

Polarization studies in multiphoton absorption spectroscopy

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Using the principles of quantum electrodynamics, the theory of two-, three-, and four-photon absorption in polyatomic gases and liquids is developed. Expressions are derived for the rates of single-frequency absorption from plane polarized, circularly polarized, and unpolarized light. It is shown that for n -photon absorption with $n \leq 3$, the rate for unpolarized radiation is in each case expressible as a linear combination of the rates for plane polarized and circularly polarized light; no such relationship exists for four-photon absorption. For each multiphoton process, it is demonstrated how the fullest information about the symmetry properties of excited states can be derived by a simple linear processing of the results from experiments with different polarizations. A detailed examination of the selection rules is made, based on a reduction of the molecular transition tensor into irreducible components, and a new classification scheme is introduced to assist with the interpretation of experimental results. Finally, it is shown that the theory may also be applied to resonance-enhanced multiphoton ionization spectroscopy.

I. INTRODUCTION

Since the arrival of tunable lasers, multiphoton absorption has become an increasingly popular area of molecular spectroscopy. The selection rules differ greatly from conventional absorption spectroscopy, and the technique therefore provides a useful means of identifying normally inaccessible electronic and vibronic excited states. The tunability of the source is especially important for multiphoton processes since it enables studies to be made using a single frequency beam, rather than by irradiation with two or more lasers of different frequencies.

A very significant development has been the utilization of tunable lasers for resonance-enhanced multiphoton ionization spectroscopy, following the pioneering work of Johnson.^{1,2} In these experiments, the variation of the molecular ionization rate with the laser frequency is used to locate multiphoton resonances with bound excited states. For example in three-photon ionization, resonance enhancement is observed when the laser frequency coincides with a one- or two-photon absorption band. Using this method new electronic states have been discovered in a variety of molecules; a recent review by Johnson cites many important examples.³

The fullest information about the excited states involved in a multiphoton absorption process can be obtained by means of a *complete polarization study*, as originally formulated by McClain.^{4,5} This method, which in general involves taking several measurements with beams of various polarizations, has been very successfully applied to two-photon absorption, as well as to resonance Raman scattering. The theory has also been applied to hyper-Raman scattering,⁶ where such experiments have yet to be performed. The information gained from such studies is particularly helpful in the determination of excited state symmetry assignments.

In this paper, we derive expressions for the rates of single-beam multiphoton absorption using plane polarized, circularly polarized and unpolarized light. We demonstrate that for n -photon absorption with $n \leq 3$ the

unpolarized measurement is redundant, since the rate is in each case expressible as a linear combination of the rates for plane polarized and circularly polarized radiation, and these measurements suffice for a full analysis. For $n=4$, however, there is no such relationship between the three polarization measurements, and only by taking all three together can a complete polarization study be accomplished.

For each multiphoton process, a detailed examination is made of the selection rules; this is facilitated by the introduction of irreducible tensors with simple transformation properties. By expressing the rate equations in terms of these tensors, we show that the results of a complete polarization study can be used to assign the multiphoton transition to a particular symmetry type, and we propose new classification schemes to assist the analysis. Finally, we draw attention to the fact that our results can in many cases be applied to resonance-enhanced multiphoton ionization studies.

II. THEORY

A. General principles

We begin with an outline of the principles used in deriving the multiphoton rate equations. For this purpose we adopt the methods of quantum electrodynamics, which enable the statistical properties of unpolarized light to be dealt with in a rigorous way. In quantum electrodynamics the dynamical system comprises both the molecules and the radiation, and the Hamiltonian for the system is

$$H = H_0 + \sum_{\xi} H_{1nt}(\xi), \quad (2.1)$$

where

$$H_0 = H_{\text{rad}} + \sum_{\xi} H_{\text{mol}}(\xi). \quad (2.2)$$

Here H_{rad} is the second-quantized radiation field Hamiltonian, $H_{\text{mol}}(\xi)$ is the nonrelativistic Schrödinger operator for the molecule ξ with position vector R_{ξ} , and

$H_{\text{int}}(\xi)$ is a term representing the interaction of this molecule with the radiation. Generally, H_{int} may be treated as a perturbation which induces transitions between the eigenstates of H_0 , and hence the multiphoton transition rates can be determined using time-dependent perturbation theory.

In the electric dipole approximation H_{int} is given by

$$H_{\text{int}}(\xi) = -\mu(\xi) \cdot \mathbf{e}^{\dagger}(\mathbf{R}_j), \quad (2.3)$$

where \mathbf{e}^{\dagger} is the microscopic transverse electric field operator and μ is the electric dipole moment operator. The electric field is expressible as a sum of components for each radiation mode characterized by wave vector and polarization;

$$\mathbf{e}^{\dagger}(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} \left(\frac{2\pi\hbar\omega}{V} \right)^{1/2} i [\mathbf{e}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) a^{\dagger(\lambda)}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}}]; \quad (2.4)$$

here $a^{(\lambda)}(\mathbf{k})$ and $a^{\dagger(\lambda)}(\mathbf{k})$ are the annihilation and creation operators, respectively, for photons of wave vector \mathbf{k} , circular frequency $\omega = c|\mathbf{k}|$, and polarization vector $\mathbf{e}^{(\lambda)}(\mathbf{k})$. The quantization volume V is here defined as the volume within which the expectation value of H_{rad} is $n\hbar\omega$, in the case of an n -photon absorption process.

The rate of multiphoton absorption is calculated using the Fermi rule,

$$\Gamma = (2\pi/\hbar) |\mathfrak{M}_{fi}|^2 \rho_f, \quad (2.5)$$

where ρ_f is the density of final states and \mathfrak{M}_{fi} is the matrix element connecting the initial state $|i\rangle$ and the final state $|f\rangle$ of the dynamical system. In the dilute gas approximation, \mathfrak{M}_{fi} may be written as a sum of contribu-

tions M_{fi}^{ξ} from each molecule ξ ;

$$\mathfrak{M}_{fi} = \sum_{\xi} M_{fi}^{\xi}. \quad (2.6)$$

Because multiphoton absorption is a nonparametric process, each contribution M_{fi}^{ξ} to \mathfrak{M}_{fi} carries a different phase factor associated with the electric field expansion of Eq. (2.4), and consequently the overall interference between matrix elements for different molecules gives a vanishing result; hence the cross terms in Eq. (2.5) disappear. If there are N molecules in the interaction volume, we therefore have

$$\Gamma = (2\pi N/\hbar) |M_{fi}|^2 \rho_f, \quad (2.7)$$

where the label ξ has been dropped from $|M_{fi}^{\xi}|^2$ since the value is the same for each molecule.

The matrix element M_{fi} has the usual time-dependent perturbation theory expansion;

$$M_{fi} = \langle f_s | H_{\text{int}} | i_s \rangle + \sum_{I_s} \frac{\langle f_s | H_{\text{int}} | I_s \rangle \langle I_s | H_{\text{int}} | i_s \rangle}{E(i_s) - E(I_s)} + \sum_{I_s, II_s} \frac{\langle f_s | H_{\text{int}} | II_s \rangle \langle II_s | H_{\text{int}} | I_s \rangle \langle I_s | H_{\text{int}} | i_s \rangle}{[E(i_s) - E(II_s)][E(i_s) - E(I_s)]} + \dots \quad (2.8)$$

In this equation states and energies, for example, $|i_s\rangle$ and $E(i_s)$, relate to the system comprising one molecule plus the radiation; hence the introduction of the subscript s . The primes denote omission from the intermediate state summations of the initial and final states of the system. The leading contribution for n -photon absorption comes from the n th term in Eq. (2.8), and this has to be separately evaluated for polarized and unpolarized light.

B. Multiphoton absorption of polarized light

For the molecular absorption of n photons with identical polarization and frequency, we have the following result:

$$M_{fi} = \sum_{I_1} \sum_{I_2} \dots \sum_{I_{n-1}} \frac{\langle 0; f | -\mu \cdot \mathbf{e}^{\dagger} | I_{n-1}; 1 \rangle \langle 1; I_{n-1} | -\mu \cdot \mathbf{e}^{\dagger} | I_{n-2}; 2 \rangle \dots \langle n-1; I_1 | -\mu \cdot \mathbf{e}^{\dagger} | i; n \rangle}{[E_i - E_{I_{n-1}} + (n-1)\hbar\omega][E_i - E_{I_{n-2}} + (n-2)\hbar\omega] \dots [E_i - E_{I_1} + \hbar\omega]}. \quad (2.9)$$

Here the ket $|\alpha; p\rangle$ represents the system with the molecule in state $|\alpha\rangle$ and p photons in the incident radiation mode. After carrying out the electric field expansion, we obtain the result

$$M_{fi} = (-i)^n (2\pi\hbar\omega/V)^{n/2} (n!)^{1/2} T_{i_1 \dots i_n} e_{i_1} \dots e_{i_n}, \quad (2.10)$$

using the repeated index summation convention for the inner product of the molecular transition tensor $T_{i_1 \dots i_n}$ with the polarization vector product $e_{i_1} \dots e_{i_n}$. The explicit form of the molecular tensor is given by

$$T_{i_1 \dots i_n} = \sum_{I_1} \sum_{I_2} \dots \sum_{I_{n-1}} \frac{\mu_{i_1}^{I_{n-1}} \mu_{i_2}^{I_{n-2}} \dots \mu_{i_n}^{I_1}}{[E_i - E_{I_{n-1}} + (n-1)\hbar\omega][E_i - E_{I_{n-2}} + (n-2)\hbar\omega] \dots [E_i - E_{I_1} + \hbar\omega]}. \quad (2.11)$$

Since $e_{i_1} \dots e_{i_n}$ is symmetric with respect to interchange of any two indices, only the fully index-symmetric part $T_{i_1 \dots i_n}^s$ of $T_{i_1 \dots i_n}$ contributes to the final result given by Eq. (2.10). Hence we can replace $T_{i_1 \dots i_n}$ by $T_{i_1 \dots i_n}^s$ in this equation, noting that $T_{i_1 \dots i_n}^s$ is obtained from $T_{i_1 \dots i_n}$ by summing over all index permutations and dividing by $n!$. This has important implications for the selection rules, as will become evident later. From Eq. (2.7), we can now write down the rate of n -photon absorption as

$$\Gamma^{(n\phi)} = \frac{2\pi N n! \rho_f}{\hbar} \left(\frac{2\pi\hbar\omega}{V} \right)^n |T_{i_1 \dots i_n}^s e_{i_1} \dots e_{i_n}|^2. \quad (2.12)$$

Since the irradiance of the light is given by

$$I = n\hbar c \omega / V, \quad (2.13)$$

we thus obtain

$$\Gamma^{(n\phi)} = \frac{2\pi N n! \rho_f}{\hbar} \left(\frac{2\pi I}{nc} \right)^n \times T_{i_1 \dots i_n}^s \bar{T}_{i_{n+1} \dots i_{2n}}^s e_{i_1} \dots e_{i_n} \bar{e}_{i_{n+1}} \dots \bar{e}_{i_{2n}}. \quad (2.14)$$

The polarization vector is regarded as a complex quantity in order to admit the possibilities of either plane or circular polarization.

The final stage in obtaining a physically meaningful result involves performing a rotational average of the tensor product in Eq. (2.14); this is necessary to account for the random orientations of molecules in liquids, solutions, and gases where rotational fine structure is unresolved.⁷ The detailed procedure for dealing with the rotational average of a Cartesian tensor product as in Eq. (2.14) has been discussed in a previous paper⁸; the result may be written as

$$\Gamma^{(n\phi)} = \frac{2\pi N n! \rho_f}{\hbar} \left(\frac{2\pi I}{nc}\right)^n \times T_{\lambda_1 \dots \lambda_n}^s \bar{T}_{\lambda_{n+1} \dots \lambda_{2n}}^s e_{i_1} \dots e_{i_n} \bar{e}_{i_{n+1}} \dots \bar{e}_{i_{2n}} I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)}. \quad (2.15)$$

Here the components of the molecular tensor are referred to a molecule-fixed frame, and components of the polarization vector are referred to a space-fixed frame; $I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)}$ is the rotational average of a product of direction cosines $l_{i_p \lambda_p}$ relating coordinates in the two frames, and defined by

$$I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)} = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \prod_{p=1}^{2n} l_{i_p \lambda_p}(\varphi, \theta, \psi) \times \sin\theta \, d\varphi \, d\theta \, d\psi, \quad (2.16)$$

where φ , θ , and ψ are the Euler angles for the frame transformation. Explicit results for the rotational averages with $2n \leq 8$ have recently been calculated^{8,9}; for the present we simply note that $I^{(2n)}$ is generally expressible in the form

$$I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)} = \sum_{rs} m_{rs}^{(2n)} f_{i_1 \dots i_{2n}; r}^{(2n)} g_{\lambda_1 \dots \lambda_{2n}; s}^{(2n)}, \quad (2.17)$$

where $f_{i_1 \dots i_{2n}; r}^{(2n)}$ and $g_{\lambda_1 \dots \lambda_{2n}; s}^{(2n)}$ are isotropic tensors referred to the space-fixed and molecule-fixed frames, respectively, and $m_{rs}^{(2n)}$ are real coefficients.

C. Multiphoton absorption of unpolarized light

It is helpful when dealing with unpolarized light to begin with a phenomenological treatment of the problem. Unpolarized light can be regarded as a stochastic mixture with equal weights of two orthogonal polarizations, for example of left- and right-handed helicity. Since each of the absorbed photons can have either polarization, the rate of n -photon absorption of unpolarized light is given by

$$\Gamma_u^{(n\phi)} = \frac{1}{2^n} \sum_{m=0}^n {}^n C_m \gamma[mL, (n-m)R], \quad (2.18)$$

where $\gamma[mL, (n-m)R]$ denotes the rate associated with absorption of m photons of left-handed helicity, followed by $(n-m)$ photons of right-handed helicity. In writing Eq. (2.18), use has been made of the fact that the rate for a particular combination of left- and right-handed photons is the same regardless of the ordering. For example the absorption sequences (LLR), (LRL), and (RLL) all have the same rate, represented by $\gamma[2L, 1R]$. Since such processes are physically indistinguishable in a concerted multiphoton transition, the rates are given

the lower-case symbol γ to denote the fact that they cannot be separately evaluated. The corresponding physically identifiable rate is a sum of these indistinguishable rates, and may be denoted by the usual symbol Γ ; hence we have

$$\Gamma[mL, (n-m)R] = {}^n C_m \gamma[mL, (n-m)R]. \quad (2.19)$$

The expressions for $\Gamma[nL, 0R]$ and $\Gamma[0L, nR]$ can be written down immediately from the results of Sec. II B, but evaluation of all the terms in Eq. (2.18) requires a different procedure.

From a quantum electrodynamical point of view, the rate $\Gamma[mL, (n-m)R]$ is given by the Fermi rule, with a matrix element $M_{fi}[mL, (n-m)R]$ consisting of a sum of ${}^n C_m$ terms corresponding to the various time-orderings of the photon absorptions. These terms are most readily identified with the aid of time-ordered diagrams, and the results have the general form

$$M_{fi}[mL, (n-m)R] = (-i)^n \left(\frac{2\pi \hbar \omega}{V}\right)^{n/2} [m!(n-m)!]^{1/2} T_{i_1 \dots i_n} \times (e_{i_1}^L \dots e_{i_m}^L e_{i_{m+1}}^R \dots e_{i_n}^R + \text{index permutations}). \quad (2.20)$$

In view of the complete index symmetry of the sum of polarization vector component permutations, $T_{i_1 \dots i_n}$ can once again be replaced by $T_{i_1 \dots i_n}^s$ in Eq. (2.20), and then since each of the ${}^n C_m$ terms gives an equal contribution to the result we can simply write

$$M_{fi}[mL, (n-m)R] = (-i)^n \left(\frac{2\pi \hbar \omega}{V}\right)^{n/2} [m!(n-m)!]^{1/2} {}^n C_m T_{i_1 \dots i_n}^s \times e_{i_1}^L \dots e_{i_m}^L e_{i_{m+1}}^R \dots e_{i_n}^R. \quad (2.21)$$

Use of the Fermi rule then leads to the following rotationally averaged rate:

$$\Gamma[mL, (n-m)R] = \frac{2\pi N n! \rho_f}{\hbar} \left(\frac{2\pi I}{nc}\right)^n {}^n C_m T_{\lambda_1 \dots \lambda_n}^s \bar{T}_{\lambda_{n+1} \dots \lambda_{2n}}^s \times e_{i_1}^L \dots e_{i_m}^L e_{i_{m+1}}^R \dots e_{i_n}^R \bar{e}_{i_{n+1}}^L \dots \bar{e}_{i_{n+m}}^L \times \bar{e}_{i_{n+m+1}}^R \dots \bar{e}_{i_{2n}}^R I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)}, \quad (2.22)$$

corresponding to ${}^n C_m \gamma[mL, (n-m)R]$. By making further use of the index symmetry of $T_{\lambda_1 \dots \lambda_n}^s$, we can now show that the result for $\Gamma_u^{(n\phi)}$ given by Eq. (2.18) takes the form

$$\Gamma_u^{(n\phi)} = \frac{2\pi N n! \rho_f}{\hbar} \left(\frac{\pi I}{nc}\right)^n T_{\lambda_1 \dots \lambda_n}^s \bar{T}_{\lambda_{n+1} \dots \lambda_{2n}}^s \times \sum_{\lambda_1=L,R} \dots \sum_{\lambda_n=L,R} e_{i_1}^{\lambda_1} \dots e_{i_n}^{\lambda_n} \bar{e}_{i_{n+1}}^{\lambda_1} \dots \bar{e}_{i_{2n}}^{\lambda_n} I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)}, \quad (2.23)$$

and the result is readily evaluated by making use of the relation¹⁰

$$\sum_{\lambda=L,R} e_i^\lambda \bar{e}_j^\lambda = \delta_{ij} - \hat{k}_i \hat{k}_j. \quad (2.24)$$

It is important to note that in Eq. (2.23) the rate is again expressed in terms of the fully index-symmetric

molecular transition tensor, just as in the case of polarized light.

D. Determination of molecular parameters

One of the most significant differences between the expressions for the rates of single-photon and multiphoton absorption is the number of molecular parameters involved. For single-photon absorption, Eqs. (2.15) and (2.23) yield the result

$$\Gamma_p^{(1\phi)} = \Gamma_c^{(1\phi)} = \Gamma_u^{(1\phi)} = (4\pi^2 N I \rho_f / 3\hbar c) |\mu^{fi}|^2, \quad (2.25)$$

where $\Gamma_p^{(1\phi)}$ denotes the rate of single-photon absorption of plane polarized light and $\Gamma_c^{(1\phi)}$ denotes the rate of absorption of circularly polarized light of either handedness—note that the equivalence of these results with the rate $\Gamma_u^{(1\phi)}$ for unpolarized light is a unique feature of single-photon absorption. Whereas Eq. (2.25) involves a single molecular parameter $|\mu^{fi}|^2$, the corresponding rate equations for multiphoton absorption generally involve two or more independent transition tensor parameters.

The general form of these parameters follows from Eqs. (2.17), (2.15), and (2.23). In each case, the summation over the molecular frame tensor indices results in a linear combination of terms

$$T_{\lambda_1 \dots \lambda_n}^s \bar{T}_{\lambda_{n+1} \dots \lambda_{2n}}^s g_{\lambda_1 \dots \lambda_{2n}}^{(2n;s)}, \quad (2.26)$$

where each isotropic tensor $g_{\lambda_1 \dots \lambda_{2n}}^{(2n;s)}$ consists of a product of n Kronecker delta tensors such as $\delta_{\lambda_1 \lambda_2} \dots \delta_{\lambda_{2n-1} \lambda_{2n}}$ and its index permutations. In view of the complete index symmetry of the molecular transition tensor, it is readily shown that there are only $[n/2] + 1$ different scalars which can result from the index contractions; with $n=2$, for example, we have just two independent parameters $T_{\lambda\lambda}^s \bar{T}_{\mu\mu}^s$ and $T_{\lambda\mu}^s \bar{T}_{\lambda\mu}^s$.

Knowledge of the relative values of these parameters provides important information about the symmetry properties of excited states; the adoption of irreducible tensors simplifies this procedure, as will be demonstrated later. In order to obtain the requisite data it is necessary to perform a suitable set of $[n/2] + 1$ separate studies with different polarizations, and then solve the rate equations for the unknown parameters. For two- and three-photon absorption where there are only two parameters to be determined, two experiments with circular and plane polarizations suffice; however for four-photon absorption the additional measurement with unpolarized light is necessary to complete the determination. The relevant expressions are examined in detail in the next three sections.

III. TWO-PHOTON ABSORPTION

A. Rate equations

Using the results of Sec. II, it is a straightforward matter to calculate the rates of two-photon absorption for plane polarized, circularly polarized and unpolarized light. The results, which are expressed in terms of the two molecular parameters $T_{\lambda\lambda}^s \bar{T}_{\mu\mu}^s$ and $T_{\lambda\mu}^s \bar{T}_{\lambda\mu}^s$, are as follows:

$$\Gamma_p^{(2\phi)} = \frac{8\pi^3 N I^2 \rho_f}{15\hbar c^2} [T_{\lambda\lambda}^s \bar{T}_{\mu\mu}^s + 2T_{\lambda\mu}^s \bar{T}_{\lambda\mu}^s], \quad (3.1)$$

$$\Gamma_c^{(2\phi)} = \frac{8\pi^3 N I^2 \rho_f}{15\hbar c^2} [-T_{\lambda\lambda}^s \bar{T}_{\mu\mu}^s + 3T_{\lambda\mu}^s \bar{T}_{\lambda\mu}^s], \quad (3.2)$$

$$\Gamma_u^{(2\phi)} = \frac{2\pi^3 N I^2 \rho_f}{15\hbar c^2} [T_{\lambda\lambda}^s \bar{T}_{\mu\mu}^s + 7T_{\lambda\mu}^s \bar{T}_{\lambda\mu}^s]. \quad (3.3)$$

Unlike the case of single-photon absorption, here each of the three results is different. However $\Gamma_u^{(2\phi)}$ is expressible as a linear combination of $\Gamma_p^{(2\phi)}$ and $\Gamma_c^{(2\phi)}$ through the equation

$$\Gamma_u^{(2\phi)} = \frac{1}{4}(2\Gamma_p^{(2\phi)} + \Gamma_c^{(2\phi)}); \quad (3.4)$$

thus measurement of $\Gamma_u^{(2\phi)}$ is redundant once $\Gamma_p^{(2\phi)}$ and $\Gamma_c^{(2\phi)}$ are known. In passing, it is worth mentioning that a result of exactly the same form has also been established for second harmonic light scattering processes, which again involve the annihilation of two incident photons.¹¹

B. Selection rules

In order to deal with the selection rules for any multiphoton process, it is instructive to introduce irreducible molecular tensors. These tensors have well-defined transformation properties under the symmetry operations of molecular point groups, and are therefore ideally suited for a discussion of selection rules. Although the selection rules for two-photon absorption are well known, this section will provide a useful introduction to the methodology used in considering three- and four-photon absorption in Secs. IV and V.

The irreducible parts of a symmetric second-rank Cartesian tensor are given by¹²

$$T_{\lambda\mu}^{(0)} = \frac{1}{3} \delta_{\lambda\mu} T_{\nu\nu}^s, \quad (3.5)$$

$$T_{\lambda\mu}^{(2)} = T_{\lambda\mu}^s - T_{\lambda\mu}^{(0)}. \quad (3.6)$$

The components of $T_{\lambda\mu}^{(0)}$ and $T_{\lambda\mu}^{(2)}$ transform among themselves under the operations of the rotation group and form bases for representations of a scalar and a deviator, i. e., a traceless symmetric second rank tensor, respectively. Because of the connection with angular momentum theory,¹³ they are said to have *weights* $j=0$ and $j=2$, each having $(2j+1)$ components, thus accounting for the six independent components of a symmetric second rank tensor. Two conclusions immediately follow. First, since the weight-0 tensor components transform like scalars, they can only assume nonzero values in symmetry-preserving two-photon transitions, i. e., those which terminate in a totally symmetric excited state.¹⁴ Secondly, the weight-2 tensor components are always nonzero in such transitions, with the sole exception of molecules belonging to one of the cubic or icosahedral point groups.

In Table I, the irreducible representations spanned by weight-0 and weight-2 tensor components 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 use of correlation tables. Two-photon absorption processes can thus be classified into three types as

TABLE I. Representations of selected point groups spanned by components of irreducible tensors. Weights 0 and 2 relate to two-photon absorption; weights 1 and 3 relate to three-photon absorption, and weights 0, 2, and 4 together relate to four-photon absorption.

Group	Weight-0	Weight-1	Weight-2	Weight-3	Weight-4
D_{5h}	A'_1	$A'_2 + E'_1$	$A'_1 + E'_1 + E'_2$	$A'_2 + E'_1 + E'_2 + E'_3$	$A'_1 + E'_1 + E'_2 + E'_3 + E'_4$
D_{6h}	A_{1g}	$A_{2u} + E_{1u}$	$A_{1g} + E_{1g} + E_{2g}$	$A_{2u} + B_{1u} + B_{2u} + E_{1u} + E_{2u}$	$A_{1g} + B_{1g} + B_{2g} + E_{1g} + 2E_{2g}$
D_{4d}	A_1	$B_2 + E_1$	$A_1 + E_2 + E_3$	$B_2 + E_1 + E_2 + E_3$	$A_1 + B_1 + B_2 + E_1 + E_2 + E_3$
D_{6d}	A_1	$B_2 + E_1$	$A_1 + E_2 + E_5$	$B_2 + E_1 + E_3 + E_4$	$A_1 + E_2 + E_3 + E_4 + E_5$
O_h	A_{1g}	T_{1u}	$E_g + T_{2g}$	$A_{2u} + T_{1u} + T_{2u}$	$A_{1g} + E_g + T_{1g} + T_{2g}$
I_h	A_g	T_{1u}	H_g	$T_{2u} + G_u$	$G_g + H_g$
$D_{\infty h}$	Σ_g^+	$\Sigma_u^+ + \Pi_u$	$\Sigma_g^+ + \Pi_g + \Delta_g$	$\Sigma_u^+ + \Pi_u + \Delta_u + \Phi_u$	$\Sigma_g^+ + \Pi_g + \Delta_g + \Phi_g + \Gamma_g$

shown in Table II.

Class I. This class comprises transitions for which the molecular transition tensor has both weight-0 and weight-2 components; only transitions to totally symmetric excited states fall into this class.

Class II. In this class the transition tensor has weight-2 components alone; the majority of two-photon transitions fall into this category.

Class III. Here the transition tensor has weight-0 components alone, and the case only arises for transitions to totally symmetric states in molecules of cubic or icosahedral symmetry.

To apply the selection rules and differentiate the properties of these three classes, we now return to the two-photon rate equations and re-express them in terms of the irreducible tensors.

C. Polarization studies

From Eqs. (3.1)–(3.3), (3.5), and (3.6) we find that the two-photon absorption rates may be written in terms of two new molecular parameters $T_{\lambda\lambda}^{(0)}\bar{T}_{\mu\mu}^{(0)}$ and $T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)}$ as follows;

$$\Gamma_p^{(2\phi)} = \frac{8\pi^3 N I^2 \rho_f}{45\hbar c^2} [5T_{\lambda\lambda}^{(0)}\bar{T}_{\mu\mu}^{(0)} + 6T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)}], \quad (3.7)$$

$$\Gamma_c^{(2\phi)} = \frac{8\pi^3 N I^2 \rho_f}{5\hbar c^2} T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)}, \quad (3.8)$$

$$\Gamma_u^{(2\phi)} = \frac{2\pi^3 N I^2 \rho_f}{45\hbar c^2} [10T_{\lambda\lambda}^{(0)}\bar{T}_{\mu\mu}^{(0)} + 21T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)}]. \quad (3.9)$$

Whilst there are no immediate conclusions to be drawn from these equations for class I transitions, comments can be made concerning the other two classes.

Firstly, for a class II transition the weight-0 tensor product $T_{\lambda\lambda}^{(0)}\bar{T}_{\mu\mu}^{(0)}$ is zero, and hence we obtain the well-known result¹⁵

$$\Gamma_p^{(2\phi)} = \frac{2}{3}\Gamma_c^{(2\phi)}. \quad (3.10)$$

We also find that in this case

$$\Gamma_u^{(2\phi)} = \frac{7}{8}\Gamma_p^{(2\phi)}. \quad (3.11)$$

Secondly, for a class III transition $T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)}$ is zero so that we find

$$\Gamma_u^{(2\phi)} = \frac{1}{2}\Gamma_p^{(2\phi)}, \quad (3.12)$$

and

$$\Gamma_c^{(2\phi)} = 0. \quad (3.13)$$

Thus the absorption of two circularly polarized photons of the same handedness is forbidden in any class III transition.

For two-photon absorption, a complete polarization study need only consist of measurements of $\Gamma_p^{(2\phi)}$ and $\Gamma_c^{(2\phi)}$, since Eqs. (3.7) and (3.8) can be solved for the two molecular parameters as below;

$$T_{\lambda\lambda}^{(0)}\bar{T}_{\mu\mu}^{(0)} = 3\mathcal{K}^{(2\phi)}(3\Gamma_p^{(2\phi)} - 2\Gamma_c^{(2\phi)}), \quad (3.14)$$

$$T_{\lambda\mu}^{(2)}\bar{T}_{\lambda\mu}^{(2)} = 5\mathcal{K}^{(2\phi)}\Gamma_c^{(2\phi)}, \quad (3.15)$$

where

$$\mathcal{K}^{(2\phi)} = \hbar c^2 / 8\pi^3 N I^2 \rho_f. \quad (3.16)$$

Since the classification scheme of Sec. III B depends only on knowledge of whether the weight-0 and weight-2 components of the transition tensor are zero or nonzero, the above results can be utilized without any necessity for evaluating $\mathcal{K}^{(2\phi)}$; the experimental values for $\Gamma_c^{(2\phi)}$ and $(3\Gamma_p^{(2\phi)} - 2\Gamma_c^{(2\phi)})$ are sufficient to provide an unambiguous assignment of the excited state to one of the three symmetry classes.

TABLE II. Classification of two-photon transitions according to the excited state symmetry.

	Class I	Class II	Class III
Weights	0, 2	2	0
D_{5h}	A'_1	E'_1, E'_2	...
D_{6h}	A_{1g}	E_{1g}, E_{2g}	...
D_{4d}	A_1	E_2, E_3	...
D_{6d}	A_1	E_2, E_5	...
O_h	...	E_g, T_{2g}	A_{1g}
I_h	...	H_g	A_g
$D_{\infty h}$	Σ_g^+	Π_g, Δ_g	...

IV. THREE-PHOTON ABSORPTION

A. Rate equations

The rates of three-photon absorption of plane polarized, circularly polarized and unpolarized light are as follows;

$$\Gamma_p^{(3\phi)} = \frac{16\pi^4 N I^3 \rho_f}{35\hbar c^3} [3T_{\lambda\mu\mu}^s \bar{T}_{\lambda\nu\nu}^s + 2T_{\lambda\mu\nu}^s \bar{T}_{\lambda\mu\nu}^s], \quad (4.1)$$

$$\Gamma_c^{(3\phi)} = \frac{16\pi^4 N I^3 \rho_f}{35\hbar c^3} [-3T_{\lambda\mu\mu}^s \bar{T}_{\lambda\nu\nu}^s + 5T_{\lambda\mu\nu}^s \bar{T}_{\lambda\mu\nu}^s], \quad (4.2)$$

$$\Gamma_u^{(3\phi)} = \frac{8\pi^4 N I^3 \rho_f}{35\hbar c^3} [T_{\lambda\mu\mu}^s \bar{T}_{\lambda\nu\nu}^s + 3T_{\lambda\mu\nu}^s \bar{T}_{\lambda\mu\nu}^s]; \quad (4.3)$$

again, the rates are expressible in terms of just two molecular parameters, i.e., $T_{\lambda\mu\mu}^s \bar{T}_{\lambda\nu\nu}^s$ and $T_{\lambda\mu\nu}^s \bar{T}_{\lambda\mu\nu}^s$. The result for $\Gamma_u^{(3\phi)}$ is expressible as a linear combination of $\Gamma_p^{(3\phi)}$ and $\Gamma_c^{(3\phi)}$, but the relation differs from the two-photon analog, Eq. (3.4); here we have

$$\Gamma_u^{(3\phi)} = \frac{1}{8}(2\Gamma_p^{(3\phi)} + \Gamma_c^{(3\phi)}). \quad (4.4)$$

Thus the measurement with unpolarized light is once again superfluous for three-photon absorption.

B. Selection rules

The decomposition of a fully index-symmetric third rank tensor into irreducible parts takes the form¹⁶;

$$T_{\lambda\mu\nu}^{(1)} = \frac{1}{5}(\delta_{\lambda\mu} T_{\rho\rho\nu}^s + \delta_{\lambda\nu} T_{\rho\rho\mu}^s + \delta_{\mu\nu} T_{\rho\rho\lambda}^s), \quad (4.5)$$

$$T_{\lambda\mu\nu}^{(3)} = T_{\lambda\mu\nu}^s - T_{\lambda\mu\nu}^{(1)}. \quad (4.6)$$

The components of $T_{\lambda\mu\nu}^{(1)}$ and $T_{\lambda\mu\nu}^{(3)}$ form the bases for representations of a vector and a septor, i.e., a traceless symmetric third rank tensor, and together they comprise ten independent tensor components. Since the weight-1 tensor components transform like vectors, they can only be nonzero in the case of a three-photon transition to a state which is, in principle, one-photon allowed, in the sense that absorption should also be observed at the frequency 3ω .

The irreducible representations spanned by weight-1 and weight-3 tensor components are listed in Table I for selected point groups, and we find that three-photon transitions can once more be classified into three types, as shown in Table III.

Class I. In this class the transition tensor comprises both weight-1 and weight-3 components, and the excited states generally have the same transformation properties as the translation vector components x , y , or z . An exception is found in the case of a transition to a T_{1u} state in a molecule of I_h symmetry, where the transition tensor has no weight-3 components.

Class II. Here the transition tensor has weight-3 components alone, and there are many examples shown in Table III. Transitions in this class terminate in states which are rigorously forbidden to single-photon absorption at frequency 3ω .

Class III. Finally, we have the class for which the transition tensor has weight-1 components alone. Only transitions to T_{1u} states in I_h molecules fall into this category, which is thus not in general of great chemical importance.

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

	Class I	Class II	Class III
Weights	1, 3	3	1
D_{5h}	A_2'', E_1'	E_2', E_2''	...
D_{6h}	A_{2u}, E_{1u}	B_{1u}, B_{2u}, E_{2u}	...
D_{4d}	B_2, E_1	E_2, E_3	...
D_{6d}	B_2, E_1	E_3, E_4	...
O_h	T_{1u}	A_{2u}, T_{2u}	...
I_h	...	T_{2u}, G_u	T_{1u}
$D_{\infty h}$	Σ_u^+, Π_u	Δ_u, Φ_u	...

C. Polarization studies

To apply the selection rules we return to the three-photon rate equations (4.1)–(4.3), and re-express them in terms of the irreducible tensors. The results are then written in terms of two new molecular parameters $T_{\lambda\mu\mu}^{(1)} \bar{T}_{\lambda\nu\nu}^{(1)}$ and $T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}$;

$$\Gamma_p^{(3\phi)} = \frac{16\pi^4 N I^3 \rho_f}{175\hbar c^3} [21T_{\lambda\mu\mu}^{(1)} \bar{T}_{\lambda\nu\nu}^{(1)} + 10T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}], \quad (4.7)$$

$$\Gamma_c^{(3\phi)} = \frac{16\pi^4 N I^3 \rho_f}{7\hbar c^3} T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}, \quad (4.8)$$

$$\Gamma_u^{(3\phi)} = \frac{8\pi^4 N I^3 \rho_f}{175\hbar c^3} [14T_{\lambda\mu\mu}^{(1)} \bar{T}_{\lambda\nu\nu}^{(1)} + 15T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}]. \quad (4.9)$$

Again, there are no immediate conclusions to draw for class I transitions, but the other two classes do lead to interesting results.

For class II transitions the weight-1 tensor components are zero, and hence from Eqs. (4.7)–(4.9) we find with Nieman¹⁷ that

$$\Gamma_p^{(3\phi)} = \frac{2}{5}\Gamma_c^{(3\phi)}; \quad (4.10)$$

we also have

$$\Gamma_u^{(3\phi)} = \frac{3}{4}\Gamma_p^{(3\phi)}. \quad (4.11)$$

For class III transitions, on the other hand, the weight-3 components are zero, leading to the results

$$\Gamma_u^{(3\phi)} = \frac{1}{3}\Gamma_p^{(3\phi)}, \quad (4.12)$$

and

$$\Gamma_c^{(3\phi)} = 0; \quad (4.13)$$

hence a class III transition is forbidden for circularly polarized light.

Because there are only two independent parameters in Eqs. (4.7)–(4.9), a complete polarization study need only consist of measurements of two rates, and we can solve for $T_{\lambda\mu\mu}^{(1)} \bar{T}_{\lambda\nu\nu}^{(1)}$ and $T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)}$ in terms of $\Gamma_p^{(3\phi)}$ and $\Gamma_c^{(3\phi)}$, giving the following expressions;

$$T_{\lambda\mu\mu}^{(1)} \bar{T}_{\lambda\nu\nu}^{(1)} = 5\mathcal{K}^{(3\phi)}(5\Gamma_p^{(3\phi)} - 2\Gamma_c^{(3\phi)}), \quad (4.14)$$

$$T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)} = 21\mathcal{K}^{(3\phi)}\Gamma_c^{(3\phi)}, \quad (4.15)$$

where

$$\mathcal{K}^{(3\phi)} = \hbar c^3 / 48\pi^4 N I^3 \rho_f. \quad (4.16)$$

TABLE IV. Classification of four-photon transitions according to the excited state symmetry.

	Class I	Class II	Class III	Class IV	Class V
Weights	0, 2, 4	2, 4	0, 4	4	0
D_{5h}	A_1'	E_1'', E_2''	...	E_1', E_2''	...
D_{6h}	A_{1g}	E_{1g}, E_{2g}	...	B_{1g}, B_{2g}	...
D_{4d}	A_1	E_2, E_3	...	B_1, B_2, E_1	...
D_{6d}	A_1	E_2, E_5	...	E_3, E_4	...
O_h	...	E_g, T_{2g}	A_{1g}	T_{1g}	...
I_h	...	H_g	...	G_g	A_g
$D_{\infty h}$	Σ_g^+	Π_g, Δ_g	...	Φ_g, Γ_g	...

By determining experimental values for $\Gamma_c^{(3\phi)}$ and $(5\Gamma_p^{(3\phi)} - 2\Gamma_c^{(3\phi)})$, we can therefore decide which of the tensor weights are nonzero, and hence assign the three-photon transition to one of the symmetry classes discussed in Sec. IV B.

V. FOUR-PHOTON ABSORPTION

A. Rate equations

The four-photon absorption rates calculated from equations (2.15) and (2.23) are as follows;

$$\Gamma_p^{(4\phi)} = \frac{32\pi^5 N I^4 \rho_f}{315\hbar c^4} [3T_{\lambda\mu\mu}^s \bar{T}_{\nu\nu\sigma}^s + 24T_{\lambda\lambda\mu\nu}^s \bar{T}_{\sigma\sigma\mu\nu}^s + 8T_{\lambda\mu\nu\sigma}^s \bar{T}_{\lambda\mu\nu\sigma}^s], \quad (5.1)$$

$$\Gamma_c^{(4\phi)} = \frac{32\pi^5 N I^4 \rho_f}{315\hbar c^4} [3T_{\lambda\lambda\mu\mu}^s \bar{T}_{\nu\nu\sigma}^s - 30T_{\lambda\lambda\mu\nu}^s \bar{T}_{\sigma\sigma\mu\nu}^s + 35T_{\lambda\mu\nu\sigma}^s \bar{T}_{\lambda\mu\nu\sigma}^s], \quad (5.2)$$

$$\Gamma_u^{(4\phi)} = \frac{2\pi^5 N I^4 \rho_f}{315\hbar c^4} [3T_{\lambda\lambda\mu\mu}^s \bar{T}_{\nu\nu\sigma}^s + 42T_{\lambda\lambda\mu\nu}^s \bar{T}_{\sigma\sigma\mu\nu}^s + 83T_{\lambda\mu\nu\sigma}^s \bar{T}_{\lambda\mu\nu\sigma}^s]. \quad (5.3)$$

In this case three independent molecular parameters are involved, and the three rate expressions are found to be linearly independent. Hence $\Gamma_u^{(4\phi)}$ cannot be written in terms of $\Gamma_p^{(4\phi)}$ and $\Gamma_c^{(4\phi)}$ alone; this feature represents a major departure from the behavior observed in two- and three-photon absorption. In fact, all three rate measurements are necessary in order to carry out a complete polarization study, as we shall see shortly.

B. Selection rules

Once again it is helpful to rewrite Eqs. (5.1)–(5.3) in terms of irreducible tensor parameters in order to deal with the selection rules. Using the methods of tensor reduction outlined in a previous paper⁶ and enunciated more formally by Jerphagnon *et al.*,¹⁸ it can be shown that a fully index-symmetric fourth rank Cartesian tensor reduces as follows;

$$T_{\lambda\mu\nu\sigma}^{(0)} = \frac{1}{15} (\delta_{\lambda\mu} \delta_{\nu\sigma} + \delta_{\lambda\nu} \delta_{\mu\sigma} + \delta_{\lambda\sigma} \delta_{\mu\nu}) T_{\rho\rho\sigma\sigma}^s, \quad (5.4)$$

$$T_{\lambda\mu\nu\sigma}^{(2)} = \frac{1}{7} (\delta_{\lambda\mu} T_{\rho\rho\nu\sigma}^s + \delta_{\lambda\nu} T_{\rho\rho\mu\sigma}^s + \delta_{\lambda\sigma} T_{\rho\rho\mu\nu}^s + \delta_{\mu\nu} T_{\rho\rho\lambda\sigma}^s + \delta_{\mu\sigma} T_{\rho\rho\lambda\nu}^s + \delta_{\nu\sigma} T_{\rho\rho\lambda\mu}^s) - \frac{10}{7} T_{\lambda\mu\nu\sigma}^{(0)}, \quad (5.5)$$

$$T_{\lambda\mu\nu\sigma}^{(4)} = T_{\lambda\mu\nu\sigma}^s - T_{\lambda\mu\nu\sigma}^{(0)} - T_{\lambda\mu\nu\sigma}^{(2)}, \quad (5.6)$$

where the corresponding representations of order 1, 5, and 9 together account for the 15 independent components of $T_{\lambda\mu\nu\sigma}^s$. The weight-0 tensor components transform as a scalar, and hence are only nonzero in transitions to totally symmetric excited states. The weight-2 components transform as a deviator, and are in general nonzero for four-photon transitions to states which are two-photon allowed at frequency 2ω . The only exception to this rule is that the molecular tensor has no weight-2 components in transitions to totally symmetric excited states in molecules of cubic or icosahedral symmetry, although such transitions are allowed by two-photon absorption.

The irreducible representations spanned by weight-0, -2, and -4 tensors are again given by Table I. One important conclusion can be drawn from inspection of this table; if the transition tensor contains weight-2 components, then it also contains weight-4 components. Hence there are five possible combinations of the tensor weights, providing us with a five-fold classification scheme for four-photon transitions, as shown in Table IV. The five classes are defined as follows:

Class I. In this class the molecular transition tensor has a complete set of weight-0, weight-2, and weight-4 components. Only transitions to totally symmetric states in noncubic and nonicosahedral molecules fall into this category.

Class II. Here there are only weight-2 and weight-4 contributions to the transition tensor; many examples are given in Table IV.

Class III. In this class there are weight-0 and weight-4 components alone; only transitions to totally symmetric excited states in molecules belonging to a cubic point group fall into this class.

Class IV. Transitions belonging to this class have only weight-4 contributions to the transition tensor, and a large number of cases arise as shown by Table IV.

Class V. Finally, there is the class with only weight-0 components; this only occurs for transitions to totally symmetric states in icosahedral molecules.

It is worth noting that all of the excited states associated with classes I, II, III, and V are also allowed by two-photon absorption at frequency 2ω . However, the

states which fall into class IV are all forbidden in two-photon absorption.

C. Polarization studies

The rate equations (5.1)–(5.3) may now be re-expressed in terms of the irreducible fourth rank tensors as follows:

$$\Gamma_p^{(4\phi)} = \frac{32\pi^5 N I^4 \rho_f}{11025 \hbar c^4} [441 T_{\lambda\lambda\mu\mu}^{(0)} \bar{T}_{\nu\nu\sigma\sigma}^{(0)} + 1080 T_{\lambda\lambda\mu\nu}^{(2)} \bar{T}_{\sigma\sigma\mu\nu}^{(2)} + 280 T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)}], \quad (5.7)$$

$$\Gamma_c^{(4\phi)} = \frac{32\pi^5 N I^4 \rho_f}{9 \hbar c^4} T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)}, \quad (5.8)$$

$$\Gamma_u^{(4\phi)} = \frac{2\pi^5 N I^4 \rho_f}{11025 \hbar c^4} [1176 T_{\lambda\lambda\mu\mu}^{(0)} \bar{T}_{\nu\nu\sigma\sigma}^{(0)} + 3960 T_{\lambda\lambda\mu\nu}^{(2)} \bar{T}_{\sigma\sigma\mu\nu}^{(2)} + 2905 T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)}]. \quad (5.9)$$

Certain general observations can be made; for example, $\Gamma_c^{(4\phi)}/\Gamma_p^{(4\phi)} \leq \frac{35}{8}$ for all classes; however the results are particularly interesting for class IV and class V transitions.

For the two-photon forbidden class IV transitions, the only nonzero molecular parameter is $T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)}$, and hence we find

$$\Gamma_p^{(4\phi)} = \frac{8}{35} \Gamma_c^{(4\phi)}, \quad (5.10)$$

and

$$\Gamma_u^{(4\phi)} = \frac{83}{128} \Gamma_p^{(4\phi)}. \quad (5.11)$$

For class V transitions, on the other hand, only $T_{\lambda\lambda\mu\mu}^{(0)} \bar{T}_{\nu\nu\sigma\sigma}^{(0)}$ is nonzero, so that we obtain the relations

$$\Gamma_u^{(4\phi)} = \frac{1}{6} \Gamma_p^{(4\phi)}, \quad (5.12)$$

and

$$\Gamma_c^{(4\phi)} = 0. \quad (5.13)$$

A four-photon transition to a class V excited state is therefore forbidden in the case of circularly polarized radiation.

Since there are three linearly independent molecular parameters in Eqs. (5.7)–(5.9), all three rate measurements are required for a complete polarization study. The solutions for $T_{\lambda\lambda\mu\mu}^{(0)} \bar{T}_{\nu\nu\sigma\sigma}^{(0)}$, $T_{\lambda\lambda\mu\nu}^{(2)} \bar{T}_{\sigma\sigma\mu\nu}^{(2)}$, and $T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)}$ are as follows;

$$T_{\lambda\lambda\mu\mu}^{(0)} \bar{T}_{\nu\nu\sigma\sigma}^{(0)} = 120 \mathcal{K}^{(4\phi)} (55 \Gamma_p^{(4\phi)} + 23 \Gamma_c^{(4\phi)} - 240 \Gamma_u^{(4\phi)}), \quad (5.14)$$

$$T_{\lambda\lambda\mu\nu}^{(2)} \bar{T}_{\sigma\sigma\mu\nu}^{(2)} = 35 \mathcal{K}^{(4\phi)} (-56 \Gamma_p^{(4\phi)} - 37 \Gamma_c^{(4\phi)} + 336 \Gamma_u^{(4\phi)}), \quad (5.15)$$

$$T_{\lambda\mu\nu\sigma}^{(4)} \bar{T}_{\lambda\mu\nu\sigma}^{(4)} = 648 \mathcal{K}^{(4\phi)} \Gamma_c^{(4\phi)}, \quad (5.16)$$

where

$$\mathcal{K}^{(4\phi)} = \hbar c^4 / 2304 \pi^5 N I^4 \rho_f. \quad (5.17)$$

Experimental determination of the rate combinations on the right-hand sides of Eqs. (5.14)–(5.16) thus enables any four-photon transition to be classified according to the scheme of Sec. V B, thereby providing important information about the symmetry of the excited state.

Again it should be emphasized that only *relative* rate measurements are required for this analysis.

VI. DISCUSSION

In this paper it has been demonstrated how to make the fullest use of polarization studies in molecular multiphoton absorption experiments. The new classification schemes which we have proposed provide a useful framework for the analysis of experimental results, leading to important information on excited state symmetry properties. The new results for the multiphoton absorption of unpolarized light are also shown to be particularly valuable in the case of four-photon absorption. Since the effects of unpolarized light are readily simulated by simultaneous irradiation with two laser beams having the same frequency but orthogonal polarizations, the experiments should not present any particular difficulty.

Our results can also be applied to multiphoton ionization processes in certain cases. Such studies often enable new excited states to be discovered by observation of the enhancement of the ionization rate as the laser frequency is tuned through a single- or multiphoton resonance. Under these circumstances, the ionization is generally a two-step process, usually with the initial excitation to the resonant state as the rate-determining step. Provided most of the molecules in the resonant state are ultimately ionized, the ionization rate is directly proportional to the resonance excitation rate,^{19,20} and hence our results can be used to ascertain the symmetry properties of the resonant state. The condition for this application should normally be satisfied if only one photon is required to complete the ionization; in other cases a more detailed analysis of the rates and loss mechanisms is required.²¹

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tensor, however, the components which have an odd value for $(n - j)$ vanish; this is the reason for the absence of weight-1 contributions in the reduction of the second rank tensor $T_{\lambda\mu}^s$. Note that for double-beam absorption, the molecular transition tensor is not usually fully index-symmetric, and the reduction leads to a different set of selection rules.

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¹⁴Here and throughout the paper it is assumed that transitions take place from a totally symmetric ground state, so that the final state representation must be spanned by tensor components of the appropriate weight. These principles are readily extended to molecules with ground states of lower symmetry; here, the requirement is that the *product* of initial

and final state representations is spanned by tensor components of the appropriate weight.

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