ellipticity for a particular rotational Raman transition is now

$$\begin{aligned} \sin 2\eta_{\lambda}^0 &= \sin 2\eta^1 \left[\sum_{J,M,M'} N_J \{ (\langle \nu' | \alpha_{\perp} | 0 \rangle)^2 + \langle \nu' | \alpha_{\perp} | 0 \rangle \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle \right. \\ &\quad \times \operatorname{Re} \langle J'M' | l_{2z}^2 + l_{1z}^2 | JM \rangle \delta_{R'R} + \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle^2 \\ &\quad \left. \times (\operatorname{Re} \langle J'M' | l_{2z}^2 | JM \rangle \operatorname{Re} \langle J'M' | l_{1z}^2 | JM \rangle - \operatorname{Im} \langle J'M' | l_{2z}l_{1z} | JM \rangle^2) \right] \\ &\quad \times \left[\sum_{J,M,M'} N_J \{ (\langle \nu' | \alpha_{\perp} | 0 \rangle)^2 + \langle \nu' | \alpha_{\perp} | 0 \rangle \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle \right. \\ &\quad \times \operatorname{Re} \langle J'M' | l_{1z}^2 + l_{2z}^2 | JM \rangle \delta_{R'R} + \langle \nu' | \alpha_{\parallel} - \alpha_{\perp} | 0 \rangle^2 (\operatorname{Re} \langle J'M' | l_{1z}^2 | JM \rangle^2 \\ &\quad \left. + \operatorname{Im} \langle J'M' | l_{2z}l_{1z} | JM \rangle^2) \right]^{-1} \quad (3.8) \end{aligned}$$

where $\lambda = 0, Q, S$ correspond to $\Delta J = J' - J = -2, 0, 2$, respectively: these are the only allowed transitions for hydrogen in a Σ electronic state, or any symmetric top molecule in a rotational state with $K = 0$.

Consider first the $\Delta J = +2$ transition. We must substitute into (3.8) all the non-vanishing matrix elements of l_{1z}^2 , l_{2z}^2 and $l_{2z}l_{1z}$ between $|JM\rangle$ and $\langle J+2, M' |$. After much tedious arithmetic we find

$$\sin 2\eta_s^0 = \frac{-3\alpha^2\kappa^2 \sin 2\eta^1 \sum_J N_J (J+2)(J+1)/(2J+3)}{\frac{2}{5}\alpha^2\kappa^2 \sum_J N_J (J+2)(J+1)/(2J+3)} = -\frac{5}{7} \sin 2\eta^1 \quad (3.9)$$

which is independent of J . The same result obtains for the $\Delta J = -2$ line.

The ellipticity of the $\Delta J = 0$ line is

$$\sin 2\eta_Q^0 = \frac{2\alpha^2 \sin 2\eta^1 \sum_J N_J (2J+1) \{1 - \kappa^2(J^2 + J)/(2J+1)(2J+3)\}}{\frac{2}{3}\alpha^2 \sum_J N_J (2J+1) \{5 + 7\kappa^2(J^2 + J)/(2J-1)(2J+3)\}} \quad (3.10)$$

and is temperature dependent. If $J > 3$,

$$\frac{J^2 + J}{(2J-1)(2J+3)} \sim \frac{1}{4}$$

and so

$$\sin 2\eta_Q^0 \rightarrow \frac{5(1-\kappa^2/4)}{5+7\kappa^2/4} \sin 2\eta^i \quad (3.11)$$

with increasing temperature.

It is gratifying to note that if the sum is taken over all J' in (3.8) the classical result (2.3) is recovered.

From (3.2) it can be seen that the azimuth of all rotational Raman lines is always the same as the incident azimuth.

These results will now be discussed in the light of experimental findings. Polarization studies have been reported in stimulated pure rotational Raman scattering from deuterium gas (Minck *et al.* 1966). When the laser was circularly polarized, pure rotational Raman transitions ($\Delta J = 2$) were stimulated which were found to have the opposite sense of circular polarization to the laser beam. From (3.9) we would expect a reversal, but also some decrease, of circularity. These results were explained by Minck *et al.* by invoking a $\Delta M = \pm 2$ transition: indeed by substituting in (3.8) just the matrix elements for a $\Delta M = \pm 2$ transition we predict an opposite circularity with no decrease in circularity; the inclusion of all allowed ΔM transitions reduces the circularity. The question thus arises: was the stimulated rotational Raman beam indeed pure circularly polarized, or was there some decrease in circularity that escaped observation? Similar remarks apply to the other polarization changes predicted by Minck *et al.* for various ΔM transitions, all of which can be obtained from (3.8) and (3.12) with the exception that the $\Delta M = \pm 1$ transition does not give rise to an azimuth change.

Polarization measurements on vibrational Raman scattering from hydrogen gas (Maker and Terhune 1965) show that, for pure vibrational transitions ($\Delta J = 0$) the ellipticity and sense of the stimulated Raman beam are the same as the laser beam. Equation (3.10) predicts the same sense, but since $\kappa \sim 0.8$ for the fundamental vibrational transition in hydrogen, we would expect some decrease in ellipticity, which should also be temperature dependent. The calculation of this effect in I is not quite correct since a classical rotational average is used there.

4. Polarization dependence of the power thresholds

The polarization dependence of the power thresholds for the onset of stimulated Raman scattering is treated by considering the cross section for the spontaneous scattering of photons with the appropriate polarization and wave vector from an incident beam with a particular polarization. It is then assumed that the thresholds are proportional to these cross sections.

The cross section for the scattering of photons with polarization vector π' into the forward direction from an incident beam with polarization vector π is proportional to the statistical average of $|R_{\pi'\pi}|^2$, where

$$R_{\pi'\pi} = \frac{2\pi\hbar\omega}{V} \langle \nu' R' | \alpha : (b_1'\epsilon_1 + b_2'\epsilon_2)^* (b_1\epsilon_1 + b_2\epsilon_2) | \nu R \rangle \quad (4.1)$$

with

$$\begin{aligned} \pi &= b_1\epsilon_1 + b_2\epsilon_2 \\ b_1 &= (\cos \eta \cos \theta + i \sin \eta \sin \theta) \\ b_2 &= (\cos \eta \sin \theta - i \sin \eta \cos \theta). \end{aligned}$$

For simplicity we shall use a classical Boltzmann average, which is equivalent to taking a weighted sum over all R, R' :

$$\begin{aligned}
 \langle |R_{\pi',\pi}|^2 \rangle &= \left(\frac{2\pi\hbar\omega}{V} \right)^2 \left\{ \frac{1}{15} (\langle \nu' | \alpha_{\alpha\alpha} | \nu \rangle \langle \nu' | \alpha_{\beta\beta} | \nu \rangle + 2 \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle) \right. \\
 &\quad \times (b_1 b_1^* b_1' b_1^* + b_2 b_2^* b_2' b_2^*) + \frac{1}{15} (2 \langle \nu' | \alpha_{\alpha\alpha} | \nu \rangle \langle \nu' | \alpha_{\beta\beta} | \nu \rangle \\
 &\quad - \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle) (b_1 b_1^* b_2' b_2^* + b_2 b_2^* b_1' b_1^*) \\
 &\quad + \frac{1}{30} (3 \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle \langle \nu' | \alpha_{\alpha\beta} | \nu \rangle - \langle \nu' | \alpha_{\alpha\alpha} | \nu \rangle \langle \nu' | \alpha_{\beta\beta} | \nu \rangle) (b_1 b_2^* b_1' b_2^* \\
 &\quad \left. + b_1 b_2^* b_2' b_1^* + b_2 b_1^* b_1' b_2^* + b_2 b_1^* b_2' b_1^*) \right\}. \tag{4.2}
 \end{aligned}$$

For a symmetric top molecule

$$\begin{aligned}
 \alpha_{\alpha\alpha} \alpha_{\beta\beta} + 2 \alpha_{\alpha\beta} \alpha_{\alpha\beta} &= 15\alpha^2 + \frac{4}{3}(\alpha_{\parallel} - \alpha_{\perp})^2 \\
 2 \alpha_{\alpha\alpha} \alpha_{\beta\beta} - \alpha_{\alpha\beta} \alpha_{\alpha\beta} &= 15\alpha^2 - \frac{2}{3}(\alpha_{\parallel} - \alpha_{\perp})^2 \\
 3 \alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta} &= 2(\alpha_{\parallel} - \alpha_{\perp})^2.
 \end{aligned}$$

If we consider rotational Raman scattering, only $\alpha_{\parallel} - \alpha_{\perp}$ contributes, and we obtain for the $\Delta J = \pm 2$ transition

$$\begin{aligned}
 \langle |R_{\pi',\pi}|^2 \rangle &= \frac{1}{45} \left(\frac{2\pi\hbar\omega}{V} \right)^2 (\alpha_{\parallel} - \alpha_{\perp})^2 \{ 4(b_1 b_1^* b_1' b_1^* + b_2 b_2^* b_2' b_2^*) \\
 &\quad - 2(b_1 b_1^* b_2' b_2^* + b_2 b_2^* b_1' b_1^*) + 3(b_1 b_2^* b_1' b_2^* + b_1 b_2^* b_2' b_1^* \\
 &\quad + b_2 b_1^* b_1' b_2^* + b_2 b_1^* b_2' b_1^*) \}. \tag{4.3}
 \end{aligned}$$

By substituting into (4.3) the expressions for b_1 and b_2 , we obtain for the $(\pi \rightarrow \pi') \equiv (\theta, \eta \rightarrow \theta', \eta')$ scattering event the ratio of power thresholds $4 : 3 : 6 : 1$ corresponding to $(0, 0 \rightarrow 0, 0) : (0, 0 \rightarrow \pi/2, 0) : (0, \pi/4 \rightarrow 0, -\pi/4) : (0, \pi/4 \rightarrow 0, \pi/4)$, in agreement with Minck *et al.* (1966). But the assignment of particular ΔM values to the various scattering events is not meaningful because the classical average used to obtain (4.3) is equivalent to a sum over all allowed M, M' for the ΔJ of interest. Furthermore, it is known from the results of § 3 that not all the final polarizations chosen above are possible. Thus there is never any change of azimuth, and the ellipticity changes are given by (3.9) and (3.10). The only meaningful ratio of power thresholds is therefore $(0, 0 \rightarrow 0, 0) : (0, \pi/4 \rightarrow 0, \frac{1}{2} \sin^{-1}[-5/7])$, which is found from (4.3) to be $4 : 4.57$. This is to be compared with the ratio $4 : 6$ which was previously expected to be the ratio of power thresholds for linearly and circularly polarized laser light.

Similar calculations can be performed for stimulated vibrational Raman scattering in liquids, but the cross sections for linearly and circularly polarized light will be almost the same. Other factors such as optical orientation and self focusing are probably more important in determining the polarization dependence of the power thresholds in liquids.

5. Stimulated Rayleigh scattering

Stimulated Rayleigh scattering refers to stimulated Raman scattering from unresolved rotational states of molecules in a fluid, the frequency difference being equal to a relaxation rate rather than a resonant frequency. This can produce a broadening, known as the stimulated Rayleigh wing, on the Stokes side of the laser line; but under certain conditions a sharp stimulated Rayleigh line is produced.

Foltz *et al.* (1968) have reported some interesting polarization measurements on these effects. Thus the sharp stimulated Rayleigh line is produced by circularly polarized laser light and is circularly polarized in the opposite sense; the broad stimulated Rayleigh wing can be produced by laser light of any polarization and has the same polarization as the laser.

Stimulated Rayleigh scattering in liquids comprising symmetric top molecules has been discussed by Bloembergen and Lallemand (1966). Their model involving optical orientation suggests that only $\alpha_{\parallel} - \alpha_{\perp}$ contributes to the appropriate non-linear gain. Consequently the nonrefracting forward scattering formulation involving just the anisotropy in the polarizability should be relevant here. We therefore conclude from (2.2) that the azimuth of the stimulated Rayleigh-scattered photons should be the same as that of the laser, whereas the ellipticity should be given by (2.4) as

$$\sin 2\eta^0 = -\frac{2}{3} \sin 2\eta^1.$$

This agrees with the observations on the stimulated Rayleigh line, except that some decrease in ellipticity is expected.

The present formulation does not appear to be able to explain why a plane polarized laser cannot produce the sharp Rayleigh line but only the diffuse wing, nor why above a certain power threshold the sharp line with opposite circularity gives way to a broad wing with the same polarization as the laser. To explain these features it is necessary to consider the bulk properties of the medium (Herman 1967, Chiao and Godine 1969).

6. Self focusing

A pencil of laser light above a certain power threshold collimates itself when passing through a transparent medium and produces extremely intense self-trapped filaments. This occurs because of the non-uniform intensity distribution inherent in a beam of finite cross section, so that the intensity-dependent refractive index can cause different parts of the beam to propagate with different phase velocities: a lens effect is thus produced whereby the rays move towards the region of higher intensity and further increase the intensity there.

It has been observed by Close *et al.* (1966) that a plane polarized laser beam produces plane polarized self-trapped filaments with the same azimuth as the incident beam, whereas a circularly polarized beam produces plane polarized filaments of arbitrary azimuth.

These polarizations could perhaps be explained with reference to the following model. It is assumed that as the beam starts to focus itself, some photons are scattered slightly off-axis towards the region of higher intensity. This means that the scattering becomes increasingly nonrefracting, so the polarization is more properly described by (2.1) and (2.2). This is supported by the fact that Stokes and anti-Stokes filaments also occur because the off-axis scattering is initially spontaneous, allowing Rayleigh,

Stokes, and anti-Stokes scattering to compete on more equal terms. It can be seen that the azimuth of the trapped beam will be the same as that of the incident beam, but the ellipticity will be rather less, depending on the molecular polarizability characteristics.

These results are in broad agreement with the observed polarization of the filaments. Thus if the incident beam is plane polarized, we predict that the filaments are plane polarized with the same azimuth; for a circularly polarized incident beam the filaments are predicted to be elliptically polarized with arbitrary azimuth because the incident azimuth is undefined. Furthermore the ellipticity becomes progressively less at each subsequent near-forward scattering event, so the limit of plane polarization is approached.

This analysis concerns just one of the many processes that affect the polarization of the filaments. Other important factors include the intensity-dependent rotation of the polarization ellipse, which renders the azimuth indeterminate, and the fact that a circularly polarized laser beam with a power below the threshold for self focusing of a circular beam can still contain plane polarized components with intensities that exceed the threshold for a plane polarized beam: these components can focus independently to produce plane polarized filaments (Chaban 1967).

7. Discussion

The main conclusions drawn are that the stimulated scattering process cannot produce any azimuth change; that when circularly polarized laser light is employed the stimulated Rayleigh and rotational Raman light should have an opposite circularity with an ellipticity rather less than circular; and that the ratio of the power thresholds for stimulated rotational Raman scattering using plane and circularly polarized laser light should be somewhat less than thought previously.

Interesting implications arise if in fact the stimulated Rayleigh and rotational Raman light produced by circularly polarized laser light is pure circularly polarized with no decrease in circularity. For example, it has been shown in § 3 that the reversal of circularity in stimulated rotational Raman scattering involving $\Delta J = 2$ transitions would not be accompanied by a decrease in circularity if just $\Delta M = \pm 2$ transitions were involved. This is physically realizable if the molecules are constrained to rotate in the plane of circular polarization of the laser beam, for then the only allowed values of M and M' would be $\pm J$ and $\pm(J+2)$, respectively: the inclusion of molecules not so oriented would reduce the circularity because $\Delta M = 0$ transitions would then also be possible. Consequently no observed decrease in circularity could be indicative of a saturation of the optical orientation; and the degree of ellipticity might provide a measure of the degree of optical orientation. Analogous remarks apply to stimulated Rayleigh scattering, and since the data of Foltz *et al.* (1968) indicate no decrease in ellipticity for the sharp stimulated Rayleigh line, we conclude that this scattering process involves molecules that are completely oriented in the plane of circular polarization of the laser beam. It would be interesting to have more accurate experimental polarization data on all these effects.

We have seen how the forward nonrefracting photon scattering approach to stimulated Raman and Rayleigh scattering and self focusing provides insight at the molecular level into some of the factors affecting the polarization of the scattered light, and ought to be considered in conjunction with the usual approach involving the bulk polarizations induced in the medium.

Acknowledgments

I would like to thank Professor A. D. Buckingham for many useful discussions and valuable criticism. The award of a Fellowship by the Science Research Council is also gratefully acknowledged.

Appendix

The non-vanishing matrix elements of binary products of direction cosines required in the text are listed below. These are evaluated by matrix multiplication using the table of direction cosine matrix elements given in Cross *et al.* (1944), for example. The external quantization axis is taken here as the 3 axis, being the forward scattering direction.

$$\begin{aligned} \langle J, M+2 | l_{2z} l_{1z} | JM \rangle &= -\frac{i}{2} \left\{ \frac{(J-M-1)(J-M)(J+M+1)(J+M+2)}{(2J+3)^2(2J-1)^2} \right\}^{1/2} \\ \langle J, M-2 | l_{2z} l_{1z} | JM \rangle &= \frac{i}{2} \left\{ \frac{(J-M+1)(J-M+2)(J+M-1)(J+M)}{(2J+3)^2(2J-1)^2} \right\}^{1/2} \\ \langle J+2, M+2 | l_{2z} l_{1z} | JM \rangle &= \frac{i}{4} \left\{ \frac{(J+M+1)(J+M+2)(J+M+3)(J+M+4)}{(2J+5)(2J+3)^2(2J+1)} \right\}^{1/2} \\ \langle J+2, M-2 | l_{2z} l_{1z} | JM \rangle &= -\frac{i}{4} \left\{ \frac{(J-M+1)(J-M+2)(J-M+3)(J-M+4)}{(2J+5)(2J+3)^2(2J+1)} \right\}^{1/2} \\ \langle J-2, M+2 | l_{2z} l_{1z} | JM \rangle &= \frac{i}{4} \left\{ \frac{(J-M-3)(J-M-2)(J-M-1)(J-M)}{(2J+1)(2J-1)^2(2J-3)} \right\}^{1/2} \\ \langle J-2, M-2 | l_{2z} l_{1z} | JM \rangle &= -\frac{i}{4} \left\{ \frac{(J+M-1)(J+M)(J+M-2)(J+M-3)}{(2J+1)(2J-1)^2(2J-3)} \right\}^{1/2} \\ \langle JM | l_{2z}^2 | JM \rangle &= \frac{J^2 + J + M^2 - 1}{(2J+3)(2J-1)} \\ \langle J+2, M | l_{2z}^2 | JM \rangle &= -\frac{1}{2} \left[\frac{\{(J+2)^2 - M^2\} \{(J+1)^2 - M^2\}}{(2J+5)(2J+3)^2(2J+1)} \right]^{1/2} \\ \langle J-2, M | l_{2z}^2 | JM \rangle &= -\frac{1}{2} \left[\frac{\{J^2 - M^2\} \{(J-1)^2 - M^2\}}{(2J+1)(2J-1)^2(2J-3)} \right]^{1/2} \\ \langle J, M+2 | l_{2z}^2 | JM \rangle &= -\frac{1}{2} \left\{ \frac{(J-M-1)(J-M)(J+M+1)(J+M+2)}{(2J+3)^2(2J-1)^2} \right\}^{1/2} \\ \langle J, M-2 | l_{2z}^2 | JM \rangle &= -\frac{1}{2} \left\{ \frac{(J-M+1)(J-M+2)(J+M-1)(J+M)}{(2J+3)^2(2J-1)^2} \right\}^{1/2} \\ \langle J+2, M+2 | l_{2z}^2 | JM \rangle &= \frac{1}{4} \left\{ \frac{(J+M+1)(J+M+2)(J+M+3)(J+M+4)}{(2J+5)(2J+3)^2(2J+1)} \right\}^{1/2} \\ \langle J+2, M-2 | l_{2z}^2 | JM \rangle &= \frac{1}{4} \left\{ \frac{(J-M+1)(J-M+2)(J-M+3)(J-M+4)}{(2J+5)(2J+3)^2(2J+1)} \right\}^{1/2} \end{aligned}$$

$$\begin{aligned} \langle J-2, M+2 | l_{2z}^2 | JM \rangle &= \frac{1}{4} \left[\frac{(J-M-3)(J-M-2)(J-M-1)(J-M)}{(2J+1)(2J-1)^2(2J-3)} \right]^{1/2} \\ \langle J-2, M-2 | l_{2z}^2 | JM \rangle &= \frac{1}{4} \left[\frac{(J+M-1)(J+M)(J+M-2)(J+M-3)}{(2J+1)(2J-1)^2(2J-3)} \right]^{1/2} \\ \langle J'M' | l_{1z}^2 | JM \rangle &= + \langle J'M' | l_{2z}^2 | JM \rangle \quad \text{for } M' = M \\ &= - \langle J'M' | l_{2z}^2 | JM \rangle \quad \text{for } M' = M \pm 2. \end{aligned}$$

The following sums are also required, with M taking all integral values from $-J$ to $+J$:

$$\begin{aligned} \sum_M 1 &= (2J+1) \\ \sum_M M^2 &= \frac{1}{3}(2J+1)(J^2+J) \\ \sum_M M^4 &= \frac{1}{15}(2J+1)(J^2+J)(3J^2+3J-1). \end{aligned}$$

References

- ATKINS, P. W., and BARRON, L. D., 1969, *Molec. Phys.*, **16**, 453-66.
 ——— 1970 a, *Molec. Phys.*, **18**, 721-7.
 ——— 1970 b, *Molec. Phys.*, **18**, 729-36.
 BLOEMBERGEN, N., 1967, *Am. J. Phys.*, **35**, 989-1023.
 BLOEMBERGEN, N., and LALLEMAND, P., 1966, *Phys. Rev. Lett.*, **16**, 81-4.
 BRIDGE, N. J., and BUCKINGHAM, A. D., 1966, *Proc. R. Soc. A*, **295**, 334-9.
 BUCKINGHAM, A. D., 1965, *J. chem. Phys.*, **43**, 25-31.
 CHABAN, A. A., 1967, *J.E.T.P. Lett.*, **5**, 48-50.
 CHIAO, R. Y., and GODINE, J., 1969, *Phys. Rev.*, **185**, 430-45.
 CLOSE, D. H., *et al.*, 1966, *I.E.E.E.J. Quant. Elec.*, **QE-2**, 553-7.
 CROSS, P. C., HAINER, R. M., and KING, G. W., 1944, *J. chem. Phys.*, **12**, 210-43.
 FOLTZ, N. D., CHO, C. W., RANK, D. H., and WIGGINS, T. A., 1968, *Phys. Rev.*, **165**, 396-400.
 FREEDHOFF, H. S., 1967, *J. chem. Phys.*, **47**, 2554-6.
 HERMAN, R. M., 1967, *Phys. Rev.*, **164**, 200-6.
 MAKER, P. D., and TERHUNE, R. W., 1965, *Phys. Rev.*, **137**, A801-18.
 MINCK, R. W., HAGENLOCKER, E. E., and RADO, W. G., 1966, *Phys. Rev. Lett.*, **17**, 229-31.
 PHILPOTT, M. R., 1968, *J. chem. Phys.*, **49**, 3558-60.
 WALLACE, R., 1967, *J. chem. Phys.*, **47**, 3126-9.