Second Spectral Moment of Vibrational Hyper-Raman and Hyper-Rayleigh Spectra

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Equations for the second spectral moment of vibrational hyper-Raman and hyper-Rayleigh spectra are derived. It is shown that owing to the simultaneous dependence of the hyper-Raman and hyper-Rayleigh intensities on the irreducible spherical first- and third-rank hyperpolarizability tensors, both the unnormalized and the normalized second moments of both the above types of scattering are geometry dependent. However, for some molecular symmetries and for some molecular vibrations, the irreducible first-rank hyperpolarizability tensor vanishes; then the normalized second spectral moment of the second-harmonically scattered radiation is independent of the scattering geometry, as in the linear case.

INTRODUCTION

When an intense light beam interacts with matter, numerous non-linear processes take place, including multi-harmonic scattering.[1] If the frequency of the scattered light is about twice that of the incident beam, we are dealing with hyper-Rayleigh scattering.[1-4] This type of scattering is described by the third-rank Rayleigh hyperpolarizability tensor $\mathbf{b}(-2\omega, \omega, \omega)$ of a molecule. Internal molecular vibrations can shift the observable spectral lines by hundreds or even thousands of cm^{-1} with respect to the hyper-Rayleigh line. This type of scattering is referred to as vibrational hyper-Raman scattering and is governed by the vibrationally modulated hyperpolarizability tensor $\mathbf{b}(-2\omega \pm \omega_v, \omega, \omega)$. Obviously, the rotational and translational motions of the scatterer molecules modulate the frequency of both above types of scattering.[1,5-16] The determination of the spectral distribution of the scattered radiation is, however, very difficult. It is, in fact a many-body problem, solvable in practice only with the help of high-efficiency computers. Nonetheless, some information on the spectral distribution can be gleaned from the spectral moments of the types of scattered light discussed above. This work was devoted to the calculation of the second spectral moments of hyper-Rayleigh and vibrational hyper-Raman scattering. To our knowledge, this problem has not previously been considered for these types of scattering. We show how, in some cases, the symmetry of the molecules can be determined from studies of both the hyper-Rayleigh and the hyper-Raman spectral moment.

THEORY AND CONCLUSIONS

Consider a system of N molecules in a volume V. The origin of coordinates is in the centre of V. An intense

linearly polarized coherent light wave $\mathbf{E} = \mathbf{e}E_0 \exp[i(\omega t - \mathbf{k} \cdot \mathbf{r})]$ is incident on the system. The second-harmonically scattered wave with the vector $\mathbf{k}_s$ is observed at the point $\mathbf{R}$ with the analyser set to transmit waves with polarization $\mathbf{n}$. We neglect the fine structure of the spectral line, disregarding the translational coordinates of the molecules. Moreover, we neglect coupling between the orientational motion of the molecule and its normal vibration Q_v, as well as coupling between normal vibrations of different molecules.[4a] The rotational part of the correlation function of the vibrational hyper-Raman light wave measured in the vicinity of $2\omega \pm \omega_v$ is then given by the expression

$$I_n(t) = A_\pm^{2\omega \pm \omega_v} \langle [\mathbf{n} \cdot \mathbf{b}'(i, 0) : \mathbf{ee}][\mathbf{n} \cdot \mathbf{b}'(i, t) : \mathbf{ee}] \rangle \quad (1)$$

with

$$A_\pm^{2\omega \pm \omega_v} = N \left(\frac{n_{2\omega} + 2}{3} \right)^2 \left(\frac{n_\omega + 2}{3} \right)^4 \frac{I_0^2}{R^2} \left(\frac{2\omega \pm \omega_v}{c} \right)^4 f_\pm(T)$$

$$(1a)$$

where $\mathbf{b}'(i, t)$ is the Raman hyperpolarizability tensor of the molecule i at time t; the brackets $\langle \quad \rangle$ represent the equilibrium average over the orientations of all the molecules; and $f_\pm(T)$ is a function of temperature similar to that for linear scattering.[4a]

If we consider the hyper-Rayleigh scattering measured in the vicinity of 2ω:

$$I_n(t) = A^{2\omega} \left\langle \sum_{\substack{j = i, j \neq i}} [\mathbf{n} \cdot \mathbf{b}(i, 0) : \mathbf{ee}][\mathbf{n} \cdot \mathbf{b}(j, t) : \mathbf{ee}] \right\rangle \quad (2)$$

where $\mathbf{b}(i, t)$ or $\mathbf{b}_i(-2\omega, \omega, \omega)$ denotes the Rayleigh hyperpolarizability tensor of the molecule i, $f_\pm(T) = 1$ and moreover in Eqn 2 there appears a coherent part, $i \neq j$, of hyper-Rayleigh scattering, a part absent in Eqn 1 owing to the lack of correlations between the normal vibrations of different molecules.

For simplicity, at this stage, we restrict our considerations to totally polarized hyper-Raman scattering. We assume that the incident radiation is polarized along the z-axis of the laboratory frame. The correlation function

1 of the vibrational hyper-Raman scattered light is then described by[1-10]

$$I_{\parallel}(t) = A^{2\omega \pm \omega_\nu}\langle b'_{zzz}(i, 0)b'_{zzz}(i, t)\rangle \qquad (3)$$

where $b'_{zzz}(i, 0)$ and $b'_{zzz}(i, t)$ are the laboratory zzz components of the Raman hyperpolarizability tensor at time $t = 0$ and t, respectively. The stationary property of the correlation function (3) allows us to calculate its second spectral moment, $M_2{}^{\parallel}$, as the negative second time derivative of Eqn (3) [11] at time $t = 0$ (sum rule). This derivative can be transformed to

$$M_2{}^{\parallel} = A^{2\omega \pm \omega_\nu}\left\langle \frac{d}{dt} b'_{zzz}(i, 0) \frac{d}{dt} b'_{zzz}(i, 0)\right\rangle \qquad (4)$$

We start by calculating the totally symmetric Raman hyperpolarizability tensor and then extend our results to the case when the hyperpolarizability tensor is symmetric in its last two indices only, and also to the case of hyper-Rayleigh scattering. We start from linear molecules. Taking into account the Cartesian–spherical transformation coefficients for the b'_{zzz} component of the hyperpolarizability tensor, we have[5,6,12,13]

$$b'_{zzz}(i, t) = -i\sqrt{\tfrac{3}{5}}D^1_{00}(\Omega_i(t))\tilde{B}'^1_0 + i\sqrt{\tfrac{2}{5}}D^3_{00}(\Omega_i(t))\tilde{B}'^3_0 \qquad (5)$$

where $D^J_{KM}(\Omega)$ is the Wigner function[14,15] and $\tilde{B}'^l_m$ is the mth component of the irreducible spherical hyperpolarizability tensor of lth rank in the molecular frame.[6] The relationship between the irreducible spherical molecular parameters $|\tilde{B}'^l_m|^2$ and the Cartesian Raman hyperpolarizability components b_{ijk} has been given previously for all molecular point group and all normal vibrations.[16] Since the hyperpolarizability tensor (5) does not depend explicitly on time we can calculate the time derivative in Eqn (4) by means of the Poisson bracket

$$\frac{d}{dt} = \sum_{k=1}^{N}\left(\frac{\partial H}{\partial p_k}\frac{\partial}{\partial q_k} - \frac{\partial H}{\partial q_k}\frac{\partial}{\partial p_k}\right) \qquad (6)$$

where the sum extends over all degrees of freedom of the system [over all molecules (i) and over the translational coordinates x, y, z and rotational coordinates φ, θ within the molecule].

Taking into account the properties of the canonical distribution, we easily find[17,18]

$$\left\langle \frac{\partial H}{\partial p_i^{(\theta)}}\frac{\partial H}{\partial p_k^{(\eta)}}\right\rangle = \begin{cases} \dfrac{kT}{I}\,\delta_{ik} & \text{for } \eta = \theta \\ 0 & \text{for } \eta = \varphi, x, y, z \end{cases} \qquad (7)$$

where I denotes the moment of inertia of a linear molecule, k is Boltzmann's constant and T is the temperature of the system. We calculate the derivatives of the Wigner functions in Eqn (7) as

$$\frac{\partial}{\partial \theta_i} D^1_{00}(\Omega_i) = -\sin\theta_i \qquad (8a)$$

$$\frac{\partial}{\partial \theta_i} D^3_{00}(\Omega_i) = \frac{3}{2}\sin\theta_i(1 - 5\cos^2\theta_i) \qquad (8b)$$

Averaging isotropically over θ_i in Eqn (4) we have[1,2]

$$\langle \sin^2\theta_i\rangle_{iso} = \tfrac{2}{3} \qquad (9a)$$

$$\langle [\tfrac{3}{2}\sin\theta_i(1 - 5\cos^2\theta_i)]^2\rangle_{iso} = \tfrac{12}{7} \qquad (9b)$$

The isotropic averages of the cross terms between Eqns (8a) and (8b) are zero. Therefore, for the non-normalized second moment of the hyper-Raman spectral line, we obtain

$$(M_2{}^{\parallel})_{HR} = A^{2\omega}\frac{kT}{I}\left[\frac{2}{5}|\tilde{B}'^1_0|^2 + \frac{24}{35}|\tilde{B}'^3_0|^2\right] \qquad (10)$$

The second spectral moment of a Raman line normalized to the integral intensity is $6kT/I$.[19] Normalizing Eqn (10) in a similar manner, we obtain

$$\overline{(M_2{}^{\parallel})_{HR}} = \frac{kT}{I}\frac{\dfrac{2}{5}|\tilde{B}'^1_0|^2 + \dfrac{24}{35}|\tilde{B}'^3_0|^2}{\dfrac{1}{5}|\tilde{B}'^1_0|^2 + \dfrac{2}{35}|\tilde{B}'^3_0|^2} \qquad (11)$$

The second spectral moment and the integral intensity of the hyper-Raman line are dependent simultaneously on the first- and third-rank hyperpolarizability tensors. In the case of linear Raman scattering, this dependence is restricted to the second-rank polarizability tensor only. If one component in Eqn (11) predominates, the situation is similar to the case of linear scattering. If $\tilde{B}'^1_0 \gg \tilde{B}'^3_0$, then $\overline{(M_2)_{HR}} = 2kT/I$ (as in infrared spectroscopy), whereas if $\tilde{B}'^1_0 \ll \tilde{B}'^3_0$, then $\overline{(M_2)_{HR}} = 12kT/I$. From Eqn (7), the second spectral moment of the coherent part of hyper-Rayleigh is zero. Hence the general form of the non-normalized second moment of the hyper-Rayleigh line is formally the same as in hyper-Raman scattering; however, the molecular parameters $\tilde{B}_m{}^l$ have different meanings in each case. From these considerations, both the non-normalized and the normalized second moment of the hyper-Raman line are dependent on the geometry of observation. For the depolarized component, we have

$$(M_2{}^{\perp})_{HR} = A^{2\omega}\frac{kT}{I}\left[\frac{2}{45}|\tilde{B}'^1_0|^2 + \frac{16}{35}|\tilde{B}'^3_0|^2\right] \qquad (12)$$

We now proceed to examine the influence of non-total symmetrical nature of the hyperpolarizability tensor b_{ijk} on the second moment. The irreducible spherical tensors describing the hyper-Raman scattered intensity now depend on the supplementary index s related to the symmetry of the lth-rank tensor element $B^{(l, s)}$ with respect to an interchange of the indices i, j, k. We denote[13] by $s = 1$ the irreducible spherical molecular parameters originating in the totally symmetric part of b_{ijk} and by $s = 2$ those originating in its asymmetric part (corresponding to $\overset{s}{,}$ and $\overset{c}{,}$, respectively, in the notation in Ref. 10). Therefore, in addition to the totally symmetric molecular parameters $\tilde{B}'^{(1, 1)}_0$ and $B'^{(3, 1)}_0$ ($s = 1$), two additional asymmetric molecular parameters, $\tilde{B}'^{(1, 2)}_0$ and $\tilde{B}'^{(2, 2)}_0$, appear. For the depolarized second spectral moment, we have

$$(M_2{}^{\perp})_{HR} = A^{2\omega}\frac{kT}{I}$$

$$\times \left[\frac{2}{45}|\tilde{B}'^{(1, 1)}_0 + \sqrt{5}\tilde{B}'^{(1, 2)}_0|^2 + \frac{16}{35}|\tilde{B}'^{(3, 1)}_0|^2 \right.$$

$$\left. + \frac{2}{5}|\tilde{B}'^{(2, 2)}_0|^2\right] \qquad (13)$$

Obviously, the situation is now more complicated than in Eqn (12) and there is less chance of a simple universal equation for the second spectral moment of the hyper-Raman line.

We now proceed to discuss the hyper-Raman second spectral moment for symmetric top molecules. In this case it is more convenient to calculate the time derivative in Eqn (4) in a different way. For the orientational degrees of freedom, the time derivative in Eqn (4) transforms to[20]

$$\frac{d}{dt} = i \sum_{k=1}^{N} \omega_k \cdot l_k \qquad (14)$$

where ω_k denotes the vector of orientational velocity of a molecule k and l_k its angular momentum operator. Again, we restrict ourselves to the totally symmetric tensor b_{ijk}. Using Eqn (14), after some algebra,[20,21] we obtain the following expression for the polarized non-normalized hyper-Raman second moment valid for symmetric and spherical top molecules [the generalization of Eqn (15) to a non-totally symmetric hyper-polarizability tensor is straightforward]:

$$(M_2{}^\parallel)_{HR} = A^{2\omega} \frac{kT}{I} \left[\frac{1}{5} \sum_v (2 + v^2\eta) |\tilde{B}_v'^1|^2 \right.$$
$$\left. + \frac{2}{35} \sum_\tau (12 + \tau^2\eta) |\tilde{B}_\tau'^3|^2 \right] \qquad (15)$$

where $\eta = I_{zz}/I$ denotes the ratio of the moment of inertia I_{zz} of the molecule calculated for its principal axis and its moment of inertia I calculated for an axis perpendicular thereto. In Eqn (15), as with linear molecules, the second spectral moment (15) is dependent on the first- and third-rank hyperpolarizability tensors.

However, for certain molecular symmetries and selected normal vibrations (as is given in the Table in our earlier paper[16]), only the components of the irreducible third-rank tensor $\tilde{B}_m'^3$ differ from zero. These are the parameters $|\tilde{B}_{\pm2}'^3|^2$ in the case of the molecular symmetries C_4, C_{4h} and S_4 and normal vibrations respectively B, B_u, A; and the molecular symmetries C_{4v}, D_4, D_{4h} and D_{2d} and normal vibrations respectively B_1 and B_2; B_2 and B_1; B_{2u} and B_{1u}; A_2 and A_1. The non-normalized polarized second spectral moment of these bands is now

$$(M_2{}^\parallel)_{HR} = \frac{16}{35} A^{2\omega} \frac{kT}{I} (3 + \eta) |\tilde{B}_2'^3|^2 \qquad (16)$$

On normalizing Eqn (16) to the integral intensity, we obtain

$$\overline{(M_2)_{HR}} = 4 \frac{kT}{I} (3 + \eta) \qquad (17)$$

Clearly, the value of Eqn (17) is geometry independent.

In a different case, the non-zero parameters can be $|\tilde{B}_3'^3|^2 = |\tilde{B}_{-3}'^3|^2$. This is the situation we deal with for the molecular symmetries D_3, D_{3d}, C_{3v} and the normal vibrations A_1, A_{1u}, A_2; for C_6, C_{3h}, C_{6h} and the normal vibrations B, A', B_u; as well as for D_6, D_{6h}, D_{3h}, C_{6v} and normal vibrations respectively B_1 and B_2; B_{1u} and B_{2u}; A_1' and A_2'; B_1 and B_2. Here, in accordance with Eqn (15), the non-normalized polarized second spectral moment of these bands is

$$(M_2{}^\parallel)_{HR} = \frac{12}{35} \frac{kT}{I} A^{2\omega} (4 + 3\eta) |\tilde{B}_3'^3|^2 \qquad (18)$$

On normalizing Eqn (18) to the integral intensity of the polarized component of hyper-Raman-scattered radiation, we obtain

$$\overline{(M_2{}^\parallel)_{HR}} = 3 \frac{kT}{I} (4 + 3\eta) \qquad (19)$$

Four of the above vibrations, $S_4 : A$, $D_{2d} : A_1$, $C_{3h} : A'$ and $D_{3h} : A_1'$, are totally symmetric. Hence, for the first two the second spectral moment of the hyper-Rayleigh line is given by Eqn (16), whereas for the latter two by Eqn (18). Obviously, the molecular parameters $|\tilde{B}_m'^3|^2$ are now determined by way of the Rayleigh hyperpolarizability tensor. Hyper-Rayleigh, as distinct from hyper-Raman scattering, contains a coherent part.[1,2,22] For the integral intensity, it is determined by the static function of orientational molecular correlations $g^{(3)}$ of third degree (the third-degree Kirkwood factor[6,22]). For this reason, on normalization to the integral intensity, the second moment of hyper-Rayleigh light scattered by molecules with the symmetries S_4 and D_{2d} is

$$(M_2)_{HRay} = \frac{4 \frac{kT}{I} (3 + \eta)}{1 + g^{(3)}} \qquad (20)$$

whereas for the symmetries C_{3h} and D_{3h} we have

$$\overline{(M_2)_{HRay}} = \frac{3 \frac{kT}{I} (4 + 3\eta)}{1 + g^{(3)}} \qquad (21)$$

Among other applications of our hyper-Raman and hyper-Rayleigh second-moment equations, the specific forms of the second spectral moments for certain well defined normal vibrations and molecular symmetries suggest that the as yet unknown symmetry of unstudied molecules can be accessible to approximate determination by investigations bearing on the second spectral moments of hyper-Raman and hyper-Rayleigh scattering.

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