

# Isotropic Raman scattering for non-totally symmetric vibrations of correlated molecules with intrinsic optical anisotropy<sup>a)</sup>

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The mechanism of isotropic Raman scattering for non-totally symmetric vibrations, forbidden in the absence of molecular correlations, is analyzed. It is shown that long-range molecular electric fields within the dipole-induced dipole model (DID) lead to isotropic Raman scattering in this case. By Racah algebra, the isotropic parts of the effective Raman polarizability and the intensity of scattered light are examined. The magnitude of this effect for the  $A_2$  vibration of the water molecule is estimated. It is shown that the order of this effect is the same as that of collision-induced depolarized Raman scattering for symmetric vibrations of optically isotropic molecules.

## INTRODUCTION

Long-range molecular electric fields depolarize Rayleigh<sup>1-4</sup> as well as Raman<sup>5-9</sup> scattered light in the case of optically isotropic molecules. Here, these fields are shown to lead to the emergence of an isotropic component of effective Raman polarizability for non-totally symmetric vibrations, i. e., in cases when the Raman polarizability tensor of the isolated molecule is purely anisotropic (intrinsic anisotropy). This entails the existence of isotropic Raman scattering for non-totally symmetric vibrations hitherto not considered in the theory.

## THEORY

The effective Raman polarizability  ${}_{(p)}A_{\alpha\beta}^{\nu}$  of a molecule  $p$  immersed in a medium consisting of  $N$  like anisotropic molecules can be calculated for a selected vibration  $Q_{\nu}$  in the long-range electric field dipole-induced dipole (DID) model:

$${}_{(p)}A_{\alpha\beta}^{\nu} = {}_{(p)}a_{\alpha\beta}^{\nu} Q_{\nu}^p - \sum_{q=1}^{N-1} ({}_{(p)}a_{\alpha\gamma}^{\nu} T_{\gamma\delta}^{pq} {}_{(q)}a_{\delta\beta} Q_{\nu}^q + {}_{(p)}a_{\alpha\gamma} T_{\gamma\delta}^{pq} {}_{(q)}a_{\delta\beta}^{\nu} Q_{\nu}^q) = {}_{(p)}^{(0)}A_{\alpha\beta}^{\nu} + {}_{(p)}^{(1)}A_{\alpha\beta}^{\nu}, \quad (1)$$

where  $a_{\alpha\beta}^{\nu} = [\partial a_{\alpha\beta}(\mathbf{Q}) / \partial Q_{\nu}]_{Q_{\nu}=0}$  is the tensor of Raman polarizability of the isolated molecule,  $T_{\alpha\beta}^{pq}$  that of dipole interactions between molecules  $p$  and  $q$ , and  $a_{\alpha\beta}$  that of Rayleigh polarizability.

The first term of the sum (1) is defined by the intrinsic molecular polarizability. We shall refer to it as the zeroth approximation of the effective Raman polarizabil-

ity  ${}_{(p)}A_{\alpha\beta}^{\nu}$ . The second term is due to dipole-induced dipole interaction. It is at the focus of our concern. We shall refer to it as the first approximation of  ${}_{(p)}A_{\alpha\beta}^{\nu}$ .

By Racah algebra, we can transform the tensor  ${}_{(p)}A_{\alpha\beta}^{\nu}$  to the spherical representation. Under normal scattering conditions, the tensor  ${}_{(p)}A_{\alpha\beta}^{\nu}$  is symmetric. Because of this  ${}_{(p)}A_{\alpha\beta}^{\nu}$  has irreducible spherical components of zeroth and second rank only. Here, we are interested only in the isotropic part of that tensor. It has the form (a) in the zeroth (single molecule) approximation

$${}_{(p)}^{(0)}A^{\nu(0)} = {}_{(p)}a^{\nu(0)} Q_{\nu}^p \quad (2a)$$

and (b) in the first approximation of DID

$${}_{(p)}^{(1)}A^{\nu(0)} = -(10)^{1/2} \sum_{t, l, R_1, R_2} (-)^{R_2} \Pi_t \begin{Bmatrix} 1 & l & 1 \\ t & 1 & 2 \end{Bmatrix} \begin{Bmatrix} 2 & t & l \\ R_1 & \epsilon & -R_2 \end{Bmatrix} \times \sum_{\alpha=1}^{N-1} D_{R_1 0}^2(\Omega_{pq}^p) D_{R_2 \eta}^l(\Omega_{pq}^q) \bar{a}_{\epsilon}^{t*} \bar{a}_{\eta}^{\nu(l)*} r_{pq}^{-3} (Q_{\nu}^p + Q_{\nu}^q). \quad (2b)$$

Above and thereafter,

$$\begin{Bmatrix} a & b & c \\ \alpha & \beta & \gamma \end{Bmatrix}$$

are Clebsch-Gordon coefficients,

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$$

are 6- $j$  Wigner symbols,  $\Omega_{pq}^p$  and  $\Omega_{pq}^q$  are, respectively, the Euler angles of the vector  $\mathbf{r}_{pq}$  connecting the centers of molecules  $p$  and  $q$  and of the orientation of molecule  $q$  with regard to the system of principal axes of molecule  $p$ ,  $D_{KM}^J(\Omega)$  are the Wigner functions, and  $\Pi_{ab\dots f} = [(2a+1)(2b+1)\dots(2f+1)]^{1/2}$ . Moreover,  $\bar{a}_{\eta}^{\nu(l)}$  and  $\bar{a}_{\epsilon}^t$  are spherical components of the Raman and Rayleigh polarizability tensors, respectively, in the system of principal axes of the latter.

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For totally symmetric vibrations, the molecule has a nonzero Raman polarizability tensor trace (a nonzero isotropic component  $a^{(0)}$ ) in the zeroth (one-molecule) approximation. Now, on taking into consideration, beside  ${}^{(0)}A^{(0)}$ , the quantity  ${}^{(1)}A^{(0)}$  in the formula for the scattered light intensity, we obtain in  $J_{iso}^{Raman}$  the first (cross:  ${}^{(0)}A^{(0)} {}^{(1)}A^{(0)} + {}^{(1)}A^{(0)} {}^{(0)}A^{(0)}$ ) correction, resulting from the presence of molecular fields in the medium.<sup>10</sup> However, for non-totally symmetric vibrations the tensor trace of the one-molecule case vanishes ( $a^{(0)}=0$ ), e. g., Ref. 11, so that no isotropic Raman scattering can take place in the zeroth and cross approximations. An analysis of Eq. (2b) shows that the isotropic component of the effective Raman polarizability  ${}^{(1)}A^{(0)}$  is nonzero in the first approximation also in the

case when the Raman polarizability tensor of a single molecule is purely anisotropic. This fact leads to isotropic Raman scattering even for non-totally symmetric vibrations. By formula (2b), we obtain the integrated intensity of Raman scattered light in terms of binary and ternary molecular correlations

$$J_{iso}^{Raman} = 4 {}^{(2)}J_{iso}^{Raman} + 4 {}^{(3)}J_{iso}^{Raman} \quad (3)$$

in a similar way as for depolarized Raman scattering for totally symmetric vibrations of optically symmetric molecules.<sup>5</sup>

We restrict our considerations to binary correlations. At the right angle scattering geometry we get for the intensity of isotropic Raman scattering for non-totally symmetric vibrations

$$\begin{aligned} {}^{(2)}J_{iso}^{Raman} &= \frac{10}{3} \frac{I_0}{R^2} \left(\frac{\omega}{c}\right)^4 N \langle Q_\nu^2 \rangle \sum_{\substack{l_1, l_2, t_1, t_2, J_1, J_2, x \\ \epsilon_1, \epsilon_2, \eta_1, \eta_2, R, R', \xi}} (-)^{R+\eta_2+xx+\xi} \\ &\times \Pi_{t_1 t_1 t_2 \epsilon_2 x^2} \begin{bmatrix} 2 & 2 & J_1 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} t_1 & x & t_2 \\ -\epsilon_1 & \xi & -\epsilon_2 \end{bmatrix} \begin{bmatrix} J_2 & x & J_1 \\ -R' & -\xi & R \end{bmatrix} \begin{bmatrix} l_1 & l_2 & J_2 \\ \eta_1 & -\eta_2 & \eta \end{bmatrix} \begin{Bmatrix} 1 & l_1 & 1 \\ t_1 & 1 & 2 \end{Bmatrix} \\ &\times \begin{Bmatrix} 1 & l_2 & 1 \\ t_2 & 1 & 2 \end{Bmatrix} \begin{Bmatrix} t_1 & 2 & l_1 \\ x & J_1 & J_2 \\ t_2 & 2 & l_2 \end{Bmatrix} \left\langle \sum_{\sigma \neq \rho}^N D_{R0}^{J_1}(\Omega_{\rho q}^{\sigma}) D_{R'\eta}^{J_2}(\Omega_{\rho q}^{\sigma}) r_{\rho q}^{-6} \right\rangle \bar{\alpha}_{\epsilon_1}^{t_1} \bar{\alpha}_{\eta_1}^{\nu} (t_1)^* \bar{\alpha}_{\epsilon_2}^{t_2} \bar{\alpha}_{\eta_2}^{\nu} (t_2). \end{aligned} \quad (4)$$

Above,

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & j \end{Bmatrix}$$

denotes the 9-j Wigner symbol,  $\langle Q_\nu^2 \rangle$  the mean value of the normal mode considered, and  $\langle \rangle$  equilibrium thermal averaging over all positions and orientations of the molecules. We neglect correlations of normal coordinates of different molecules and coupling between the internal vibration and overall reorientation.

In the first approximation we can take the unweighted average over the orientations  $\Omega_{\rho q}^{\sigma}$  and  $\Omega_q^{\sigma}$  in Eq. (4).

Then we obtain

$$\begin{aligned} {}^{(2)}J_{iso}^{Raman} &= \frac{2}{3} \frac{I_0}{R^2} \left(\frac{\omega}{c}\right)^4 N \langle Q_\nu^2 \rangle \\ &\times \sum_{t, t', \eta, \sigma} \begin{Bmatrix} 1 & l & 1 \\ t & 1 & 2 \end{Bmatrix}^2 |\bar{\alpha}_{\eta}^{\nu(t)}|^2 |\bar{\alpha}_{\epsilon}^t|^2 \left\langle \sum_{\sigma \neq \rho}^N r_{\rho q}^{-6} \right\rangle_{\epsilon_s}. \end{aligned} \quad (5)$$

Taking into account the full form of the correlation function  $g^{(2)}(r_{\rho q}, \Omega_{\rho q}^{\sigma}, \Omega_q^{\sigma})$ , we have additional terms, dependent on temperature and the multipolar electric moments of the molecules.<sup>1</sup> It is interesting to note that if we restrict our attention to polar fluids and average our result (4) with the help of a pair correlation function of the form<sup>12</sup>

$$g^{(2)}(pq) = g_s(r_{pq}) + g_D(r_{pq})D(pq) + g_\Delta(r_{pq})\Delta(pq), \quad (6)$$

with

$$D(pq) = 3(\hat{r}_{pq} \cdot \hat{s}_p)(\hat{r}_{pq} \cdot \hat{s}_q) - \hat{s}_p \cdot \hat{s}_q, \quad \Delta(pq) = \hat{s}_p \cdot \hat{s}_q,$$

where  $\hat{s}_i$  ( $i=p, q$ ) gives the orientation of the dipolar axes, all terms connected with  $g_D(r_{pq})$  and  $g_\Delta(r_{pq})$  vanish.

We discuss the expression (5) for a system of molecules of symmetry  $C_{2v}$ . We consider scattering for a non-totally symmetric vibration  $A_2$ . In this case the Rayleigh and Raman polarizability tensors in the system of principal axes of the molecule have, respectively, the forms<sup>13</sup>

$$\begin{pmatrix} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}. \quad (7)$$

Taking into account the relations between the irreducible components and the Cartesian elements of the Rayleigh and Raman polarizability tensors, we have from Eq. (5)

$$\begin{aligned} {}^{(2)}J_{iso}^{Raman} &= \frac{1}{45} \frac{I_0}{R^2} \left(\frac{\omega}{c}\right)^4 N \langle Q_\nu^2 \rangle \bar{a}^2 \\ &\times \left\{ \bar{a}^2 + \frac{7}{160} \left[ \frac{1}{3} (2c - a - b)^2 + (a - b)^2 \right] \right\} \left\langle \sum_{\sigma \neq \rho}^N r_{\rho q}^{-6} \right\rangle_{\epsilon_s}, \end{aligned} \quad (8)$$

where  $\bar{a}$  denotes the mean value of the Rayleigh polarizability tensor.

## DISCUSSION

For a selected non-totally symmetric vibration in the one-molecule approximation, because of the absence of the isotropic part, the polarized component of the scattered light consists of an anisotropic part only. In our case it has the form

$${}^{(1)}I_{VV}^{\text{Raman}} = \frac{1}{15} \frac{I_0}{R^2} \left(\frac{\omega}{c}\right)^4 N \langle Q_v^2 \rangle d^2. \quad (9)$$

Let us define the ratio

$$\eta = \frac{4 {}^{(2)}I_{\text{iso}}^{\text{Raman}}}{{}^{(1)}I_{VV}^{\text{Raman}}} = \frac{4}{3} \left\{ \bar{a}^2 + \frac{7}{160} \left[ \frac{1}{3} (2c - a - b)^2 + (a - b)^2 \right] \right\} \left\langle \sum_{\sigma \neq \beta}^N r_{\beta\sigma}^{-6} \right\rangle_{\epsilon_s},$$

which describes the contribution of collision-induced isotropic Raman scattering at the polarized component of that scattering. We omit here collision-induced corrections to the anisotropic part as they are small in comparison with one-molecule scattering. Let us estimate that ratio for  $T = 300$  K. We calculate the mean value  $\langle r_{\beta\sigma}^{-6} \rangle$  with the help of Eq. (C1) of Ref. 14 for a potential model of water assumed to have an orientational average of the Lennard-Jones form with  $\epsilon = 5.2605 \times 10^{-15}$  erg and  $\sigma = 3.10$  Å.<sup>15</sup> Taking into account the values of the Rayleigh polarizability tensor for the water molecule<sup>16</sup> ( $a = 1.162$  Å<sup>3</sup>,  $b = 1.069$  Å<sup>3</sup>, and  $c = 1.279$  Å<sup>3</sup>), we finally obtain  $\eta = 18 \times 10^{-3}$ . This value is comparable with  $\eta_s$  obtained for depolarized collision-induced Raman scattering for totally symmetric vibrations of optically isotropic molecules.<sup>17</sup> This suggests that mechanisms of these two effects are similar.

We can estimate the mean value of the effective Raman polarizability tensor trace by taking the square root of  $\eta$ . We have  $(\eta)^{1/2} = 0.13$ . The order of this value is in agreement with the experimental one obtained<sup>18</sup> for the non-totally symmetric vibration  $E$  of the  $\text{CDCl}_3$ -DMSO complex.

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