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D.L. Andrews<sup>a b</sup>

<sup>a</sup> Department of Mathematics, University College, Gower Street, London, WC1E 6BT, England  
Present address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England.

<sup>b</sup> Department of Chemistry, University College, Gower Street, London, WC1E 6BT, England  
Present address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England.

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**Hyper-Raman scattering by oriented molecules**

by D. L. ANDREWS

Departments of Mathematics and Chemistry, University College,  
Gower Street, London WC1E 6BT, England†*(Received 11 September 1978)*

Hyper-Raman scattering is a non-linear analogue of Raman scattering observed with intense laser radiation. It is a three-photon process involving the simultaneous absorption of two photons from an incident beam (frequency  $\omega$ ) and the emission of a third at approximately twice the frequency ( $\omega'$ ), the shift ( $2\omega - \omega'$ ) usually being associated with a vibrational transition in the scattering medium. A comprehensive treatment of the hyper-Raman selection rules has recently been given, based on a reduction of the scattering tensor into irreducible parts [1]. In this way it has been shown how hyper-Raman polarization studies supply a powerful method for the study and symmetry assignment of vibrational modes not directly amenable to conventional methods of vibrational spectroscopy.

Experimental studies of hyper-Raman scattering have usually been performed on gases and liquids [2], where the molecules are randomly oriented with respect to the incident beam. The wide scope for the hyper-Raman study of vibrations in oriented molecules has not yet received much attention; although experiments have been performed on some crystalline solids, these have generally been concerned with detecting lattice modes in ionic crystals [3-6]. Nevertheless, there is potentially much valuable information to be derived from the study of vibrations in molecules oriented in liquid or molecular crystals, for example. In this note, a general expression for the intensity of hyper-Raman scattering by oriented molecules is given, and some general conclusions are drawn regarding the polarization dependence of the scattered light. These conclusions, which are also applicable to scattering by fluid samples, are of particular significance in the search for evidence of hyper-Raman activity resulting from index dissymmetry in the scattering tensor.

It is convenient to take as our starting point the expression for the hyper-Raman scattering intensity

$$I = \mathcal{D} |\beta_{ijk}^{\text{NM}} \bar{e}'_i e_j e_k|^2, \quad (1)$$

using the implied summation convention for repeated indices. Here  $\mathbf{e}$  and  $\mathbf{e}'$  are the polarization vectors of the incident and scattered photons, and  $\beta_{ijk}^{\text{NM}}$  is the hyper-Raman scattering tensor, expressible as

$$\beta_{ijk}^{\text{NM}} = \langle \chi_{0\text{N}} | \beta_{ijk} | \chi_{0\text{M}} \rangle, \quad (2)$$

where  $|\chi_{0\text{M}}\rangle$  and  $|\chi_{0\text{N}}\rangle$  are the vibrational wavefunctions for the initial and final

† Present address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England.

states, and  $\beta_{ijk}$  is the  $j, k$ -symmetric hyperpolarizability tensor. The scattering constant  $\mathcal{D}$  is given by

$$\mathcal{D} = \frac{2\pi}{c^5} \mathcal{N} \omega'^4 g^{(2)} I_0^2, \quad (3)$$

where  $\mathcal{N}$  is the number of scattering molecules,  $\omega'$  is the scattered frequency, and  $g^{(2)}$  and  $I_0$  are the degree of second-order coherence and mean irradiance, respectively, of the incident light. A detailed discussion of the theory leading to equation (1) is given in [1].

Because of the implications for the selection rules, it may be worth mentioning the reasons behind the contrasting index symmetry properties of the hyper-Raman tensor and the conventional Raman scattering tensor. Under non-resonance conditions the Raman tensor  $\alpha_{ij}^{\text{NM}} = \langle \chi_{0\text{N}} | \alpha_{ij} | \chi_{0\text{M}} \rangle$  has  $i, j$  index symmetry because, for each electronic excited state  $|r\rangle$ , an  $i, j$ -symmetric term  $\mu_i^{\text{r}0} \mu_j^{\text{r}0}$  can be factorized from the polarizability tensor  $\alpha_{ij}$ . No such factorization is possible in the hyperpolarizability tensor  $\beta_{ijk}$ , however, and only at unrealistically low incident frequencies, when the energy denominators in the various hyperpolarizability terms become equal, can full  $i, j, k$  index symmetry ensue [7]. In general, only the  $j, k$ -symmetry which results from the equivalence of the two absorbed photons is guaranteed.

To proceed further, we note that the hyper-Raman scattering amplitude in equation (1) depends on the inner product of the  $j, k$ -symmetric tensors  $\beta_{ijk}^{\text{NM}}$  and  $S_{ijk}$ , where the latter is a polarization tensor defined by

$$S_{ijk} \equiv \vec{e}'_i \cdot \vec{e}_j \vec{e}_k. \quad (4)$$

Both these tensors can be written in terms of irreducible tensors by using the following reduction formulae for a general  $j, k$ -symmetric third rank tensor  $T_{ijk}$ :

$$T_{ijk} = {}^1A T_{ijk} + {}^1B T_{ijk} + {}^2T_{ijk} + {}^3T_{ijk}; \quad (5)$$

$${}^1A T_{ijk} = \frac{1}{10} (3\delta_{ij} T_{luk} + 3\delta_{ik} T_{luj} - 2\delta_{jk} T_{lii}), \quad (6)$$

$${}^1B T_{ijk} = \frac{1}{10} (-\delta_{ij} T_{kii} - \delta_{ik} T_{jii} + 4\delta_{jk} T_{iii}), \quad (7)$$

$${}^2T_{ijk} = \frac{1}{6} \epsilon_{ijn} (\epsilon_{lmn} T_{lmk} + \epsilon_{lmk} T_{lmn}) + \frac{1}{6} \epsilon_{ikn} (\epsilon_{lmn} T_{lmj} + \epsilon_{lmj} T_{lmn}) \quad (8)$$

and

$${}^3T_{ijk} = \frac{1}{3} (T_{ijk} + T_{jki} + T_{kij}) - \frac{1}{15} [\delta_{ij} (2T_{luk} + T_{kii}) + \delta_{ik} (2T_{luj} + T_{jii}) + \delta_{jk} (2T_{lii} + T_{iii})]. \quad (9)$$

When  $\beta_{ijk}^{\text{NM}}$  and  $S_{ijk}$  are expressed in irreducible terms using equation (5), the scattering intensity can be written as

$$I = \mathcal{D} |({}^1A \beta_{ijk}^{\text{NM}} {}^1A S_{ijk} + {}^1A \beta_{ijk}^{\text{NM}} {}^1B S_{ijk} + {}^1B \beta_{ijk}^{\text{NM}} {}^1A S_{ijk} + {}^1B \beta_{ijk}^{\text{NM}} {}^1B S_{ijk} + {}^2\beta_{ijk}^{\text{NM}} {}^2S_{ijk} + {}^3\beta_{ijk}^{\text{NM}} {}^3S_{ijk})|^2; \quad (10)$$

the cross-terms involving products of tensors with different weights vanish on

index symmetry grounds. Explicit calculation of the irreducible polarization tensors leads to the result

$$I = \mathcal{D} \left| \frac{1}{15} \{ 3 \text{}^1\text{A} \beta_{iii}^{\text{NM}} [3(\bar{\mathbf{e}}' \cdot \mathbf{e})e_i - (\mathbf{e} \cdot \mathbf{e})\bar{e}'_i] + 3 \text{}^1\text{B} \beta_{iii}^{\text{NM}} [2(\mathbf{e} \cdot \mathbf{e})\bar{e}'_i - (\bar{\mathbf{e}}' \cdot \mathbf{e})e_i] + 5 \text{}^2\beta_{kik}^{\text{NM}} \epsilon_{kij} [(\bar{\mathbf{e}}' \times \mathbf{e})_i e_j + (\bar{\mathbf{e}}' \times \mathbf{e})_j e_i] + 15 \text{}^3\beta_{ijk}^{\text{NM}} \bar{e}'_i e_j e_k \} \right|^2. \quad (11)$$

From this general expression, the intensity of hyper-Raman scattering can be calculated for any particular alignment of the molecules in the incident light. While this result is directly applicable to the case of uniformly oriented molecules, the corresponding result for media in which the molecules are randomly oriented follows from equation (11) by use of the standard rotational averaging procedure [8]. The result is equation (3.8) in [1].

In either case, it is possible to draw some general conclusions from the form of equation (11). For example, if  $(\bar{\mathbf{e}}' \cdot \mathbf{e})$  and  $(\mathbf{e} \cdot \mathbf{e})$  are both zero, then there is no weight-1 contribution to the scattering. This condition is fulfilled in right-angled scattering of circularly polarized light, with the polarization of the scattered light analysed for the in-plane component, i.e.  $I_{\pi/2}(L/R \rightarrow \parallel)$  in the terminology of [1].

Perhaps more important, however, are the conclusions which can be drawn concerning the scattering which involves the weight-2 part of the hyper-Raman tensor. This term is of particular interest since it disappears if the tensor is assumed to have full index symmetry. As shown earlier, however, only the index symmetry in the second and third tensor indices is guaranteed, and full index symmetry cannot be expected. The hyper-Raman activity of vibrational modes for which the  $\beta$ -tensor has weight-2 components alone, i.e. those belonging to class E in the scheme of [1], thus hinges on an index dissymmetry in the tensor; examples are afforded by the  $\nu_2(\text{E})$  deformation modes of tetrahedral species such as methane or the ammonium ion. Now, from equation (11), it is evident that the weight-2 contribution to the scattering vanishes if  $(\bar{\mathbf{e}}' \times \mathbf{e})$  is zero. This is the case in the commonly studied geometry where  $\mathbf{e}'$  and  $\mathbf{e}$  are parallel vectors perpendicular to the scattering plane, i.e.  $I(\perp \rightarrow \perp)$ . (It is also true for forward scattering with reversal of circular polarization, and backward scattering with retention of circular polarization.) Under these conditions, then, potentially hyper-Raman active modes belonging to class E will not appear in the spectrum. It is therefore essential that the apparent inactivity of these modes is not mistaken for an indication that the scattering tensor is fully index-symmetric. Experimental evidence should confirm the appearance of class E modes in hyper-Raman spectra where the polarization geometry is such that  $(\bar{\mathbf{e}}' \times \mathbf{e})$  is non-zero.

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