

Doubly resonant three-photon spectroscopy

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Multiphoton spectroscopy is increasingly being used for the study of molecular excited states. The increase in the transition rate under resonance conditions can be exploited as a means of locating new states, and the dependence of the rate on the photon polarizations gives information about state symmetries. In this paper, expressions for the rate of doubly resonant three-photon absorption are derived, and it is shown how these results can be applied to various other stimulated processes. It is also demonstrated how the relative orientations of molecular transition moments can be found by performing a specified set of experiments with different polarizations. In addition to providing symmetry information, this method may prove a valuable means of testing molecular wave function calculations for biological molecules.

I. INTRODUCTION

In recent years, experimental studies of the excited states of atoms and molecules have increasingly been based on multiphoton spectroscopy. As multiphoton phenomena are governed by different selection rules from one-photon processes, they are particularly useful for the study of excited states which are not accessible by conventional spectroscopic methods. Moreover, multiphoton spectroscopy has become far more practicable with the development of high intensity tunable lasers. Tunability is especially significant for resonance processes, where there is approximate conservation of energy between the initial state of the system and one of the intermediate states following the absorption of a certain number of photons. With multiphoton resonances, the resulting enhancement of the transition rate can be exploited as a means of locating new excited states; various aromatic compounds have been studied using this technique.^{1,2}

In order to ascertain the symmetry species of a given excited state, it is often necessary to examine the dependence of the transition rate on the polarizations of the incident photons. Monson and McClain³ and McClain^{4,5} have shown that studies of this kind in two- and three-photon phenomena can provide valuable information even when the molecules are randomly oriented, as in gaseous or liquid samples, and that most information can be obtained by performing a *complete polarization study* involving a number of separate experiments with different polarizations. In general, these polarization studies are used to determine the various molecular tensor products which govern the transition rate, and it is the analysis of these parameters which gives the fullest symmetry information. This method has been successfully applied in a number of two-photon absorption and resonance Raman investigations, and the application to hyper-Raman scattering has also received recent attention.⁶

In the case of three-photon phenomena the transition is usually governed by 11 tensor products, requiring 11 polarization experiments for their determination.⁵ This number can be reduced if two of the photons, or all three, have the same frequency. However, the number

of experiments is also reduced if the three photon frequencies are tuned near to resonance with particular electronic transitions. This arrangement is particularly well suited for studies of transitions to highly excited bound states, because of the increase in the transition rate associated with the resonance conditions. The relevant rate results derived in this paper show that in this case the transition is characterized by five tensor products, whose values can be determined from five specified polarization experiments. Further analysis of these parameters enables the relative orientations of transition moments to be found, giving new information about the symmetry of the excited states, and providing a novel way of testing molecular wavefunction calculations. It is shown how these methods can be applied not only to three-photon absorption, but also to a number of stimulated three-photon processes, thereby increasing the scope for studies of molecular excited states.

II. THEORY OF DOUBLY RESONANT THREE-PHOTON ABSORPTION

We start by working out a general expression for the rate of three-photon absorption in the fully resonant case. The three photons are absorbed from three different beams, and have circular frequencies ω_1 , ω_2 , and ω_3 ; their absorption results in a molecular transition from the ground state $|0\rangle$ to a final state $|n\rangle$, with the energy conservation condition

$$E_{n0} \equiv E_n - E_0 = \hbar(\omega_1 + \omega_2 + \omega_3). \quad (1)$$

We consider the case where the photon energy $\hbar\omega_1$ is tuned near to resonance with the energy difference between the ground state and a low-lying excited state $|r\rangle$, i. e., $\hbar\omega_1 \approx E_{r0}$, and $\hbar\omega_2$ is similarly tuned near to the resonance between $|r\rangle$ and a higher state $|s\rangle$, i. e., $\hbar\omega_2 \approx E_{sr}$.⁷ The third photon then supplies the remaining energy $\hbar\omega_3$ required to reach the final highly excited state $|n\rangle$. Because of the unequal spacing of electronic levels, we assume that ω_1 , ω_2 , and ω_3 are three different frequencies. We also assume that the intermediate states $|r\rangle$ and $|s\rangle$ are nondegenerate; this condition is only restrictive in molecules with rotation axes C_n , S_n of order $n \geq 3$.

To calculate the rate Γ at which the process takes place, we make use of the Fermi rule

$$\Gamma = \frac{2\pi}{\hbar} \langle |\mathfrak{M}_{ff}|^2 \rangle \rho. \quad (2)$$

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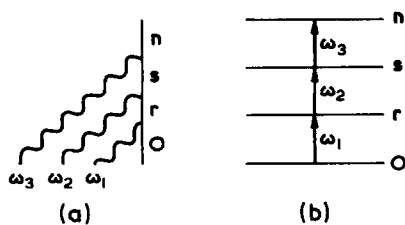


FIG. 1. Time-ordered diagram (a) and energy diagram (b) for doubly resonant three-photon absorption.

The angular brackets in this equation denote the classical rotational averaging which is necessary to account for the random orientations of molecules in a fluid sample; ρ denotes the density of states function, and \mathfrak{M}_{fi} the matrix element connecting the initial and final states of the system (molecules plus radiation). The latter may be written as a sum over the \mathfrak{N} molecules in the interaction volume of the matrix elements M_{fi}^{ξ} for the individual molecules ξ , the results for which are obtained in the usual way with the aid of time-ordered diagrams. For the doubly resonant case, one particular time-ordering corresponding to the diagram shown in Fig. 1(a) makes by far the largest contribution, and the result for M_{fi}^{ξ} is therefore well approximated by the following expression:

$$M_{fi}^{\xi} = i \left(\frac{8\pi^3 \hbar^3 n_1 n_2 n_3 \omega_1 \omega_2 \omega_3}{V^3} \right)^{1/2} T_{ijk}^{\xi} e_{3i} e_{2j} e_{1k}. \quad (3)$$

Here V is the quantization volume, n_{λ} is the occupation number of the radiation mode with frequency ω_{λ} and polarization vector e_{λ} , (the latter may be complex for circular polarizations), and there is implied summation over the component indices i, j, k . Provided the intermediate states $|r\rangle$ and $|s\rangle$ are nondegenerate, the third rank tensor T_{ijk} is simply given by

$$T_{ijk} = \frac{\mu_{if}^{\mu} \mu_{if}^{\nu} \mu_{if}^{\sigma}}{(\epsilon_2 - \frac{1}{2}i\hbar\gamma_2)(\epsilon_1 - \frac{1}{2}i\hbar\gamma_1)}, \quad (4)$$

where the μ 's are electric dipole transition moments,⁸ γ_1 and γ_2 are damping factors for states $|r\rangle$ and $|s\rangle$, respectively, and ϵ_1, ϵ_2 are energies expressible in terms of the detuning from resonance of ω_1 and ω_2 ;

$$\left. \begin{aligned} \epsilon_1 &= (E_{r0} - \hbar\omega_1), \\ \epsilon_2 &= \epsilon_1 + (E_{sr} - \hbar\omega_2). \end{aligned} \right\} \quad (5)$$

The quantities E_{r0}, E_{sr} are taken as the measured energy differences including any shifts induced by the laser radiation. Using Eqs. (2) and (3), we now find the following expression for the rate of three-photon absorption;

$$\Gamma = \mathfrak{S} \langle T_{ijk} \bar{T}_{imn} e_{3i} e_{2j} e_{1k} \bar{e}_{3i} \bar{e}_{2m} \bar{e}_{1n} \rangle, \quad (6)$$

where

$$\mathfrak{S} = \frac{16\pi^4}{\hbar^3 c^3} \rho \mathfrak{N} I_1 I_2 I_3, \quad (7)$$

and I_{λ} is the irradiance of the beam with frequency ω_{λ} .

In Eq. (6), the molecular tensor components are referred to the same Cartesian frame as the photon polarization vectors, and need to be re-expressed in terms of an appropriate molecular coordinate system. We therefore write

$$\left. \begin{aligned} T_{ijk} &= l_{i\lambda} l_{j\mu} l_{k\nu} T_{\lambda\mu\nu}, \\ \bar{T}_{imn} &= l_{i\lambda} l_{m\nu} l_{n\rho} \bar{T}_{\sigma\rho}, \end{aligned} \right\} \quad (8)$$

using Greek indices to represent components referred to the molecular frame; the l 's are direction cosines, $l_{i\lambda}$ denoting the (i, λ) element of the Euler angle matrix for the transformation between the laboratory frame and the molecular frame. Substituting these relations into (6), we have

$$\Gamma = \mathfrak{S} \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{i\sigma} l_{m\nu} l_{n\rho} \rangle T_{\lambda\mu\nu} \bar{T}_{\sigma\rho} e_{3i} e_{2j} e_{1k} \bar{e}_{3i} \bar{e}_{2m} \bar{e}_{1n}, \quad (9)$$

and the necessary rotational average can now be performed on the direction cosine product.

It is at this stage that new features, peculiar to the doubly-resonant case, become evident. The result for the rotational average,

$$I_{ijkimn; \lambda\mu\nu\sigma\rho}^{(6)} = \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{i\sigma} l_{m\nu} l_{n\rho} \rangle, \quad (10)$$

involves a basis set of 15 isotropic tensors,⁹ which would normally give a result for the three-photon absorption rate in terms of fifteen inner products of the tensor $T_{\lambda\mu\nu}$ with its complex conjugate. McClain has shown that in nonresonant cases, where $T_{\lambda\mu\nu}$ may be regarded as real, the number of such inner products reduces to 11.⁵ However, in the case of double resonance $T_{\lambda\mu\nu}$ itself reduces to the outer product of three vectors, as in Eq. (4), and assuming the transition moments are real it is readily shown that the number of independent tensor products is just five.¹⁰ These are as follows;

$$\left. \begin{aligned} \alpha &= T_{\lambda\lambda\mu} \bar{T}_{\mu\nu\nu}, \\ \beta &= T_{\lambda\lambda\mu} \bar{T}_{\nu\nu\mu}, \\ \gamma &= T_{\lambda\mu\lambda} \bar{T}_{\nu\mu\nu}, \\ \delta &= T_{\lambda\mu\mu} \bar{T}_{\lambda\nu\nu}, \\ \epsilon &= T_{\lambda\mu\nu} \bar{T}_{\lambda\mu\nu}. \end{aligned} \right\} \quad (11)$$

Using the result for the sixth rank rotational average given elsewhere,⁹ we find the explicit result for the three-photon absorption rate is

$$\Gamma = \frac{1}{210} \mathfrak{S} [(16 - 12p - 12q - 12r + 18s)\alpha + (-10 + 11p + 4q + 4r - 6s)\beta + (-10 + 4p + 11q + 4r - 6s)\gamma + (-10 + 4p + 4q + 11r - 6s)\delta + (16 - 5p - 5q - 5r + 4s)\epsilon], \quad (12)$$

where p , q , r , and s are all real parameters determined by the polarization geometry of the experiment. They are defined by

$$\left. \begin{aligned} p &= |\mathbf{e}_3 \cdot \mathbf{e}_2|^2 + |\mathbf{e}_3 \cdot \mathbf{e}_1|^2, \\ q &= |\mathbf{e}_3 \cdot \mathbf{e}_1|^2 + |\mathbf{e}_3 \cdot \mathbf{e}_2|^2, \\ r &= |\mathbf{e}_2 \cdot \mathbf{e}_1|^2 + |\mathbf{e}_2 \cdot \mathbf{e}_3|^2, \\ s &= \text{Re}[(\mathbf{e}_3 \cdot \mathbf{e}_2)(\mathbf{e}_1 \cdot \mathbf{e}_3)(\mathbf{e}_2 \cdot \mathbf{e}_1) + (\mathbf{e}_3 \cdot \mathbf{e}_2)(\mathbf{e}_1 \cdot \mathbf{e}_2)(\mathbf{e}_3 \cdot \mathbf{e}_1) \\ &\quad + (\mathbf{e}_3 \cdot \mathbf{e}_1)(\mathbf{e}_2 \cdot \mathbf{e}_3)(\mathbf{e}_2 \cdot \mathbf{e}_1) + (\mathbf{e}_3 \cdot \mathbf{e}_2)(\mathbf{e}_2 \cdot \mathbf{e}_1)(\mathbf{e}_1 \cdot \mathbf{e}_3)]. \end{aligned} \right\} \quad (13)$$

We conclude this section by noting that the five molecular tensor products $\alpha - \epsilon$ may be written as follows:

$$\left. \begin{aligned} \alpha &= K \cos \phi_1 \cos \phi_2 \cos \phi_3, \\ \beta &= K \cos^2 \phi_1, \\ \gamma &= K \cos^2 \phi_2, \\ \delta &= K \cos^2 \phi_3, \\ \epsilon &= K, \end{aligned} \right\} \quad (14)$$

where

$$K = \frac{|\mu^{ns}|^2 |\mu^{sr}|^2 |\mu^{r0}|^2}{(\epsilon_2^2 + \frac{1}{4}\hbar^2\gamma_2^2)(\epsilon_1^2 + \frac{1}{4}\hbar^2\gamma_1^2)}, \quad (15)$$

and ϕ_1 , ϕ_2 , ϕ_3 are the angles between the three transition moments;

$$\left. \begin{aligned} \hat{\mu}^{ns} \cdot \hat{\mu}^{sr} &= \cos \phi_1, \\ \hat{\mu}^{ns} \cdot \hat{\mu}^{r0} &= \cos \phi_2, \\ \hat{\mu}^{sr} \cdot \hat{\mu}^{r0} &= \cos \phi_3. \end{aligned} \right\} \quad (16)$$

III. OTHER DOUBLY RESONANT THREE-PHOTON PROCESSES

Thus far we have been considering the case where each interaction with the radiation is absorptive, so that the molecular energy increases at each stage of the three-photon transition. In this section, we consider an extension of the theory to encompass the situation where one or more of the interactions is a radiative emission stimulated by a beam of the appropriate frequency. If the transition is doubly resonant and the molecule is initially in its ground state, at least one absorption must take place before emission can occur; the various possibilities are illustrated by the time-ordered diagrams 2(a), 3(a), and 4(a). It should be noted that there are two energy level diagrams (b) and (c) corresponding to each of the time-ordered diagrams in Figs. 2 and 3, and there are important differences in the processes these

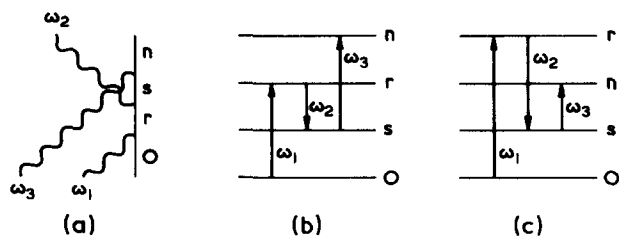


FIG. 2. Three-photon processes with stimulated emission of the second photon.

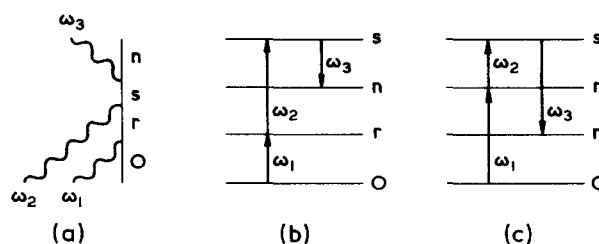


FIG. 3. Three-photon processes with stimulated emission of the third photon.

represent.¹¹ Only the process represented by Fig. 2(b), for example, can be monitored by photoionization of the final state, since in every other case there is an intermediate state of higher energy. Nevertheless, both processes 2(b) and 2(c) are amenable to study by measurement of the absorption from the beam of frequency ω_3 .

The theory of these stimulated three-photon processes can be developed in much the same way as for three-photon absorption in the last section. As an illustrative example, we briefly consider the process represented by Fig. 2(b). Here the energy conservation is expressed through the relation

$$E_{r0} = \hbar(\omega_1 - \omega_2 + \omega_3), \quad (17)$$

and the resonance conditions are $\hbar\omega_1 \approx E_{r0}$, $\hbar\omega_2 \approx E_{rs}$. The transition rate again follows from Eq. (2), and the matrix element M_{fi}^t is given by

$$M_{fi}^t = -i \left(\frac{8\pi^3 \hbar^3 n_1 (n_2 + 1) n_3 \omega_1 \omega_2 \omega_3}{V^3} \right)^{1/2} T_{ijk}^t e_{3i} \bar{e}_{2j} e_{1k}; \quad (18)$$

the molecular tensor T_{ijk} can be written in the form of Eq. (4), provided ϵ_1 and ϵ_2 are redefined as

$$\left. \begin{aligned} \epsilon_1 &= (E_{r0} - \hbar\omega_1), \\ \epsilon_2 &= \epsilon_1 - (E_{rs} - \hbar\omega_2). \end{aligned} \right\} \quad (19)$$

Because we are dealing with stimulated emission of ω_2 , we can make the approximation $(n_2 + 1) \approx n_2$, and the three-photon transition rate is then given by

$$\Gamma = \mathcal{G} \langle T_{ijk}^t T_{lmn}^t e_{3i} \bar{e}_{2j} e_{1k} \bar{e}_{3l} e_{2m} \bar{e}_{1n} \rangle, \quad (20)$$

with \mathcal{G} defined as before. Performing the rotational average finally leads to precisely the result of Eq. (12), with the parameters $\alpha - \epsilon$ and $p - s$ again defined by Eqs. (11) and (13). A similar analysis of the other types of

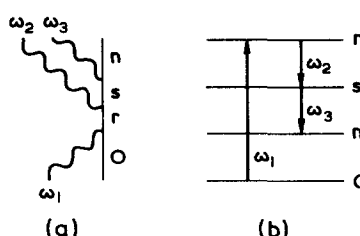


FIG. 4. Three-photon process with stimulated emission of both the second and third photons.

three-photon process in fact shows that these equations are of general validity, provided only that ϵ_1 and ϵ_2 are given the appropriate definitions in each case. In the next section, Eq. (12) is used as the starting point for a general discussion of how these processes depend on the polarizations of the incident beams.

IV. POLARIZATION STUDIES

As seen in Sec. II, the five molecular parameters α – ϵ appearing in Eq. (12) are expressible in terms of the four independent quantities ϕ_1 , ϕ_2 , ϕ_3 , and K . Now K cannot be obtained from the three-photon experiments unless absolute rate measurements are made and a precise value is known for \mathcal{S} , and in general this is not possible. Nevertheless, linear processing of the results from experiments with various polarizations of the incident beams can be used to obtain *relative* values for α – ϵ , and hence *absolute* values for the cosines of ϕ_1 , ϕ_2 , and ϕ_3 . Since α – ϵ are linearly independent, five such experiments are required by this method.

A convenient set of experiments involving only plane polarized light can be specified as follows. The first measurement, denoted by Γ_1 , is made with parallel polarizations,

$$\Gamma_1 = \Gamma(\mathbf{e}_1 \parallel \mathbf{e}_2 \parallel \mathbf{e}_3); \quad (21)$$

another three result from having two parallel, and one perpendicular polarization,

$$\left. \begin{aligned} \Gamma_2 &= \Gamma(\mathbf{e}_1 \perp \mathbf{e}_2 \parallel \mathbf{e}_3), \\ \Gamma_3 &= \Gamma(\mathbf{e}_1 \parallel \mathbf{e}_3 \perp \mathbf{e}_2), \\ \Gamma_4 &= \Gamma(\mathbf{e}_1 \parallel \mathbf{e}_2 \perp \mathbf{e}_3), \end{aligned} \right\} \quad (22)$$

and the fifth measurement is made with a completely orthogonal set of polarizations,

$$\Gamma_5 = \Gamma(\mathbf{e}_1 \perp \mathbf{e}_2 \perp \mathbf{e}_3 \perp \mathbf{e}_1). \quad (23)$$

It should be noted that since the polarization directions are specified, but not the directions of propagation of the incident light, there is some freedom in the choice of beam geometry for each experiment. A coplanar arrangement is likely to be most practical; although measurements Γ_1 – Γ_4 could be obtained with collinear beams, it is necessary to use non-collinear beams for the fifth experiment in order for the molecular parameters α – ϵ to be determined.

The explicit results for Γ_1 – Γ_5 are readily found from Eqs. (12) and (13), and are as follows;

$$\left. \begin{aligned} \Gamma_1 &= \frac{1}{10\mathcal{S}} \mathcal{G}(8\alpha + 2\beta + 2\gamma + 2\delta + \epsilon), \\ \Gamma_2 &= \frac{1}{10\mathcal{S}} \mathcal{G}(-4\alpha + 6\beta - \gamma - \delta + 3\epsilon), \\ \Gamma_3 &= \frac{1}{10\mathcal{S}} \mathcal{G}(-4\alpha - \beta + 6\gamma - \delta + 3\epsilon), \\ \Gamma_4 &= \frac{1}{10\mathcal{S}} \mathcal{G}(-4\alpha - \beta - \gamma + 6\delta + 3\epsilon), \\ \Gamma_5 &= \frac{1}{10\mathcal{S}} \mathcal{G}(8\alpha - 5\beta - 5\gamma - 5\delta + 8\epsilon). \end{aligned} \right\} \quad (24)$$

These form a regular system of equations in α – ϵ , and the inverse relations enable values for these parameters to be determined from the five rate measurements; we have

$$\left. \begin{aligned} \alpha &= \frac{3}{4} \mathcal{S}^{-1}(11\Gamma_1 - 3\Gamma_2 - 3\Gamma_3 - 3\Gamma_4 + 2\Gamma_5), \\ \beta &= 3\mathcal{S}^{-1}(2\Gamma_1 + 4\Gamma_2 - \Gamma_3 - \Gamma_4 - \Gamma_5), \\ \gamma &= 3\mathcal{S}^{-1}(2\Gamma_1 - \Gamma_2 + 4\Gamma_3 - \Gamma_4 - \Gamma_5), \\ \delta &= 3\mathcal{S}^{-1}(2\Gamma_1 - \Gamma_2 - \Gamma_3 + 4\Gamma_4 - \Gamma_5), \\ \epsilon &= 3\mathcal{S}^{-1}(\Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + 2\Gamma_4 + 2\Gamma_5). \end{aligned} \right\} \quad (25)$$

The values for α – ϵ give important information about the symmetries of the excited states involved in the three-photon transition. For example, in a transition to an A_u state in a D_{2h} molecule, the three transition moments would have to be mutually perpendicular, so that α – δ would all be zero. On the other hand, in a transition where states $|n\rangle$ and $|r\rangle$ were of the same symmetry species, and $|s\rangle$ was an A_g state, all transition moments would be parallel, resulting in equal values for each of the five parameters.

While this kind of symmetry analysis should prove useful for molecules possessing a number of symmetry elements, it is superfluous for asymmetric molecules, where no *a priori* predictions can be made concerning the values of α – ϵ . Nevertheless, it is possible to derive data of another kind for these molecules, which may prove useful in testing electronic wavefunction calculations. These are the values for the cosines defined by Eq. (16), which can readily be determined from the results for α – ϵ , since we have

$$\left. \begin{aligned} \cos\phi_1 &= (\beta/\epsilon)^{1/2}, \\ \cos\phi_2 &= (\gamma/\epsilon)^{1/2}, \\ \cos\phi_3 &= (\delta/\epsilon)^{1/2}. \end{aligned} \right\} \quad (26)$$

It is important to note that even when only relative values for Γ_1 – Γ_5 are obtainable, the corresponding relative values for α – ϵ as given by (25) may still be used in (26) to give the correct absolute values for the cosines.

Finally, we note that the relation

$$\alpha = \left(\frac{\beta\gamma\delta}{\epsilon} \right)^{1/2} \quad (27)$$

can be used as a check on the consistency of results obtained from experiments on a particular system. Again, this equation holds not only for the absolute values of α – ϵ but also for their experimentally determined relative values.

V. CONCLUSION

In this paper it has been shown how doubly resonant three-photon spectroscopy can be used to provide important information about the excited states of molecules. In addition to providing a means for locating new states, it should also be possible to ascertain their symmetry by carrying out the polarization experiments described in the last section. For asymmetric molecules, where the excited states are equally accessible by conventional one-photon absorption methods, resonance multiphoton spectroscopy still has the advantage of providing information concerning the relative orientations of transition moments. It is worth emphasizing

that this information can be derived from studies of randomly oriented systems such as gases or solutions, whereas to obtain similar data from absorption experiments usually requires the study of crystalline samples. The transition moment data should prove useful in testing electronic wavefunction calculations, and this may be especially significant in view of the growing interest in calculations on biological and pharmaceutical substances.

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¹P. M. Johnson, J. Chem. Phys. **64**, 4143 (1976).

²R. E. Turner, V. Vaida, C. A. Molini, J. O. Berg, and D. H. Parker, Chem. Phys. **28**, 47 (1978).

³P. R. Monson and W. M. McClain, J. Chem. Phys. **53**, 29 (1970).

⁴W. M. McClain, J. Chem. Phys. **55**, 2789 (1971).

⁵W. M. McClain, J. Chem. Phys. **57**, 2264 (1972).

⁶D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **68**, 2941 (1978).

⁷The intermediate states will usually be vibrationally excited. We therefore assume that the detuning from resonance is much smaller than any of the vibrational frequencies, so that only one level effectively contributes to the resonance.

⁸In the absence of vibronic interactions, μ^{ab} can be written in the Born-Oppenheimer approximation as $\langle \phi_a | \mu | \phi_b \rangle \langle \chi_a^A | \chi_b^B \rangle$; here the first Dirac bracket is the electronic transition moment, and the second is the overlap between the vibrational wavefunctions for the levels connected by the transition.

⁹D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **67**, 5026 (1977).

¹⁰The number of tensor products involved in two-photon excited fluorescence is also reduced to five under resonance conditions. See for example Yu. T. Mazyrenko, Opt. Spectrosc. **31**, 413 (1971); W. M. McClain, J. Chem. Phys. **58**, 324 (1973).

¹¹Although these stimulated processes are essentially nonlinear inelastic scattering phenomena, it seems best not to use the term *hyper-Raman* to describe them, since in current usage this usually refers to the case where the two absorbed photons have the same frequency.