SPECTRAL THEORY OF MOLECULAR ROTATION-INDUCED BROADENING OF HYPER-RAMAN LINES IN LIQUIDS

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Abstract. The spectral line shape of hyper-Raman light scattering in liquids is calculated by the method of irreducible spherical tensors and the theory of rotational Brownian motion. The line broadening due to rotational molecular motion in the liquid is expressed by way of relaxation times τ_M^J and is found to depend on nonlinear molecular parameters $\bar{B}_M^{J\,2}$, which are quadratic functions of the derivatives with respect to appropriate normal coordinates of the hyperpolarizability tensor elements $b_{ijk}^{2\omega}$. Tables of $|\bar{B}_M^{J}|^2$ are adduced for all vibration symmetries of spherical-top and symmetric-top molecules. The tensor elements of scattered light intensity are calculated for linearly and circularly polarized incident light. Investigation of hyper-Raman spectral line broadening is seen as a source of new data on the dynamics of molecules in the liquid state and on their nonlinear optical properties.

1. Introduction

The advent of laser techniques permitted the extension of theory of Raman light scattering, as proposed by Placzek [1], to nonlinear scattering [2], referred to as hyper-Raman scattering [3, 4]. Let ω denote the circular vibration frequency of the laser beam, and ω_r a vibrational eigen-frequency of the molecule. Then light scattering at frequencies $\omega_s^{(1)} = 2\omega \pm \omega_r$ is the hyper-Raman effect of order 1; scattering at frequencies $\omega_s^{(2)} = 3\omega \pm \omega_r$ is the hyper-Raman effect of order 2; and, quite generally, scattering at frequencies $\omega_s^{(n)} = (n+1)\omega \pm \omega_r$ is what can be termed an nth order hyper-Raman effect. If the scattered light observed is not modulated by molecular vibrations, we simply write $\omega_r = 0$ and refer to the phenomenon as a hyper-Rayleigh effect of the nth order, since now $\omega_s^{(n)} = (n+1)\omega$. The present paper is restricted to the hyper-Raman effect of order 1, to which we shall refer simply as hyper-Raman scattering.

The phenomena of hyper-Raman and hyper-Rayleigh light scattering are sources of highly relevant information concerning the motions and mutual interactions of molecules in liquids [2-5]. Studies of their line shapes permit the determination of molecular relaxation times of higher orders. The problem is accessible to a general description by angular momentum and irreducible spherical tensor methods [6-8] in conjunction with the theory of rotational Brownian motions [9]. With respect to hyper-Rayleigh light scattering, the problem was studied closely by Maker [7], whose calculations for symmetric-top molecules have recently been extended to the case of asymmetric-top ones [10].

Hyper-Raman spectroscopy extends our range of investigation by permitting us to

analyze a far richer set of spectral lines; moreover, it provides the key to the study of liquids composed of centro-symmetric molecules where first-order hyper-Rayleigh scattering is intrinsically absent [2]. The coherent part of hyper-Raman scattered light related to scattering by statistically correlated molecules is, contrary to hyper-Rayleigh scattering [11], vanishingly small owing to the circumstance that the phases of normal vibrations of the individual molecules in the liquid are statistically independent. As a result, hyper-Raman line shape studies will permit a more accurate description of the motion of the individual molecules of the liquid.

The hyper-Raman spectral line shape is predominantly defined by orientational motions of the molecules and their internal vibrations. The contribution from molecular vibrational motion cannot be separated from that of orientational motion by first-order hyper-Raman spectral analysis alone. This is because it is impossible to separate the isotropic component, which is independent of molecular orientational motion and yields directly the intrinsic line shape. This contribution can be determined from absorption studies in IR or Raman scattering covering many of the normal vibrations active in one of these two effects.

The present paper is aimed at the investigation of the hyper-Raman line shape for the cases of incident linearly polarized light as well as incident circularly polarized light. Derivatives of hyperpolarizability tensor elements accounting for all types of vibrations of symmetric-top and spherical-top molecules are calculated and tabulated in the form of molecular parameters $|\tilde{B}_u^J|^2$ well-adapted for the direct analysis of hyper-Raman light scattering by liquids.

2. Theory of Hyper-Raman Line Shape Broadening in Liquids

In dealing with hyper-Raman light scattering, we shall proceed similarly to Placzek's [1] treatment of linear polarizability theory. The conditions for its applicability to nonlinear Raman scattering are analyzed in Refs [2–4]. In the case of small vibrations of the nuclei, the appropriate tensor $b_{ijk}^{2\omega}$ of the electric molecular hyperpolarizability can be expanded in a Taylor series:

$$b_{ijk}^{2\omega}(t) = b_{ijk}^0(t) + \sum_r b_{ijk}^r(t)\, q_r(t) + \cdots . \tag{1}$$

The tensor $b_{ijk}^0(t)$ accounts for hyper-Rayleigh scattering, whereas the tensor:

$$b_{ijk}^r(t) = \left(\frac{\partial b_{ijk}(t)}{\partial q_r} \right)_{q_r=0}$$

describes light scattering at the hyper-Raman frequency $\omega_s = 2\omega \pm \omega_r$, where ω_r is an eigen-frequency of the normal vibration q_r.

We consider an isotropic liquid, composed of a large number N of generally anisotropic molecules on which a linearly polarized light wave, of frequency ω and electric field $E_i(t) = E_0\, e_i \cos \omega t$, is incident (e is the unit vector of light polarisation). The

hyper-Raman spectral line shape is given by the tensor $I_{ij}(\Delta\omega)$. The latter is the Fourier transform of the tensor $I_{ij}(t)$ of scattered light intensity:

$$I_{ij}(\Delta\omega) = \frac{1}{2\pi} \int\limits_{-\tau}^{\tau} dt\, I_{ij}(t) \exp(i\Delta\omega t). \qquad (2)$$

$\Delta\omega$ is a measure of the distance, in units of frequency from the centre $\omega_s^{(1)}$ of the spectral line. On neglecting coupling between the orientational motion of the molecule and its vibrations q_r, the tensor $I_{ij}(t)$ can be written in the following form [2]:

$$I_{ij}(t) = \frac{\pi}{2c^5} (2\omega \pm \omega_r)^4 I_0^2 \sum_m \sum_n \langle b_{ik\rho}^{r(m)}(0)\, b_{jl\tau}^{r(n)*}(t) \rangle \times$$
$$\times \langle q_r^{(m)}(0)\, q_r^{(n)*}(t) \rangle e_k e_l^* e_\rho e_\tau^*, \qquad (3)$$

where $\langle\ \rangle$ denotes statistical averaging, and I_0 is the incident light intensity; the indices m, n label the molecules of the liquid.

On the assumption of mutually independent phases of the normal vibrations of any two molecules, we can write:

$$\langle q_r^{(m)}(0)\, q_r^{(n)*}(t) \rangle = 0, \qquad m \neq n,$$

and Equation (2) becomes (omitting the molecular indices m, n):

$$I_{ij}(\Delta\omega) = A_\pm(T) \int\limits_{-\infty}^{\tau} dt\, C_{ij}(t) \langle q_r(0)\, q_r^*(t) \rangle \exp(i\Delta\omega t), \qquad (4)$$

where

$$C_{ij}(t) = \langle b_{ik\rho}^r(0)\, b_{jl\tau}^{r*}(t) \rangle_\Omega\, e_k e_l^* e_\rho e_\tau^* \qquad (4a)$$

is the orientational autocorrelation tensor, and

$$A_\pm(T) = \frac{N I_0^2}{4c^5} (2\omega \pm \omega_r)^4 f_\pm(T) \qquad (4b)$$

with $f_\pm(T)$ a function of temperature similar to that for linear scattering [1].

From Equation (4), the hyper-Raman line shape depends on the orientational as well as the vibrational motions of the molecules. It is thus essential to resolve these two contributions. The vibrational autocorrelation functions $\langle q_v(0)\, q_v^*(t) \rangle$ are accessible to determination from absorption in IR or from Raman scattering, which yield the intrinsic line shape, defined by the function [5]:

$$I_v(\Delta\omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\tau} dt\, \langle q_v(0)\, q_v^*(t) \rangle \exp(i\Delta\omega t). \qquad (5)$$

The preceding procedure is justified since, in general, some normal vibrations q_v are active in at least one of the two effects. Accordingly, we shall henceforth restrict our discussion to the orientational autocorrelation matrix $C_{ij}(t)$ which, from experimental results, can be obtained in the following form:

$$C_{ij}(t) = \frac{\int\limits_{-\infty}^{\infty} d(\Delta\omega)\, I_{ij}(\Delta\omega)\exp(-i\Delta\omega t)}{A_{\pm}(T)\int\limits_{-\infty}^{\infty} d(\Delta\omega)\, I_v(\Delta\omega)\exp(-i\Delta\omega t)}. \tag{6}$$

On neglecting translational motion of the molecules, one can assume the tensor elements $b_{ijk}^v(t)$ to be time-dependent only by way of variations in molecular orientation $\Omega(t)$:

$$b_{ijk}^v(t) = b_{ijk}^v[\Omega(t)].$$

The mean value of the time-dependent tensor product $\langle b_{ikp}^v(0)\, b_{jlr}^{v*}(t)\rangle$ is given by the expression:

$$\langle b_{ikp}^v(0)\, b_{jlr}^{v*}(t)\rangle_\Omega = \frac{1}{8\pi^2}\int\limits_{\Omega(0)}\int\limits_{\Omega(t)} b_{ikp}^v(0)\, b_{jlr}^{v*}(t)\, f(\Delta\Omega, t)\, d\Omega(0)\, d\Omega(t), \tag{7}$$

where

$$\int d\Omega = \int\limits_0^{2\pi} d\alpha \int\limits_0^{\pi} d\beta\, \sin\beta \int\limits_0^{2\pi} d\gamma = 8\pi^2,$$

the Euler angles α, β, γ being defined as in Reference 6, and $f(\Delta\Omega, t)$ denoting the conditional singlet probability function, defining the probability of a change in molecular orientation by the angle $\Delta\Omega = \Omega(t) - \Omega(0)$ in the interval of time t.

The function $f(\Delta\Omega, t)$ can be expanded in a power series in Wigner functions $D_{KM}^J(\Delta\Omega)$ [6]:

$$f(\Delta\Omega, t) = \sum_{J, M} D_{MM}^J(\Delta\Omega)\, f_M^J(t). \tag{8}$$

The expansion coefficients $f_M^J(t)$, with $|M| \leqslant J$, are functions of the time; their shape depends on the nature of the rotational motion of the molecules in the liquid.

Applying the particularly simple model of Debye's rotational diffusion, the function $f(\Delta\Omega, t)$ can be found by solving the following equation [9]:

$$\frac{\partial f(\Delta\Omega, t)}{\partial t} = -\sum_i L_i^2 D_i f(\Delta\Omega, t), \tag{9}$$

where the L_i's are components of the angular momentum operator $\hat{L}$ and the D_i's are diagonal elements of the molecular rotational diffusion tensor ($i = x, y, z$). In the case

of axially-symmetric molecules $D_x = D_y \neq D_z$, and the solution of Equation (9) is obtained in the form:

$$f_M^J(t) = \frac{2J + 1}{8\pi^2} \exp\left(-\frac{t}{\tau_M^J}\right). \tag{10}$$

with the molecular relaxation time τ_M^J equal to:

$$\tau_M^J = [J(J + 1) D_x + M^2(D_z - D_x)]^{-1}. \tag{11}$$

In the case of spherical molecules $D_x = D_y = D_z = D$, and the relaxation times are found not to depend on the number M:

$$\tau^J = [J(J + 1) D]^{-1}. \tag{12}$$

We now proceed to write out explicitly the autocorrelation matrix (4a) and its Fourier transform determining the hyper-Raman spectral line shape, for selected experimental geometries and states of incident light polarization.

Assume the incident beam to propagate in the direction of the Y-axis with electric vector linearly polarized along the Z-axis. For observation in the direction of the X-axis, the polarized component $I_Z(\Delta\omega)$ and unpolarized component $I_Y(\Delta\omega)$ of scattered light are described by the autocorrelation functions:

$$C_{a-Z, Y}(t) = \langle b_{nZZ}^r(0) \, b_{nZZ}^{r*}(t)\rangle_\Omega. \tag{13}$$

In the case of right-circular polarization $(e_{+1} = -(i/\sqrt{2})(x + iy))$ of the incident light wave, at observation along the propagation direction of the latter, the co-rotating $(+)$ and contra-rotating $(-)$ scattered spectra are given by [8]:

$$C_{a+1, -1}(t) = \langle b_{a-1-1}^r(0) \, b_{a-1-1}^{r*}(t)\rangle_\Omega. \tag{14}$$

To calculate the autocorrelation functions (13) and (14), the tensor elements b_{ijk}^r have to be expressed in the form of spherical tensors B_M^J by means of the transformation matrices of References 7 and 8.

A tensor b_{ijk}, if symmetric in all its indices, involves no invariant part of zero-th rank in its spherical representation.* Hence, no isotropic term independent of orientational molecular motion can be picked out in Equation (4). As a consequence of this, contrary to the case of normal Raman scattering, observations of hyper-Raman scattering do · not permit the determination of $I_v(\Delta\omega)$, the function describing the vibrational contribution to line broadening. The assumption of time-independence, made in Reference 5 with respect to the expression $b_{iij}^r(0) \, b_{jkk}^r(t)$, led to the conclusion that it was possible to resolve an isotropic part in the spectrum of scattered hyper-Raman radiation. Now from what has been said above, that assumption appears to be unjustified.

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* Which involves only parts of ranks 1 and 3 [7].

TABLE I

Nonzero molecular parameters $|\bar{B}^{J}_{M}|^2$ as quadratic functions of b^{v}_{ijk}

Notation

$a = b_{xxx}$,	$e = b_{xxz}$,	$i = b_{yyz}$,
$b = b_{yyy}$,	$f = b_{xyy}$,	$j = b_{yzz}$.
$c = b_{zzz}$,	$g = b_{xyz}$,	
$d = b_{xxy}$,	$h = b_{xzz}$.	

Point groups	Symmetry of vibration		The form of the non-zero parameters $|\bar{B}^{J}_{M}|^2$
C_3	A		$|\bar{B}^1_0|^2 = \frac{1}{3}(c+2e)^2$, $|\bar{B}^3_0|^2 = \frac{2}{3}(c-3e)^2$, $|\bar{B}^3_{\pm 3}|^2 = 2(a^2+b^2)$
	E	1	$|\bar{B}^3_{\pm 2}|^2 = 3(e^2+g^2)$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}[(4a+3h)^2+(4b+3j)^2]$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}[(a-3h)^2+(b-3j)^2]$
		2	$|\bar{B}^3_{\pm 2}|^2 = 3(e^2+g^2)$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}[(4a+3h)^2+(4b+3j)^2]$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}[(a-3h)^2+(b-3j)^2]$
D_3, D_{3d}	A_1, A_{1u}		$|\bar{B}^3_{\pm 3}|^2 = 2a^2$
	A_2, A_{2u}		$|\bar{B}^1_0|^2 = \frac{1}{3}(c+2e)^2$, $|\bar{B}^3_0|^2 = \frac{2}{3}(c-3e)^2$, $|\bar{B}^3_{\pm 3}|^2 = 2b^2$
	E, E_u	1	$|\bar{B}^3_{\pm 2}|^2 = 3g^2$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}(4a+3h)^2$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}(a-3h)^2$
		2	$|\bar{B}^3_{\pm 2}|^2 = 3e^2$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}(4b+3j)^2$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}(b-3j)^2$
C_{3v}	A_1		$|\bar{B}^1_0|^2 = \frac{1}{3}(c-2e)^2$, $|\bar{B}^3_0|^2 = \frac{2}{3}(c+3e)^2$, $|\bar{B}^3_{\pm 3}|^2 = 2a^2$
	A_2		$|\bar{B}^3_{\pm 3}|^2 = 2b^2$
	E	1	$|\bar{B}^3_{\pm 2}|^2 = 3e^2$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}(4a+3h)^2$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}(a-3h)^2$
		2	$|\bar{B}^3_{\pm 2}|^2 = 3g^2$, $|\bar{B}^1_{\pm 1}|^2 = \frac{1}{30}(4b+3j)^2$, $|\bar{B}^3_{\pm 1}|^2 = \frac{2}{15}(b-3j)^2$

Table 1 (Continued)

Point groups	Symmetry of vibration	The form of the non-zero parameters $B_{M}^{J}{}^{2}$
C_4, C_{4h}, S_4	A, A_u, B	$|\tilde{B}_0^1|^2 = \frac{1}{3}(c + 2e)^2, \quad |\tilde{B}_0^3|^2 = \frac{2}{3}(c - 3e)^2$
	B, B_u, A	$|\tilde{B}_{\pm2}^3|^2 = 3(e^2 + g^2)$
	E, E_u, E	1 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{3}{10}[(a + f + h)^2 + (b + d + j)^2],$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}[(a + f - 4h)^2 + (b + d - 3j)^2],$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}[(a - 3f)^2 + (b - 3d)^2]$ 2 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{3}{10}[(a + f + h)^2 + (b + d + j)^2],$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}[(a + f - 4h)^2 + (b + d - 3j)^2],$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}[(a - 3f)^2 + (b - 3d)^2]$
$C_{4v}, D_4,$ D_{4h}, D_{2d}	A_1, A_2, A_{2u}, B_2	$|\tilde{B}_0^1|^2 = \frac{1}{3}(c + 2e)^2, \quad |\tilde{B}_0^3|^2 = \frac{2}{3}(c - 3e)^2$
	B_1, B_2, B_{2u}, A_2	$|\tilde{B}_{\pm2}^3|^2 = 3e^2$
	B_2, B_1, B_{1u}, A_1	$|\tilde{B}_{\pm2}^3|^2 = 3g^2$
	E, E, E_u, E	1 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{3}{10}(a + f + h)^2,$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}(a + f - 4h)^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}(a - 3f)^2$ 2 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{3}{10}(b + d + j)^2,$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}(b + d - 3j)^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}(b - 3d)^2$
C_6, C_{3h}, C_{6h}	A, A'', A_u	$|\tilde{B}_0^1|^2 = \frac{1}{3}(c + 2e)^2, \quad |\tilde{B}_0^3|^2 = \frac{2}{3}(c - 3e)^2$
	B, A', B_u	$|\tilde{B}_{\pm3}^3|^2 = 2(a^2 + b^2)$
	E_1, E', E_{1u}	1 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{1}{30}[(4a + 3h)^2 + (4b + 3j)^2],$ $|\tilde{B}_{\pm1}^3|^2 = \frac{2}{15}[(a - 3h)^2 + (b - 3j)^2]$ 2 $\quad |\tilde{B}_{\pm1}^1|^2 = \frac{1}{30}[(4a + 3h)^2 + (4b + 3j)^2],$ $|\tilde{B}_{\pm1}^3|^2 = \frac{2}{15}[(a - 3h)^2 + (b - 3j)^2]$

Table I (Continued)

Point groups	Symmetry of vibration	The form of the non-zero parameters $\left| B_M^J \right|^2$	
	E_2, E'', E_{2u}	1	$\left| \tilde{B}_{\pm 2}^3 \right|^2 = 3 \left(e^2 + g^2 \right)$
		2	$\left| \tilde{B}_{\pm 2}^3 \right|^2 = 3 \left(e^2 + g^2 \right)$
D_6, D_{6h}, D_{3h}, C_{6v}	A_2, A_{2u}, A_2'', A_1		$\left| \tilde{B}_0^1 \right|^2 = \tfrac{3}{5} \left(c + 2e \right)^2, \quad \left| \tilde{B}_0^3 \right|^2 = \tfrac{2}{5} \left(c - 3e \right)^2$
	B_1, B_{1u}, A_1', B_1		$\left| \tilde{B}_{\pm 3}^3 \right|^2 = 2a^2$
	B_2, B_{2u}, A_2', B_2		$\left| \tilde{B}_{\pm 3}^3 \right|^2 = 2b^2$
	E_1, E_{1u}, E', E_1	1	$\left| \tilde{B}_{\pm 1}^1 \right|^2 = \tfrac{3}{10} \left(4a + 3h \right)^2,$ $\left| \tilde{B}_{\pm 1}^3 \right|^2 = \tfrac{2}{15} \left(a - 3h \right)^2$
		2	$\left| \tilde{B}_{\pm 1}^1 \right|^2 = \tfrac{3}{10} \left(4b + 3j \right)^2,$ $\left| \tilde{B}_{\pm 1}^3 \right|^2 = \tfrac{2}{15} \left(b - 3j \right)^2$
	E_2, E_{2u}, E'', E_2	1	$\left| \tilde{B}_{\pm 3}^3 \right|^2 = 3g^2$
		2	$\left| \tilde{B}_{\pm 3}^3 \right|^2 = 3e^2$
T, T_h	A, A_u		$\left| \tilde{B}_{\pm 3}^3 \right|^2 = 3g^2$
	F, F_u	1	$\left| \tilde{B}_{\pm 1}^1 \right|^2 = \tfrac{3}{10} \left(a + f + h \right)^2,$ $\left| \tilde{B}_{\pm 1}^3 \right|^2 = \tfrac{3}{40} \left(a + f - 4h \right)^2,$ $\left| \tilde{B}_{\pm 3}^3 \right|^2 = \tfrac{1}{8} \left(a - 3f \right)^2$
		2	$\left| \tilde{B}_{\pm 1}^1 \right|^2 = \tfrac{3}{10} \left(b + d + j \right)^2,$ $\left| \tilde{B}_{\pm 1}^3 \right|^2 = \tfrac{3}{40} \left(b + d - 4j \right)^2,$ $\left| \tilde{B}_{\pm 3}^3 \right|^2 = \tfrac{1}{8} \left(b - 3j \right)^2$
		3	$\left| \tilde{B}_0^1 \right|^2 = \tfrac{3}{5} \left(c + e + i \right)^2,$ $\left| \tilde{B}_0^3 \right|^2 = \tfrac{1}{10} \left(2c + 3e + 3i \right)^2,$ $\left| \tilde{B}_{\pm 2}^3 \right|^2 = \tfrac{3}{4} \left(e - i \right)^2$
T_d, O, O_h	A_1, A_2, A_{2u}		$\left| \tilde{B}_{\pm 2}^3 \right|^2 = 3g^2$

Table I (Continued)

Point groups	Symmetry of vibration	The form of the non-zero parameters $|\tilde{B}_M^J|^2$
F_2, F_1, F_{1u}	1	$|\tilde{B}_{\pm1}^1|^2 = \frac{3}{16}(a + 2f)^2,$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}(a - 3f)^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}(a - 3f)^2$
	2	$|\tilde{B}_{\pm1}^1|^2 = \frac{3}{16}(b + 2d)^2,$ $|\tilde{B}_{\pm1}^3|^2 = \frac{3}{40}(b - 3d)^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{1}{8}(b - 3d)^2$
	3	$|\tilde{B}_0^1|^2 = \frac{3}{5}(c + 2e)^2,$ $|\tilde{B}_0^3|^2 = \frac{2}{5}(c - 3e)^2$
F_1, F_2, F_{2u}	1	$|\tilde{B}_{\pm1}^3|^2 = \frac{15}{8}f^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{9}{8}f^2$
	2	$|\tilde{B}_{\pm1}^3|^2 = \frac{15}{8}j^2,$ $|\tilde{B}_{\pm3}^3|^2 = \frac{9}{8}j^2$
	3	$|\tilde{B}_{\pm2}^3|^2 = 3e^2$

By taking the Fourier transforms of the autocorrelation functions $C_n(t)$, we now can obtain expressions for the hyper-Raman line broadening due only to orientational molecular motion. For the various states of polarization of the incident light beam, we thus obtain:

$$C_Z(\Delta\omega) = \tfrac{1}{3}\sum_M |\tilde{B}_M^1|^2\, g_M^1(\Delta\omega) + \tfrac{3}{35}\sum_M |\tilde{B}_M^3|^2\, g_M^3(\Delta\omega),$$

$$C_Y(\Delta\omega) = \tfrac{1}{45}\sum_M |\tilde{B}_M^1|^2\, g_M^1(\Delta\omega) + \tfrac{4}{105}\sum_M |\tilde{B}_M^3|^2\, g_M^3(\Delta\omega),$$

$$C_{+1}(\Delta\omega) = \tfrac{4}{45}\sum_M |\tilde{B}_M^1|^2\, g_M^1(\Delta\omega) + \tfrac{1}{105}\sum_M |\tilde{B}_M^3|^2\, g_M^3(\Delta\omega), \tag{15}$$

$$C_{-1}(\Delta\omega) = \tfrac{1}{7}\sum_M |\tilde{B}_M^3|^2\, g_M^3(\Delta\omega),$$

where

$$g_M^J(\Delta\omega) = \frac{2(\tau_M^J)}{1 + (\Delta\omega\tau_M^J)^2} \tag{16}$$

is a Lorentz function, of halfwidth equal to the reciprocal of the relaxation time τ_M^J. C_Y and C_Z are functions analogous to ones derived by Maker [7].

Analytically, the shape of the molecular parameters $|\tilde{B}_M^J|^2$ is determined by the symmetry of the molecule as well as that of the normal vibration q_v. Table I gives the

parameters $|\tilde{B}_M^J|^2$ in explicit form for all vibration symmetries of symmetric-top and spherical-top molecules as functions of derivatives $b_{i j \lambda}^r$. The index v, labelling the normal coordinate q_v with respect to which the derivative is taken, is omitted, since the latter can be easily and uniquely identified from the notations in Column 2. Our calculations show that, for doubly degenerate normal vibrations, the values of the parameters $|\tilde{B}_M^J|^2$ are always equal in spite of their different analytical form. For triply degenerate vibrations, the values of the parameters $|\tilde{B}_M^J|^2$ are mutually equal for two of the coordinates whereas the value of $|\tilde{B}_M^J|^2$ for the third coordinate is different.

3. Discussion and Conclusions

From Table I and Equations (15), the hyper-Raman line broadening due to orientational molecular motion alone is in general a sum of several Lorentz functions (16) and can be of a non-Lorentz shape. Of especial interest are those normal vibrations to which there corresponds only one nonzero parameter $|\tilde{B}_M^J|^2$; the corresponding line broadening depends on a single relaxation time τ_M^J, the numerical value of which can be obtained directly by measuring the halfwidth $(\Delta\omega)_{1/2}$.

As an example, we adduce the line shape functions (15) for all hyper-Raman active vibrations of molecules having the properties of the symmetry group D_{6h}. Since they possess a centre of symmetry, all their electric hyperpolarizability tensor elements $b_{i j \lambda}^0(t)$ vanish and they can cause no hyper-Rayleigh light scattering. Hence, one has to have recourse to hyper-Raman scattering studies in order to obtain information as to their molecular third-order relaxation times τ_M^3.

For vibrations B_{1u}, B_{2u}, E_{2u} the spectral shape is defined by a single line shape function, $g_3^3(\Delta\omega)$, and the following, simple relation holds:

$$C_Z(\Delta\omega) = \tfrac{3}{2}C_Y(\Delta\omega) = 6C_{+1}(\Delta\omega) = \tfrac{3}{2}C_{-1}(\Delta\omega) = \tfrac{4}{35}|\tilde{B}_3^3|^2\, g_3^3(\Delta\omega). \quad (17)$$

For vibrations E_{1u}, we have the relations:

$$\begin{aligned}
C_Z(\Delta\omega) &= \tfrac{2}{5}|\tilde{B}_1^1|^2\, g_1^1(\Delta\omega) + \tfrac{4}{35}|\tilde{B}_1^3|^2\, g_1^3(\Delta\omega), \\
C_Y(\Delta\omega) &= \tfrac{2}{15}|\tilde{B}_1^1|^2\, g_1^1(\Delta\omega) + \tfrac{8}{105}|\tilde{B}_1^3|^2\, g_1^3(\Delta\omega), \\
C_{+1}(\Delta\omega) &= \tfrac{8}{45}|\tilde{B}_1^1|^2\, g_1^1(\Delta\omega) + \tfrac{2}{105}|\tilde{B}_1^3|^2\, g_1^3(\Delta\omega), \\
C_{-1}(\Delta\omega) &= \tfrac{2}{7}|\tilde{B}_1^3|^2\, g_1^3(\Delta\omega).
\end{aligned} \quad (18)$$

For vibrations A_{2u}, the relations are:

$$\begin{aligned}
C_Z(\Delta\omega) &= \tfrac{2}{5}|\tilde{B}_0^1|^2\, g_0^1(\Delta\omega) + \tfrac{4}{35}|\tilde{B}_0^3|^2\, g_0^3(\Delta\omega), \\
C_Y(\Delta\omega) &= \tfrac{2}{15}|\tilde{B}_0^1|^2\, g_0^1(\Delta\omega) + \tfrac{8}{105}|\tilde{B}_0^3|^2\, g_0^3(\Delta\omega), \\
C_{+1}(\Delta\omega) &= \tfrac{4}{45}|\tilde{B}_0^1|^2\, g_0^1(\Delta\omega) + \tfrac{1}{105}|\tilde{B}_0^3|^2\, g_0^3(\Delta\omega), \\
C_{-1}(\Delta\omega) &= \tfrac{1}{7}|\tilde{B}_0^3|^2\, g_0^3(\Delta\omega).
\end{aligned} \quad (19)$$

The preceding formulae show that it is feasible to determine the values of the molecular relaxation times τ_M^J and nonlinear molecular parameters $|\tilde{B}_M^J|^2$ from vibrational

hyper-Raman spectra. Spectra $I_{-1}(\Delta\omega)$ related to the vibration E_{1u} yield directly τ_1^3 whereas those related to vibrations of the type A_{2u} permit the determination of τ_0^3. Hyper-Raman scattering makes possible the direct study of vibrations of the types B_{1u}, B_{2u} and E_{2u} and the determination of $|\bar{B}_3^3|^2$; however, difficulties arise with regard to τ_3^3, since these vibrations are not active either in IR absorption or Raman scattering.

By having recourse to Table I, a similar analysis can be performed for other symmetry groups of symmetric-top and spherical-top molecules. In the case of liquids composed of asymmetric-top molecules the spectra will be more complicated; as is the case for hyper-Rayleigh scattering [10], they will be dependent on a larger number of relaxation times τ_L'.

In our considerations we assumed the hyperpolarizability tensor $b_{ijk}^{2\omega}$ as real, and symmetric in all its indices. This is a good approximation as long as the frequencies of incident and scattered light are remote from regions of electron absorption and dispersion. Analogous calculations on b_{ijk} without the assumption of total symmetry lead to results involving a larger number of molecular parameters [12]. Divergences from total symmetry of $b_{ijk}^{2\omega}$ require, for their description, two more spherical tensors, of degrees 1 and 2, respectively.

Since the coherent part of hyper-Raman scattering, related to scattering by mutually correlated molecules is (contrary to hyper-Rayleigh scattering) negligible, investigation of the relaxation times τ_M' by hyper-Raman scattering is seen to present particularly important advantages. The study of completely symmetric vibrations by the method of hyper-Raman light scattering provides information on molecular dynamics similar to that gleaned from hyper-Rayleigh scattering. With respect to molecular vibrations of different symmetry, hyper-Raman spectroscopy permits the determination of further relaxation times, reaching deeper into the molecular dynamics of liquids.

Maker's [7] measurements of hyper-Rayleigh scattering spectra, as well as those of Verdieck *et al.* [13] and Peterson [14] of hyper-Raman scattering spectra, are examples of the high degree of perfection achieved in the technique of nonlinear molecular spectroscopy. It thus appears that, at present, experimental techniques are fully available for hyper-Raman line shape studies – a method more potent than others for obtaining novel information regarding the structure of individual molecules and their motions in liquids.

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