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The theory of double-beam three-photon absorption

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This paper deals with the theory of double-beam three-photon absorption, in which the excitation process involves the concerted absorption of three photons from two laser beams which simultaneously irradiate the sample. Equations are derived for the rate of absorption under various polarization conditions, and the dependence on the angle between the two beams is examined in detail. It is shown how a set of experiments at a suitable angle with specified polarizations allows the determination of five molecular parameters which characterize the symmetry of the excited state. It is demonstrated how the results thereby provide for an unambiguous assignment of the excited state to one of six different symmetry classes. It is also shown that the double-beam experiment allows access to excited states which are forbidden under single-beam excitation.

I. INTRODUCTION

Multiphoton spectroscopy is now recognized as a powerful method for the discovery and characterization of molecular excited states. Two-photon absorption spectroscopy has received widespread application in recent years despite the technical difficulties associated with its observation, and three- and four-photon absorption processes are now also becoming increasingly practicable through the advances in laser technology. Recent discoveries of new excited states in comparatively simple molecules like ammonia^{1,2} give clear evidence for the importance of these higher order multiphoton studies.

The theory of molecular three-photon absorption is still in its infancy. Friedrich has recently presented a detailed analysis of the three-photon absorption tensor,³ and in another recent paper we have shown how to derive detailed information about the symmetry properties of three-photon excited states by a simple linear processing of results from single-beam experiments with different polarizations.⁴ In the present paper, it is shown how a similar analysis may be applied to double-beam three-photon absorption, where the excitation process involves the concerted absorption of three photons from two laser beams which simultaneously irradiate the sample. There are two important reasons for performing such an experiment with lasers of differing wavelengths;

(a) Since the only requirement imposed by energy matching is that the sum of the three photon energies equals the transition energy, there is considerable flexibility in the choice of irradiation wavelengths for one of the lasers. This facilitates exploitation of a resonance enhancement of the three-photon absorption rate by choosing a wavelength close to a one- or two-photon absorption band.

(b) The selection rules for double-beam three-photon absorption are different from those which govern single-beam excitation. In particular, transitions to certain excited states which are forbidden under single-beam conditions are allowed under double-beam conditions; hence the double-beam method increases the scope for characterization of new excited states. Even for those transitions which are allowed via single-beam excitation,

the double-beam experiment in many cases provides more detailed symmetry information.

With these objectives in mind, this paper develops the theory of double-beam three-photon absorption, and provides a framework for the analysis and interpretation of experimental results.

II. THEORY

In this section the basic theory is outlined, and the various parameters which appear in the rate equations are introduced and defined. We first label the two laser beams $\alpha = 1$ and 2, such that one photon from beam 1 with frequency ω_1 and two photons from beam 2 with frequency ω_2 are absorbed in the excitation process. This gives us the overall energy conservation relation

$$E_{f0} \equiv E_f - E_0 = \hbar\omega_1 + 2\hbar\omega_2. \quad (2.1)$$

Further parameters are required to complete the specification of the absorbed photons; these are the propagation vectors \mathbf{k}_α and the unit polarization vectors $\mathbf{e}^{(\alpha)}$.

For the full characterization of the radiation we define I_α as the mean irradiance and $g_\alpha^{(n)}$ as the degree of n th order coherence of beam α . In order to specify the relation between the polarizations of the two beams, it is convenient to introduce a set of Cartesian axes for each beam as shown in Fig. 1; in each right-handed set $(\hat{i}_\alpha, \hat{j}_\alpha, \hat{k}_\alpha)$ the \hat{i}_α direction is perpendicular to the $\mathbf{k}_1, \mathbf{k}_2$ plane. We also define θ as the angle between the two beams.

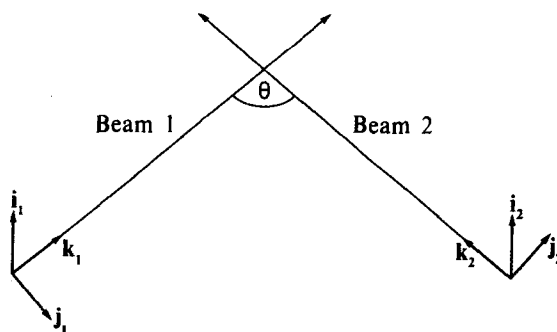


FIG. 1. Laser beam geometry.

The starting point for a discussion of the three-photon absorption rate equations is the general expression for the rate Γ , derived using standard quantum electrodynamical methods discussed in earlier papers^{4,6},

$$\Gamma = \mathcal{G} \langle |T_{\lambda\mu\nu} e_{\lambda}^{(1)} e_{\mu}^{(2)} e_{\nu}^{(3)}|^2 \rangle. \quad (2.2)$$

Here the angular brackets denote the rotational averaging required to account for the random orientations of the molecules in any fluid sample, and the implied summation convention for repeated tensor indices is employed. The factor \mathcal{G} is given by

$$\mathcal{G} = \frac{16N\pi^4\rho}{\hbar c^3} I_1 I_2^2 g_2^{(2)}, \quad (2.3)$$

and N is the number of molecules in the interaction volume; ρ is a density of states for the excited molecule.

Equation (2.2) immediately exhibits the expected linear dependence of the absorption rate on the irradiance I_1 and the quadratic dependence on I_2 ; the appearance of $g_2^{(2)}$ marks the influence of the coherence properties of beam 2 on the absorption process.⁵ Note that this coherence dependence is predicted on the assumption that the two beams have no phase correlation; otherwise a third order degree of coherence may be implicated.

The principal interest in Eq. (2.2) is the molecular response tensor $T_{\lambda\mu\nu}$, defined as

$$T_{\lambda\mu\nu} = \frac{1}{2} \sum_{r,s} \left[\frac{\mu_{\lambda}^{fs} \mu_{\mu}^{sr} \mu_{\nu}^{r0}}{(\bar{E}_{s0} - 2\hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_2)} + \frac{\mu_{\mu}^{fs} \mu_{\lambda}^{sr} \mu_{\nu}^{r0}}{(\bar{E}_{s0} - \hbar\omega_1 - \hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_2)} + \frac{\mu_{\mu}^{fs} \mu_{\nu}^{sr} \mu_{\lambda}^{r0}}{(\bar{E}_{s0} - \hbar\omega_1 - \hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_1)} \right. \\ \left. + \frac{\mu_{\lambda}^{fs} \mu_{\nu}^{sr} \mu_{\mu}^{r0}}{(\bar{E}_{s0} - 2\hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_2)} + \frac{\mu_{\nu}^{fs} \mu_{\lambda}^{sr} \mu_{\mu}^{r0}}{(\bar{E}_{s0} - \hbar\omega_1 - \hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_2)} + \frac{\mu_{\nu}^{fs} \mu_{\mu}^{sr} \mu_{\lambda}^{r0}}{(\bar{E}_{s0} - \hbar\omega_1 - \hbar\omega_2)(\bar{E}_{r0} - \hbar\omega_1)} \right], \quad (2.4)$$

where \bar{E}_{r0} and \bar{E}_{s0} are complex energy terms which incorporate damping factors to model the resonance line shape, i.e., $\bar{E}_{r0} = E_{r0} - \frac{1}{2}i\hbar\gamma_r$ and $\bar{E}_{s0} = E_{s0} - \frac{1}{2}i\hbar\gamma_s$. The tensor defined by Eq. (2.4), which has index symmetry in its last two indices, may be written as a sum of four terms, each of which is an irreducible Cartesian tensor with well-defined transformation properties. Full details of the reduction procedure are given in Refs. 6 and 7; the equations are as follows:

$$T_{\lambda\mu\nu}^{(1A)} = \frac{1}{10} (3\delta_{\lambda\mu} T_{\rho\rho\nu} + 3\delta_{\lambda\nu} T_{\rho\rho\mu} - 2\delta_{\mu\nu} T_{\rho\rho\lambda}), \quad (2.5)$$

$$T_{\lambda\mu\nu}^{(1B)} = \frac{1}{10} (-\delta_{\lambda\mu} T_{\nu\rho\rho} - \delta_{\lambda\nu} T_{\mu\rho\rho} + 4\delta_{\mu\nu} T_{\lambda\rho\rho}), \quad (2.6)$$

$$T_{\lambda\mu\nu}^{(2)} = \frac{1}{8} \epsilon_{\lambda\mu\tau} (\epsilon_{\rho\sigma\tau} T_{\rho\sigma\nu} + \epsilon_{\rho\sigma\nu} T_{\rho\sigma\tau}) + \frac{1}{8} \epsilon_{\lambda\nu\tau} (\epsilon_{\rho\sigma\tau} T_{\rho\sigma\mu} + \epsilon_{\rho\sigma\mu} T_{\rho\sigma\tau}), \quad (2.7)$$

$$T_{\lambda\mu\nu}^{(3)} = T_{\lambda\mu\nu} - T_{\lambda\mu\nu}^{(1A)} - T_{\lambda\mu\nu}^{(1B)} - T_{\lambda\mu\nu}^{(2)}. \quad (2.8)$$

The two independent weight-1 tensors $T_{\lambda\mu\nu}^{(1A)}$ and $T_{\lambda\mu\nu}^{(1B)}$ have the transformation properties of polar vectors; $T_{\lambda\mu\nu}^{(2)}$ transforms as a traceless symmetric second rank axial tensor, and $T_{\lambda\mu\nu}^{(3)}$ transforms as a fully traceless and index symmetric third rank polar tensor. The virtue of decomposing $T_{\lambda\mu\nu}$ into these four parts will become evident when we turn to the selection rules later.⁸

Returning to the rate equation (2.2), however, and explicitly performing the rotational average, again using standard procedures described elsewhere,⁹ we obtain the following general expression for the rate of three-photon absorption with arbitrary beam directions and either plane or circular polarizations:

$$\Gamma = \frac{\mathcal{G}}{525} [14\{7(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) - 3(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - 2(\mathbf{e}_2 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2)\} Re T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 7\{-6(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) \\ + 9(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) + (\mathbf{e}_2 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2)\} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 7\{-4(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) + (\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) + 4(\mathbf{e}_2 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2)\} \\ \times T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 35\{2(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) - (\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - (\mathbf{e}_2 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) - 2(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) + 2\} T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} \\ + 5\{-4(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) - 4(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - (\mathbf{e}_2 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_2 \cdot \bar{\mathbf{e}}_2) + 10(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) + 5\} T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}]. \quad (2.9)$$

III. POLARIZATION STUDIES

Using Eq. (2.9), expressions may be derived for the rate of three-photon absorption under various polarization conditions, and for an arbitrary beam geometry. Each beam is allowed to have either plane polarization perpendicular to or parallel to the $\mathbf{k}_1, \mathbf{k}_2$ plane, i.e.,

$$\mathbf{e}^{(\alpha, \perp)} = \hat{\mathbf{i}}_{\alpha}, \quad (3.1)$$

$$\mathbf{e}^{(\alpha, \parallel)} = \hat{\mathbf{j}}_{\alpha}, \quad (3.2)$$

or else left- or right-handed circular polarization;

$$\mathbf{e}^{(\alpha, L)} = \frac{1}{\sqrt{2}}(\hat{\mathbf{i}}_\alpha + i\hat{\mathbf{j}}_\alpha), \quad (3.3)$$

$$\mathbf{e}^{(\alpha, R)} = \frac{1}{\sqrt{2}}(\hat{\mathbf{i}}_\alpha - i\hat{\mathbf{j}}_\alpha). \quad (3.4)$$

Each of the 16 different polarization combinations has a corresponding rate given by Table I. In fact, there are only nine distinct results, denoted by Γ_1 – Γ_9 , and of these only Γ_1 – Γ_5 are genuinely independent for arbitrary beam angle θ . The results are as follows:

$$\Gamma_1 = \frac{S}{525} (28 \operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 28 T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 7 T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 30 T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}), \quad (3.5)$$

$$\Gamma_2 = \frac{S}{525} (-28 \operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 7 T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 28 T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 35 T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} + 20 T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}), \quad (3.6)$$

$$\Gamma_3 = \frac{S}{1050} (-42 \operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 63 T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 7 T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 35 T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} + 80 T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}), \quad (3.7)$$

$$\Gamma_4(\theta) = \frac{S}{1050} \{-42 \cos^2 \theta \operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 63 \cos^2 \theta T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 7 \cos^2 \theta T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 35(4 - 3 \cos^2 \theta) \times T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} + 10(5 + 3 \cos^2 \theta) T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}\}, \quad (3.8)$$

$$\Gamma_5(\theta) = \frac{S}{2100} \{-42(1 - \cos \theta)^2 \operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} + 63(1 - \cos \theta)^2 T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} + 7(1 - \cos \theta)^2 T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} + 35(5 + 3 \cos \theta)(1 - \cos \theta) T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} + 10(13 + 14 \cos \theta + 3 \cos^2 \theta) T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}\}, \quad (3.9)$$

The expressions for Γ_6 – Γ_9 can be obtained from the supplementary relations

$$\Gamma_6(\theta) = \Gamma_2 + (\Gamma_1 - \Gamma_2) \cos^2 \theta, \quad (3.10)$$

$$\Gamma_7(\theta) = \Gamma_3(\theta) + \Gamma_4(\theta) - \Gamma_5(\theta), \quad (3.11)$$

$$\Gamma_8 = \frac{1}{2}(\Gamma_1 + \Gamma_2), \quad (3.12)$$

$$\Gamma_9(\theta) = \frac{1}{2}[\Gamma_2 + \Gamma_6(\theta)]. \quad (3.13)$$

Note the θ independence of all the results relating to experiments with either beam polarized perpendicular to the $\mathbf{k}_1, \mathbf{k}_2$ plane.

A complete polarization study can be carried out to determine whether each of the five distinct molecular parameters in the rate equations, i.e., $T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)}$, $T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)}$, $T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)}$, $T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)}$, and $T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}$, is zero or nonzero; this facilitates the application of selection rules, as shown in the next section. It is readily established that if the beam geometry is such that $\theta = 0^\circ$, 90° , or 180° , then only four of the 16 rate equations for the various polarization combinations are linearly independent, and hence the five molecular parameters cannot be fully determined. A convenient angle at which Γ_1 – Γ_5 are all linearly independent is $\theta = 60^\circ$, leading to the following solution for the molecular parameters:

$$\operatorname{Re} T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\mu\nu\nu}^{(1B)} = \frac{1}{2} S^{-1} (21 \Gamma_1' - 3 \Gamma_2' - 20 \Gamma_3' + 8 \Gamma_4'), \quad (3.14)$$

$$T_{\lambda\lambda\mu}^{(1A)} \bar{T}_{\nu\nu\mu}^{(1A)} = \frac{1}{2} S^{-1} (12 \Gamma_1' - 6 \Gamma_2' + 25 \Gamma_3' + 11 \Gamma_4' - 30 \Gamma_5'), \quad (3.15)$$

$$T_{\lambda\mu\mu}^{(1B)} \bar{T}_{\lambda\nu\nu}^{(1B)} = S^{-1} (9 \Gamma_1' + 18 \Gamma_2' - 10 \Gamma_3' - 8 \Gamma_4'), \quad (3.16)$$

$$T_{\lambda\mu\nu}^{(2)} \bar{T}_{\lambda\mu\nu}^{(2)} = \frac{5}{2} S^{-1} (5 \Gamma_4' - \Gamma_5' - 2 \Gamma_6'), \quad (3.17)$$

$$T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)} = 7 S^{-1} (2 \Gamma_5' - \Gamma_4'). \quad (3.18)$$

In each equation, the prime on the rates Γ_1' – Γ_5' is a

reminder that all measurements relate to experiments with a beam angle of 60° .

Hence, by reference to Table I we see that the five experiments (\perp_1, \perp_2) , (\perp_1, \parallel_2) , (\perp_1, L_2) , (\parallel_1, L_2) , and (L_1, L_2) corresponding to Γ_1' – Γ_5' , respectively, enable all five molecular parameters to be determined from Eqs. (3.14)–(3.18). The usefulness of these parameters will now be demonstrated as we turn to an examination of the selection rules.

IV. SELECTION RULES

For three-photon transitions originating from a totally symmetric ground state, the excited state symmetry dictates the representation under which the components of the molecular response tensor must transform. In this section, we shall concentrate on the application of this selection rule to the analysis of the results given in Sec. III. It is worth noting that the following discussion can easily be extended to cases where the molecular ground state has lower symmetry; then it is the product of the initial and final state representations

TABLE I. Rates of double-beam three-photon absorption.

Beam 1	Beam 2			
	\perp	\parallel	L	R
\perp	Γ_1	Γ_2	Γ_3	Γ_3
\parallel	Γ_2	Γ_6	Γ_4	Γ_4
L	Γ_8	Γ_9	Γ_5	Γ_7
R	Γ_8	Γ_9	Γ_7	Γ_5

TABLE II. Representations of selected point groups spanned by irreducible components of the molecular response tensor.

Group	Weight-1	Weight-2	Weight-3
D_{5h}	$A_2'' + E_1'$	$A_1'' + E_1' + E_2''$	$A_2'' + E_1' + E_2' + E_2''$
D_{6h}	$A_{2u} + E_{1u}$	$A_{1u} + E_{1u} + E_{2u}$	$A_{2u} + B_{1u} + B_{2u} + E_{1u} + E_{2u}$
D_{4d}	$B_2 + E_1$	$B_1 + E_1 + E_2$	$B_2 + E_1 + E_2 + E_3$
D_{6d}	$B_2 + E_1$	$B_1 + E_1 + E_4$	$B_2 + E_1 + E_3 + E_4$
O_h	T_{1u}	$E_u + T_{2u}$	$A_{2u} + T_{1u} + T_{2u}$
I_h	T_{1u}	H_u	$T_{2u} + G_u$
$D_{\infty h}$	$\Sigma_u^+ + \Pi_u$	$\Sigma_u^- + \Pi_u + \Delta_u$	$\Sigma_u^+ + \Pi_u + \Delta_u + \Phi_u$

which determines the transformation properties of the tensor components.

In Table II, the irreducible representations spanned by the weight-1, weight-2, and weight-3 components of the molecular response tensor are listed for molecules belonging to the point groups D_{5h} , D_{6h} , D_{4d} , D_{6d} , O_h , I_h , and $D_{\infty h}$; the corresponding representations for molecules of lower symmetry are readily obtained by the use of correlation tables. Using Table II, it is possible to classify all three-photon transitions observed in a double-beam experiment into one of six classes characterized by the particular combination of tensor weights allowed in the absorption process. The sixfold classification shown in Table III is based on an extension of the threefold classification discussed previously for three-photon transitions observed by single-beam excitation.

A. Classes IA and IB

These classes correspond to subclasses of Class I for single-beam three-photon absorption, and they together comprise those transitions for which the molecular response tensor has both weight-1 and weight-3 components: the distinction is that in class IA the tensor also possesses weight-2 components, whereas in class IB, these components are forbidden. Both classes represent transitions which are allowed by single-photon absorption at frequency $\omega_1 + 2\omega_2$.

B. Classes IIA and IIB

These classes correspond to subclasses of class II for single-beam excitation, and are characterized by having allowed weight-3 components, but forbidden weight-1 components; again the distinction is that class IIA additionally possesses weight-2 components. Both classes are rigorously *forbidden* to single-photon absorption at frequency $\omega_1 + 2\omega_2$.

C. Class III

In this class the transition tensor has weight-1 components alone, exactly as in class III for single-beam excitation. Only transitions to T_{1u} states in I_h molecules fall into this category, which are also allowed by single-photon absorption.

D. Class IV

Finally, we have the class for which the response tensor has weight-2 components alone. This class is absolutely forbidden for single-beam three-photon absorption, and also for single-photon absorption. In all centrosymmetric molecules, the ungerade nature of the excited state also precludes the possibility of two-photon excitation. Hence, class IV transitions are uniquely accessible by double-beam three-photon absorption.

Having established the classification, it is now apparent how the results of Sec. III can be utilized. By performing the five different polarization experiments specified and determining the values of the five molecular parameters given by Eqs. (3.14)–(3.18), then it can be ascertained whether each of the three weights 1, 2, and 3 is allowed in the transition. For example, if $2\Gamma_5' = \Gamma_4'$, then from Eq. (3.18), $T_{\lambda\mu\nu}^{(3)} T_{\lambda\mu\nu}^{(3)}$ is zero and hence the weight-3 tensor components are evidently forbidden. Note that this procedure only requires measurement of relative rates, and not absolute absorption cross sections.

Once it has been established whether each of the three possible weights is allowed or forbidden, the transition can be unambiguously assigned to one of the six classes discussed above. For the classes comprising transitions which are allowed via single-beam

TABLE III. Classification of double-beam three-photon transitions according to the excited state symmetry.

Weights	1, 2, 3	1, 3	2, 3	3	1	2
Group	Class IA	Class IB	Class IIA	Class IIB	Class III	Class IV
D_{5h}	E_1'	A_2''	E_2''	E_2'	...	A_1''
D_{6h}	E_{1u}	A_{2u}	E_{2u}	B_{1u}, B_{2u}	...	A_{1u}
D_{4d}	E_1	B_2	E_2	E_3	...	B_1
D_{6d}	E_1	B_2	E_4	E_3	...	B_1
O_h	...	T_{1u}	T_{2u}	A_{2u}	...	E_u
I_h	T_{2u}, G_u	T_{1u}	H_u
$D_{\infty h}$	Π_u	Σ_u^+	Δ_u	Φ_u	...	Σ_u^-

three-photon absorption, the additional information about the weight-2 tensor components removes some of the ambiguity in the single-beam classification scheme; e.g., a distinction can be made between transitions to A_{2u} and E_{1u} states in D_{6h} molecules. Perhaps more important, however, is the facility for obtaining access to the class IV states which cannot be excited by any other simple method.

In this connection, we note that the class IV transitions are in principle allowed even if the two laser beams are collinear. However, in this case it is necessary that the beams have different polarizations. We also note that with a collinear geometry the ratio $p = \Gamma(L_1, L_2)/\Gamma(\perp_1, \perp_2)$ assumes the value of 5/2 for both class IIA and class IIB transitions. This corresponds exactly to the class II result $\Gamma_o/\Gamma_p = 5/2$ in the case of single-beam excitation,⁴ despite the fact that in the double-beam case two different irradiation frequencies are employed. The ratio does, however, depend on the angle θ between the two beams, and this dependence is expressed by the simple result

$$p = \frac{1}{12}(13 + 14 \cos \theta + 3 \cos^2 \theta), \quad (4.1)$$

in the case of class IIB transitions.

DISCUSSION

Throughout this paper it has been assumed that the two laser beams have different frequencies as well as different directions of propagation. It is worth emphasizing that the requirement for different frequencies is a crucial one. If both beams are of the same frequency, then the molecular response tensor becomes fully index-symmetric, and its weight-2 components vanish: hence transitions to class IV states are forbidden, and the distinction between classes IA and IB, and between classes IIA and IIB is lost. Given two beams of different frequency, however, the double-beam experiment certainly increases the scope for observation of new excited states, and provides more informa-

tion about excited state symmetries than a single-beam study.

The only transitions which remain forbidden, although in principle allowable by the absorption of three photons, are those of weight-0 character—e.g., any transition to an A_{1u} state in a molecule of O_h symmetry. Since such states are not accessible by single- or two-photon absorption either, they should only be observable in a three-photon experiment where *three* different beams are employed, unless the electric dipole selection rules are broken. However, very few transitions are of this weight-0 type, and the double-beam experiment remains the most attractive proposition for extending the scope of three-photon spectroscopy. In view of the additional possibility of utilizing resonance conditions to amplify the absorption rates, the process promises to be an important tool for the molecular spectroscopist.

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