

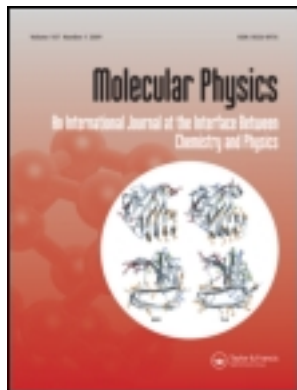
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### Integrated double-beam hyper-Raman spectroscopy

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## Integrated double-beam hyper-Raman spectroscopy

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This paper deals with the theory of double-beam hyper-Raman spectroscopy and provides expressions for the radiant power of hyper-Raman emission as a function of polarization parameters. Selection rules are discussed, with particular reference to the vibronic spectrum of benzene, and a 'magic-angle' configuration is analysed.

### 1. INTRODUCTION

In most experimental studies of hyper-Raman scattering a sample is irradiated by a single, highly intense, laser source and the process takes place by the absorption of two laser photons coupled with the emission of a single photon at approximately twice the frequency; the energy mismatch between the absorbed and emitted radiation results from a transition in the sample being studied [1]. The type of transition which is allowed in hyper-Raman scattering is governed by selection rules which have been discussed in detail previously [2]. Because of the difference in these rules from those which apply to absorption or Raman scattering, hyper-Raman spectroscopy can provide information on excited states and vibrations not accessible by conventional spectroscopic methods.

In principle, three-photon processes originating in totally symmetric ground states provide access to excited states which have the symmetry properties of irreducible tensors of weights 0, 1, 2 or 3. To be more precise, any transition giving rise to a feature in a three-photon spectrum must satisfy the condition that the product of the initial and final state representations is spanned by components of one or more of these irreducible tensors. The weight-0 tensor transforms as a pseudoscalar, weight-1 as a polar vector, weight-2 as a traceless symmetric second rank axial tensor, and weight-3 as a traceless fully index-symmetric third rank polar tensor. In the most general case, where the two absorbed photons have different frequencies  $\omega_1$  and  $\omega_2$ , and the emitted photon has frequency  $\omega_3$ , the hyper-Raman tensor thus has the decomposition:

$$\beta_{ijk}^{NM}(-\omega_3; \omega_1, \omega_2) = \beta_{ijk}^{(0)} + \beta_{ijk}^{(1)} + \beta_{ijk}^{(2)} + \beta_{ijk}^{(3)}, \quad (1)$$

where  $N$  and  $M$  identify final and initial states. Explicit expressions for each of the terms in equation (1) are given in [3], and the existence or non-existence of each term is in general determined by the transformation properties of the excited state under the symmetry operations of the appropriate molecular point group.

Special attention must be paid to the weight-0 term in the reduction however ;  $\beta_{ijk}^{(0)}$  is antisymmetric with respect to interchange of any pair of indices and thus vanishes if the two absorbed photons have the same frequency, as in single-beam experiments. As an illustration of the practical significance of this, consider the vibronic hyper-Raman spectrum of benzene. In principle, we should expect to see vibronic progressions in the 260 nm  $\tilde{A} \leftarrow \tilde{X}$  band ( ${}^1B_{2u} \leftarrow {}^1A_{1g}$ ) due to coupling with ring-puckering vibrations  $\nu_7$  and  $\nu_8$  ( $b_{2g}$ ), since the weight-0 pseudoscalar part of the hyper-Raman tensor  $\beta_{ijk}^{(0)}$  spans the product representation  $A_{1u}$  ( $=A_{1g} \times B_{2u} \times b_{2g}$ ). This feature should prove useful since  $\nu'_7$  and  $\nu'_8$  are not well known in the  $\tilde{A}$  state. However, although these progressions should indeed be observable under the conditions of double-beam excitation, they are forbidden if the hyper-Raman spectrum is observed using a single laser beam, since the  $\beta_{ijk}^{(0)}$  contribution then vanishes.

This point illustrates one of the motivations for performing double-beam hyper-Raman spectroscopy, namely the facility for observing transitions which are not only forbidden in conventional absorption or Raman spectra, but also in the single-beam hyper-Raman spectrum. A second motivation is the fact that with two beams incident on the sample, the frequency of each beam can be independently chosen to optimize any resonance enhancement mechanisms [4].

There is, however, one further method by which it should be possible to increase greatly the intensity of any hyper-Raman spectrum. This method involves obtaining the spectrum of the total hyper-Raman emission over  $4\pi$  steradians, in contrast to the small solid angle over which the spectrum is usually measured. Both this method and the possibility of resonance enhancement are particularly significant for hyper-Raman spectroscopy ; the principal reason for the relative paucity of hyper-Raman spectra appears to be the experimental difficulties associated with the very low emission intensities normally encountered. In this paper, the theory of integrated double-beam hyper-Raman spectroscopy is developed from well-established quantum electrodynamical principles [5, 6].

## 2. THEORY

Consider first a hyper-Raman experiment in which sample molecules each absorb two photons from independent beams with wave-vectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$ , polarization vectors  $\mathbf{e}_1$ ,  $\mathbf{e}_2$ , and intensities  $I_1$ ,  $I_2$ , and emit a third photon of wave-vector  $\mathbf{k}_3$  and polarization  $\mathbf{e}_3$ . The energy of the emitted photon is given by  $\hbar c k_3 = \hbar c k_1 + \hbar c k_2 - (E_N - E_M)$ . By methods described in detail previously [2], it is readily shown that if there are  $N_m$  molecules in the initial state within the laser beam intersection, the radiant intensity of emission (power per unit solid angle in the  $\mathbf{k}_3$  direction) is given by

$$I(\mathbf{k}_3) = D |\bar{e}_{3i} e_{2j} e_{1k} \beta_{ijk}^{NM}|^2, \quad (2)$$

where  $D$  is a scattering constant defined by

$$D = \frac{2\pi}{c} N_m k_3^4 I_1 I_2 \quad (3)$$

and the superior bar indicates the complex conjugate. The implied summation convention for repeated indices is used in equation (2), which may thus be expressed as

$$I(\mathbf{k}_3) = D \bar{e}_{3i} e_{2j} e_{1k} e_{3l} \bar{e}_{2m} \bar{e}_{1n} \beta_{ijk}^{NM} \bar{\beta}_{lmn}^{NM}. \quad (4)$$

A general result for the intensity of double-beam hyper-Raman emission from an assembly of randomly oriented molecules can be obtained from equation (4) by performing a sixth rank rotational average [7]. However the resulting expression contains 225 terms and is not of much practical interest. Let us therefore concentrate on the case where the emission is integrated over all possible scattering angles, as mentioned earlier.

The integration procedure is most simply carried out by summing over all polarizations of the emitted light for a given emission direction, and then spherically averaging the hyper-Raman intensity over all emission directions, and multiplying by the total solid angle of  $4\pi$  steradians. The polarization summation is given by the formula [8]

$$\sum_{\lambda} \bar{e}_{3i}^{(\lambda)} e_{3l}^{(\lambda)} = \delta_{il} - \hat{k}_{3i} \hat{k}_{3l} \quad (5)$$

and for the spherical average we have

$$\langle (\delta_{il} - \hat{k}_{3i} \hat{k}_{3l}) \beta_{ijk}^{NM} \bar{\beta}_{imn}^{NM} \rangle = \frac{2}{3} \beta_{ijk}^{NM} \bar{\beta}_{imn}^{NM}. \quad (6)$$

Hence the integrated hyper-Raman intensity, or radiant power, is given by

$$\phi = \int I(\mathbf{k}_3) d\Omega = \frac{8\pi}{3} D e_{2j} e_{1k} \bar{e}_{2m} \bar{e}_{1n} \beta_{ijk}^{NM} \bar{\beta}_{imn}^{NM}. \quad (7)$$

Once again, this equation has to be rotationally averaged for a randomly oriented assembly of molecules; in this case, however, the calculation involves only a fourth rank average [7] and yields the simple result which follows:

$$\phi = \frac{4\pi}{45} D [(4p_1 - 1 - p_2) \beta_{\lambda\mu\mu}^{NM} \bar{\beta}_{\lambda\nu\nu}^{NM} + (-p_1 + 4 - p_2) \beta_{\lambda\mu\nu}^{NM} \bar{\beta}_{\lambda\mu\nu}^{NM} + (-p_1 - 1 + 4p_2) \beta_{\lambda\mu\nu}^{NM} \bar{\beta}_{\lambda\nu\mu}^{NM}]. \quad (8)$$

Here  $p_1$  and  $p_2$  are experimentally determined parameters, dependent on the polarizations of the two beams and their angle of intersection:

$$p_1 = |\mathbf{e}_1 \cdot \mathbf{e}_2|^2, \quad (9)$$

$$p_2 = |\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2|^2; \quad (10)$$

clearly both  $p_1$  and  $p_2$  have values in the range (0, 1).

By applying the tensor reduction methods mentioned earlier, it is readily shown that whilst the first tensor product  $\beta_{\lambda\mu\mu}^{NM} \bar{\beta}_{\lambda\nu\nu}^{NM}$  in equation (8) contains only weight-1 contributions, the other two contain contributions from weights 0, 1, 2 and 3. Since there are only three distinct molecular parameters appearing in equation (8), it is therefore not possible to devise a set of polarization experiments which result in the separate evaluation of the contributions from each weight. However it is possible to identify pure weight-0 transitions (such as the vibronic band in benzene discussed earlier) on the basis of their polarization behaviour, since these will disappear from the spectrum when both beams are polarized with parallel polarization vectors (then  $p_1 = p_2 = 1$ , and the weight-0 parts of  $\beta_{\lambda\mu\nu}^{NM} \bar{\beta}_{\lambda\mu\nu}^{NM}$  and  $\beta_{\lambda\mu\nu}^{NM} \bar{\beta}_{\lambda\nu\mu}^{NM}$  in (8) completely cancel out). Although the integrated two-beam experiment generally provides little further help with the symmetry assignment of hyper-Raman transitions, the spectrum is obviously much stronger than one collected over the usual small solid angle of

emission, and the single-beam methods developed recently can subsequently be used to assist with the peak assignment [9].

One other feature of equation (8) is of interest, and that is the fact that both the first and last terms vanish when  $p_1 = p_2 = \frac{1}{3}$ . This situation may be realized when both beams are plane polarized, and their planes of polarization intersect at an angle of  $54.7^\circ$ , the so-called 'magic angle'  $\beta$  of nuclear magnetic resonance spectroscopy [10]. Under these conditions, we have simply

$$\phi^\beta = \frac{8\pi}{27} D\beta_{\lambda\mu\nu}{}^{NM} \bar{\beta}_{\lambda\mu\nu}{}^{NM}. \quad (11)$$

The tensor product  $\beta_{\lambda\mu\nu}{}^{NM} \bar{\beta}_{\lambda\mu\nu}{}^{NM}$  represents the sum of the square modulus of all 27 components of the transition tensor, and thus contains contributions from each irreducible weight. Hence in the magic-angle configuration, all potentially hyper-Raman active transitions appear in the spectrum, and integration provides the best means of obtaining absolute values for the radiant power of hyper-Raman emission.

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