

Theory of electro-optical effects in two-photon spectroscopy

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This paper develops the general theory of electro-optical effects in two-photon molecular spectroscopy. Two distinct mechanisms can play a role in these nonlinear interactions with an external static electric field. One relates specifically to polar fluids and is associated with the partial molecular alignment produced by the applied field. The resultant anisotropy produces a relaxation of symmetry restrictions on the allowed two-photon transitions. The other mechanism directly involves a nonlinear electro-optical channel and is associated with quite distinct selection rules. Both mechanisms induce changes in line intensities and can under suitable polarization conditions enable certain transitions to be "switched into" the spectra. Generalized rate equations are derived using standard quantum electrodynamical procedures. The results, which are applicable to any required laser beam configuration, are cast in terms of irreducible Cartesian tensors. This facilitates the elucidation of the selection rules appropriate for molecules of any given symmetry. A comprehensive tabulation of the transformation properties of the relevant molecular tensors under the operations of the common molecular point groups is also presented, paving the way for the subsequent application of the results specifically to two-photon absorption and Raman scattering processes.

I. INTRODUCTION

Electrically driven two-photon processes play a central role in the field of modern electro-optics. Kerr and Pockels cells for example, which are widely used for the fast switching of laser beams, both involve the effect of an electric field on an elastic light scattering process (forward Rayleigh scattering) which at the quantum level is a two-photon interaction.¹ From a spectroscopic point of view, such a process is fairly uninteresting as there is no net exchange of energy between the radiation and the medium, the incident and emergent photons having the same frequency. However, the influence of a static field on other kinds of two-photon interaction, such as two-photon absorption and inelastic Stokes (Raman) scattering in which there is an uptake of energy by the medium, has not as yet received much attention from spectroscopists. Studies of both these processes in a field-free environment provide key information on two-photon allowed transitions, and both have found numerous and diverse applications ranging from speciation to the determination of molecular structure. It is the purpose of this paper and the two which follow^{2,3} to demonstrate the large amount of additional information which can be obtained by studying the electric field dependence of these interactions.

A static electric field can influence two-photon interactions by two distinct mechanisms. The first is an *electrical polarization effect*, and relates specifically to fluids containing dipolar molecules. Here, application of the field can produce macroscopic anisotropy by inducing a degree of molecular alignment. This results in a relaxation of the symmetry restrictions on the allowed transitions, so changing the line intensities in the two-photon spectra. The other mechanism, which is of more universal application, is one in which two-photon molecular transitions proceed through an *electro-optical interaction* which is normally absent. Here the static field perturbs and partially mixes the molecular wave functions, thereby allowing some transitions to take place which are otherwise forbidden. This can give rise to a novel effect

wherein application of the field enables certain lines to be "switched into" the spectra. The distinct roles of these two mechanisms in conventional (single-photon) absorption spectroscopy have been discussed in two earlier papers.^{4,5}

In this introductory paper, the general theory underlying these new electro-optical effects is delineated. Generalized rate equations are derived using quantum electrodynamics and, with the introduction of irreducible Cartesian tensors, the results are cast in a form which facilitates a subsequent symmetry analysis. The spectroscopic selection rules for field-induced two-photon processes are described in detail, and illustrated by reference to common molecular point groups. The two following papers detail the application of the general theory to two-photon absorption² and vibrational Raman scattering,³ and include explicit intensity expressions for specific laser polarizations.

II. QUANTUM MECHANICS

The starting point for the calculation is the quantum electrodynamical Hamiltonian for the system comprising the molecules and the electromagnetic radiation, modified to incorporate the effect of the static field:

$$H = H'_{\text{mol}} + H_{\text{int}} + H_{\text{rad}}, \quad (2.1)$$

where H'_{mol} is the molecular Hamiltonian in the presence of the static electric field \mathbf{E} ; H_{int} represents the perturbation associated with the electromagnetic radiation, and H_{rad} is the Hamiltonian for the radiation itself. A two-photon interaction may now be formulated in terms of time-dependent perturbation theory with the dressed eigenstates of H'_{mol} and H_{rad} as a basis. The dressed molecular eigenstates are given by the following equation:

$$|r'\rangle = |r\rangle - \sum_{s \neq r} (\boldsymbol{\mu}^{sr} \cdot \mathbf{E}) E_{rs}^{-1} |s\rangle + \dots, \quad (2.2)$$

where $|r\rangle$ represents an eigenstate of the conventional Schrödinger operator H_{mol} for the molecule in the absence of the

applied electric field, E_{rs} denotes the difference $E_r^{(0)} - E_s^{(0)}$ between the zeroth-order energies associated with the states $|r\rangle$ and $|s\rangle$, and μ^{sr} is the transition electric dipole moment for the $|s\rangle \leftarrow |r\rangle$ transition. In writing Eq. (2.2) it is assumed that the static electric field \mathbf{E} is not only temporally but also spatially homogeneous across the laser beam. This assumption is reviewed in a later section. Within the electric dipole ($E1$) approximation the interaction Hamiltonian may be written as

$$H_{\text{int}} = -\epsilon_0^{-1} \boldsymbol{\mu} \cdot \mathbf{d}^\perp, \quad (2.3)$$

where $\boldsymbol{\mu}$ is the molecular electric dipole moment operator and \mathbf{d}^\perp the transverse electric displacement operator for the radiation field. The dipole approximation is sufficient for considering the majority of cases in which electronic excitations of molecules are restricted to regions much smaller than a typical wavelength for optical-frequency radiation. The transverse electric displacement operator can be written in terms of a summation over radiation modes as follows⁶:

$$\mathbf{d}^\perp(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} (\pi \hbar c k \epsilon_0 / 2V) \{ e^{(\lambda)}(\mathbf{k}) \mathbf{a}^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} - \bar{e}^{(\lambda)}(\mathbf{k}) \mathbf{a}^{\dagger(\lambda)}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} \}. \quad (2.4)$$

Here $e^{(\lambda)}(\mathbf{k})$ is the unit polarization vector for the mode characterized by propagation vector \mathbf{k} and polarization λ , with frequency given by $\omega = c|\mathbf{k}|$; $a^{(\lambda)}(\mathbf{k})$ and $a^{\dagger(\lambda)}(\mathbf{k})$ are the corresponding annihilation and creation operators which operate on the eigenstates of H_{rad} ; V is the quantization volume.

The rate of an electro-optical interaction can be calculated from the Fermi Golden Rule,

$$\Gamma = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho_f, \quad (2.5)$$

where ρ_f is a density of final states for the process, and the matrix element M_{fi} is given by the series

$$M_{fi} = \langle f_s | H_{\text{int}} | i_s \rangle + \sum_r \frac{\langle f_s | H_{\text{int}} | r_s \rangle \langle r_s | H_{\text{int}} | i_s \rangle}{\bar{E}_{ir}} + \sum_{r,s} \frac{\langle f_s | H_{\text{int}} | s_s \rangle \langle s_s | H_{\text{int}} | r_s \rangle \langle r_s | H_{\text{int}} | i_s \rangle}{\bar{E}_{is} \bar{E}_{ir}} + \dots, \quad (2.6)$$

where the subscript s within the Dirac brackets denotes the fact that the states and the energies relate to the *system* comprising both the molecule and the radiation. The energy denominators in the above expression are complex to ensure that even near to resonance the series for the matrix element converges. Thus, $\bar{E}_{ri} = E_{ri} - \frac{1}{2} i \hbar \gamma_r$, where the imaginary term is a damping factor associated with state r . This effectively models the time dependences of the virtual intermediate states when decay processes are taken into account. When frequencies of irradiation are close to a single resonance, the matrix element becomes almost entirely imaginary, but well away from resonance the imaginary component of the energy denominators can be ignored and the matrix element can be considered real.

For normal Raman scattering and two-photon absorption the first term in Eq. (2.6) vanishes and the leading contribution arises from the second-order term. The third-order

term then represents the leading correction due to involvement of the static electric field. For the special case of two-photon transitions which are allowed even in the *absence* of the field, the second-order term will naturally dominate even when the field is *present*, and under these conditions the higher-order terms will not be significant. However, certain two-photon transitions which would normally be forbidden in the $E1$ approximation may be induced by the static field through the third-order term. The result for the matrix element may, in general, conveniently be expressed as follows:

$$M_{fi} = K(S_{ij} e_{1i} e'_{2j} - T_{ijk} e_{1i} e'_{2j} E_k + \dots), \quad (2.7)$$

where the exact form of the constant K is given for each process in the subsequent papers,^{2,3} and the molecular response tensors S_{ij} and T_{ijk} are derived from the appropriate time-ordered diagrams. The former tensor results from the coupling of two electric-dipole interactions with the radiation ($E1 \times E1$), and the latter a coupling of three electric dipole interactions ($E1 \times E1 \times E1$), of which the third is associated with the static field. The polarization vectors e_1 and e'_2 relate to the two photons involved in the interaction, and the prime on the e_2 component signifies that the complex conjugate is to be taken in the case of Raman scattering, where it is associated with the emitted photon. In Eq. (2.7), and subsequently, we adopt the implied summation convention for repeated tensor indices. In passing we note that *undressed* molecular states are used as the basis for the calculation with the *full* interaction Hamiltonian,

$$H_{\text{int}} = -\epsilon_0^{-1} \boldsymbol{\mu} \cdot \mathbf{d}^\perp - \boldsymbol{\mu} \cdot \mathbf{E}, \quad (2.8)$$

then precisely the same result ensues.

Equations (2.5) and (2.7) lead to the following result for the rate,

$$\Gamma = L |S_{ij} e_{1i} e'_{2j} - T_{ijk} e_{1i} e'_{2j} E_k|^2, \quad (2.9)$$

where

$$L = 2\pi K^2 \rho_f / \hbar. \quad (2.10)$$

The major contribution to the rate for a transition allowed in the absence of the static field thus results from the square modulus of the first term in Eq. (2.9). In this case the higher order correction terms are not of much interest, other than in representing small corrections to the exact transition rate. For a transition which is *induced* by the field, the leading contribution to the rate comes from the square modulus of the second term in Eq. (2.9).

III. ROTATIONAL AVERAGING

The result represented by Eq. (2.9), as it stands, is valid for application to solid media in which the molecules have a fixed orientation relative to the radiation. For the case of partially ordered molecules absorbed on substrates, the appropriate result can be developed using the methods recently described by Mazely and Hetherington.⁷ However for application to fluid media, the distribution of molecular orientations has to be modeled by rotationally averaging the result. At this point, it becomes necessary to consider the anisotropy which the static electric field induces in the sample if the constituent molecules are polar.

In general, polar molecules will experience a torque of

magnitude $\mu^{00} \times \mathbf{E}$ in the static field, where μ^{00} is the permanent molecular electric dipole moment, and \mathbf{E} is the electric field. The resultant anisotropic distribution of orientations is associated with an interaction energy $\Delta E = -\mu^{00} \cdot \mathbf{E}$ and a Boltzmann-weighting factor $\exp(\mu^{00} \cdot \mathbf{E}/kT)$. The correctly averaged result for the rate is thus given by,

$$\Gamma = L \langle |S_{ij} e_{1i} e'_{2j} - T_{ijk} e_{1i} e'_{2j} E_k|^2 \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle / \langle \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle, \quad (3.1)$$

where the angular brackets denote the rotational average. The electric field strength \mathbf{E} which appears in the calculations above is strictly the field \mathbf{E}_{mol} experienced by each sample molecule, in other words the applied field \mathbf{E}_{app} modified by the electrostatic environment produced by surrounding molecules. For a continuous medium of dielectric constant κ , these are related by the well-known Lorentz local-field equation,

$$\mathbf{E}_{\text{mol}} = \frac{1}{3}(\kappa + 2)\mathbf{E}_{\text{app}}. \quad (3.2)$$

However, this equation is only correct at electric field strengths of less than $\approx 10^5 \text{ V m}^{-1}$ where the two fields \mathbf{E}_{mol} and \mathbf{E}_{app} are approximately proportional to one another. At large electric field strengths the correct field-dependent expression for the dielectric constant must be adopted and Eq. (3.2) becomes

$$\mathbf{E}_{\text{mol}} = \mathbf{E}_{\text{app}} + \frac{1}{3}\mu^{00}\epsilon_0^{-1}NL(\gamma), \quad (3.3)$$

where N is the number density, and $L(\gamma)$ is the Langevin function which is defined as

$$L(\gamma) = \coth(\gamma) - 1/\gamma, \quad (3.4)$$

and where

$$\gamma = \mu^{00}E_{\text{mol}}/kT. \quad (3.5)$$

For nitrobenzene at 300 K in an external field of 10^8 V m^{-1} , the local fields are in excess of 10^9 V m^{-1} , and the Boltzmann-weighting exponent, $\mu \cdot \mathbf{E}_{\text{mol}}/kT$, takes the value of 4.8.

Before proceeding further it is worth assessing the validity of the electric-dipole approximation for the interaction energy. First, this rests on the assumption that spatial inhomogeneities in the applied field are small enough that higher order electric multipolar interactions will be insignificant compared to the dipolar coupling. This should normally be the case where the electric field results from applying a potential difference across a pair of parallel electrode plates. In the special case of an electrolyte, however, in which the maximum degree of molecular orientation occurs close to the surface of an electrode, the local field may be highly inhomogeneous, and quadrupolar effects may need to be considered. Secondly, it is assumed that the interaction energy is linear in the applied field. In general the nonlinear correction terms will be small; the leading correction involves the molecular polarizability α and is given by

$$\Delta E = -\alpha_{ij}E_iE_j. \quad (3.6)$$

It can readily be shown that, under nonresonant conditions, this contribution to the interaction energy must be at least a factor of $\gamma/100$ smaller than the dipolar term; hence it is

normally sufficient to adopt the dipole approximation for the Boltzmann weighting. The other factor which is worth considering is the possibility of laser-induced molecular orientation due to a coupling with the electric field of the light itself. Here, molecular orientation will not be possible within the short duration of an optical cycle, and the time average is clearly zero. Thus, only the quadratic term can produce any nonzero time-averaged response, and once again it is readily shown that for the typical laser intensities used in two-photon absorption, the size of this effect will be entirely negligible.

Returning to the rate equation, we can now consider in detail the two cases mentioned earlier.

A. Two-photon interactions allowed in the absence of the static electric field

For two-photon transitions which are allowed in the absence of the static field, the leading S_{ij} term in Eq. (3.1) is nonzero, and greatly outweighs the contribution from the T_{ijk} term. Hence, to a good approximation, we have

$$\Gamma = L \langle |S_{ij} e_{1i} e'_{2j}|^2 \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle / \langle \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle. \quad (3.7)$$

The procedure for evaluating this type of weighted rotational average has been described in earlier work.⁸ The calculation proceeds as follows:

$$\begin{aligned} \Gamma &= L \langle S_{ij} e_{1i} e'_{2j} \bar{S}_{kl} \bar{e}_{1k} \bar{e}'_{2l} \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle / \langle \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle \\ &= LS_{\lambda\mu} \bar{S}_{\nu\sigma} e_{1i} e'_{2j} \bar{e}_{1k} \bar{e}'_{2l} \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{l\sigma} \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle / \langle \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle, \end{aligned} \quad (3.8)$$

where the polarization vectors are now referred to a laboratory-fixed Cartesian frame denoted by Latin indices, and the molecular response tensors are referred to a molecule-fixed frame, denoted by Greek indices. The direction cosines such as $l_{i\lambda}$ refer to the (i, λ) elements of the Euler angle matrix for the transformation between the two sets of axes. In the shorthand terminology developed previously, we thus have

$$\Gamma = LS_{\lambda\mu} \bar{S}_{\nu\sigma} e_{1i} e'_{2j} \bar{e}_{1k} \bar{e}'_{2l} I'_{ijkl;\lambda\mu\nu\sigma}^{(4)\varphi} (-i\gamma, \hat{\mathbf{E}}, \hat{\boldsymbol{\mu}}^{00}), \quad (3.9)$$

where

$$I'_{ijkl;\lambda\mu\nu\sigma}^{(4)\varphi} (-i\gamma, \hat{\mathbf{E}}, \hat{\boldsymbol{\mu}}^{00}) = I_{ijkl;\lambda\mu\nu\sigma}^{(4)\varphi} (-i\gamma, \hat{\mathbf{E}}, \hat{\boldsymbol{\mu}}^{00}) / I^{(0)\varphi}. \quad (3.10)$$

The results for $I^{(n)\varphi}$ involve expansions in terms of spherical Bessel functions $j_{0-n}(-i\gamma)$, and explicit expressions are given in Ref. 8. It is the fact that the calculation involves *weighted* averages which results in the appearance of features differing from the case where the static field is absent and the medium is isotropic. The leading field-independent contribution in the expansion of $I'^{(4)\varphi}$ is the isotropic average $I^{(4)}$. Thus it is the higher-order correction terms involving $J'_n = j_n/j_0$ ($1 \leq n \leq 4$), which produce the novel features. The functions involved in the weighting of the higher order terms are given explicitly in Table I. The interesting features that arise as a result of these further correction terms are detailed in the following papers.

TABLE I. The explicit form of the reduced spherical Bessel functions, $j'_n = j_n/j_0$.

Full expression for $j_n(-i\gamma)$	Low-field limit, $\gamma \ll 1$	High-field limit, $\gamma \gg 1$
$j'_0 = 1$	$j'_0 = 1$	$j'_0 = 1$
$j'_1 = i(1/\gamma - \coth \gamma)$	$j'_1 = -i(\gamma/3 - \gamma^3/45 + 2\gamma^5/945\dots)$	$j'_1 = i(1/\gamma - 1)$
$j'_2 = -1 - 3/\gamma^2 + (3/\gamma)\coth \gamma$	$j'_2 = -\gamma^2/15 + 2\gamma^4/315\dots$	$j'_2 = -1 + 3/\gamma - 3/\gamma^2$
$j'_3 = i[(1 + 15/\gamma^2)\coth \gamma - 6/\gamma - 15/\gamma^3]$	$j'_3 = i(\gamma^3/105 - \gamma^5/945\dots)$	$j'_3 = i(1 - 6/\gamma + 15/\gamma^2 - 15/\gamma^3)$
$j'_4 = 1 + 45/\gamma^2 + 105/\gamma^4 - (10/\gamma + 105/\gamma^3)\coth \gamma$	$j'_4 = \gamma^4/945\dots$	$j'_4 = 1 - 10/\gamma + 45/\gamma^2 - 105/\gamma^3 + 105/\gamma^4$

B. Two-photon interactions forbidden in the absence of the static electric field

In the case where the static field induces transitions which are forbidden in its absence, the leading S_{ij} term in Eq. (3.1) is zero, and the rate is thus given by

$$\Gamma = L \langle |T_{ijk} e_{1i} e'_{2j} E_k|^2 \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle / \langle \exp(\mu^{00} \cdot \mathbf{E}/kT) \rangle. \tag{3.11}$$

Following the same procedure as before we obtain

$$\Gamma = LT_{\lambda\mu\nu} \bar{T}_{\sigma\tau\rho} e_{1i} e'_{2j} E_k \bar{e}_{1l} \bar{e}_{2m} E_n \times I'_{ijklmn;\lambda\mu\nu\sigma\tau\rho}(-i\gamma, \hat{\mathbf{E}}, \hat{\boldsymbol{\mu}}^{00}). \tag{3.12}$$

Once again the result involves weighted averages. However, in this case, since there is no field-independent rate, the most significant term in the expansion of $I^{(6\varphi)}/I^{(0\varphi)}$ is the leading term, equivalent to the isotropic result $I^{(6)}$. The formula for this is as follows²:

$$I'_{ijklmn;\lambda\mu\nu\sigma\tau\rho} = \sum_{p,q}^{15} m_{pq}^{(6)} f_{ijklmn}^{(6;p)} g_{\lambda\mu\nu\sigma\tau\rho}^{(6;q)}, \tag{3.13}$$

where m_{pq} are numerical coefficients and $f^{(6;p)}$ and $g^{(6;q)}$ denote sixth-rank isotropic tensors, which are triple products of Kronecker deltas, such as $\delta_{ij}\delta_{kl}\delta_{mn}$ and $\delta_{\lambda\mu}\delta_{\nu\sigma}\delta_{\tau\rho}$. From Eqs. (3.12) and (3.13) we obtain a rate equation given by

$$\Gamma = L \sum_{p,q}^{15} a_p m_{pq}^{(6)} t_q. \tag{3.14}$$

where a_p form a set of 15 parameters determined by polarization conditions, and given by

$$a_p = f_{ijklmn}^{(6;p)} e_i e_j E_k \bar{e}_l \bar{e}_m \bar{E}_n. \tag{3.15}$$

The t_q form a corresponding set of linearly independent molecular invariants defined by

$$t_q = g_{\lambda\mu\nu\sigma\tau\rho}^{(6;q)} T_{\lambda\mu\nu} \bar{T}_{\sigma\tau\rho}, \tag{3.16}$$

as listed in Table II.

IV. REPRESENTATION OF RESULTS IN TERMS OF IRREDUCIBLE TENSORS

In order to clarify the selection rules it is preferable to express results in terms of irreducible tensors. The irreducible parts of the S_{ij} and T_{ijk} tensors are as follows. For $S_{\lambda\mu}$ we have the well-known results

$$S_{\lambda\mu} = S_{\lambda\mu}^{(0+)} + S_{\lambda\mu}^{(1+)} + S_{\lambda\mu}^{(2+)}, \tag{4.1}$$

$$S_{\lambda\mu}^{(0+)} = \frac{1}{3} \delta_{\lambda\mu} S_{\nu\nu}, \tag{4.2}$$

$$S_{\lambda\mu}^{(1+)} = \frac{1}{2} \epsilon_{\lambda\mu\nu} (\epsilon_{\sigma\tau\nu} S_{\sigma\tau}) \equiv \frac{1}{2} (S_{\lambda\mu} - S_{\mu\lambda}), \tag{4.3}$$

$$S_{\lambda\mu}^{(2+)} = \frac{1}{2} (S_{\lambda\mu} + S_{\mu\lambda}) - \frac{1}{3} \delta_{\lambda\mu} S_{\nu\nu}, \tag{4.4}$$

where $\delta_{\lambda\mu}$ is the Kronecker delta and the plus sign in the superscript signifies even parity. Clearly the weight-1 term vanishes if $S_{\lambda\mu}$ is index symmetric, as it is for nonresonant Raman scattering, and for single-beam two-photon absorption. The rate equation for the optically allowed channel, Eq. (3.9), is readily recast in terms of these irreducible tensors; explicit results are given in the following papers.^{2,3}

The decomposition into irreducible parts of the electro-optical tensor $T_{\lambda\mu\nu}$ is less well known and takes the form¹⁰

$$T_{\lambda\mu\nu} = T_{\lambda\mu\nu}^{(0-)} + \sum_{\rho=\alpha,\beta,\gamma} T_{\lambda\mu\nu}^{(1-;\rho)} + \sum_{q=\alpha,\beta} T_{\lambda\mu\nu}^{(2-;q)} + T_{\lambda\mu\nu}^{(3-)}, \tag{4.5}$$

$$T_{\lambda\mu\nu}^{(0-)} = \frac{1}{6} \epsilon_{\lambda\mu\nu} \epsilon_{\rho\sigma\tau} T_{\rho\sigma\tau}, \tag{4.6}$$

$$T_{\lambda\mu\nu}^{(1\alpha-)} = \frac{1}{10} (4\delta_{\lambda\mu} T_{\rho\rho\nu} - \delta_{\lambda\nu} T_{\rho\rho\mu} - \delta_{\mu\nu} T_{\rho\rho\lambda}), \tag{4.7}$$

$$T_{\lambda\mu\nu}^{(1\beta-)} = \frac{1}{10} (-\delta_{\lambda\mu} T_{\rho\rho\nu} + 4\delta_{\lambda\nu} T_{\rho\rho\mu} - \delta_{\mu\nu} T_{\rho\rho\lambda}), \tag{4.8}$$

$$T_{\lambda\mu\nu}^{(1\gamma-)} = \frac{1}{10} (-\delta_{\lambda\mu} T_{\nu\rho\rho} - \delta_{\lambda\nu} T_{\mu\rho\rho} + 4\delta_{\mu\nu} T_{\lambda\rho\rho}), \tag{4.9}$$

$$T_{\lambda\mu\nu}^{(2\alpha-)} = \frac{1}{6} \epsilon_{\lambda\mu\tau} (2\epsilon_{\rho\sigma\tau} T_{\rho\sigma\nu} + 2\epsilon_{\rho\sigma\nu} T_{\rho\sigma\tau} + \epsilon_{\rho\sigma\tau} T_{\nu\rho\sigma} + \epsilon_{\rho\sigma\nu} T_{\tau\rho\sigma} - 2\delta_{\nu\tau} \epsilon_{\rho\sigma\tau} T_{\rho\sigma}), \tag{4.10}$$

TABLE II. Linearly independent basis sets of the isotropic molecular parameters; t_q are inner products of the reducible tensor $T_{\lambda\mu\nu}$ with itself, and t'_q are the nonzero inner products of the irreducible tensor.

q	t_q	t'_q
1	$T_{\lambda\lambda\mu} \bar{T}_{\mu\nu\nu}$	$T_{\lambda\mu\nu}^{(0-)} \bar{T}_{\lambda\mu\nu}^{(0-)}$
2	$T_{\lambda\lambda\mu} \bar{T}_{\nu\mu\nu}$	$T_{\lambda\mu\nu}^{(1-\alpha)} \bar{T}_{\lambda\mu\nu}^{(1-\alpha)}$
3	$T_{\lambda\lambda\mu} \bar{T}_{\nu\mu}$	$\bar{T}_{\lambda\mu\nu}^{(1-\alpha)} \bar{T}_{\lambda\mu\nu}^{(1-\beta)}$
4	$T_{\lambda\mu\lambda} \bar{T}_{\mu\nu\nu}$	$T_{\lambda\mu\nu}^{(1-\alpha)} \bar{T}_{\lambda\mu\nu}^{(1-\gamma)}$
5	$T_{\lambda\mu\lambda} \bar{T}_{\nu\mu\nu}$	$T_{\lambda\mu\nu}^{(1-\beta)} \bar{T}_{\lambda\mu\nu}^{(1-\alpha)}$
6	$T_{\lambda\mu\lambda} \bar{T}_{\nu\mu}$	$T_{\lambda\mu\nu}^{(1-\beta)} \bar{T}_{\lambda\mu\nu}^{(1-\beta)}$
7	$T_{\lambda\mu\lambda} \bar{T}_{\lambda\nu\nu}$	$T_{\lambda\mu\nu}^{(1-\beta)} \bar{T}_{\lambda\mu\nu}^{(1-\gamma)}$
8	$T_{\lambda\mu\nu} \bar{T}_{\lambda\mu\nu}$	$T_{\lambda\mu\nu}^{(1-\gamma)} \bar{T}_{\lambda\mu\nu}^{(1-\alpha)}$
9	$T_{\lambda\mu\nu} \bar{T}_{\lambda\nu\mu}$	$T_{\lambda\mu\nu}^{(1-\gamma)} \bar{T}_{\lambda\mu\nu}^{(1-\beta)}$
10	$T_{\lambda\mu\nu} \bar{T}_{\nu\lambda\nu}$	$T_{\lambda\mu\nu}^{(1-\gamma)} \bar{T}_{\lambda\mu\nu}^{(1-\gamma)}$
11	$T_{\lambda\mu\nu} \bar{T}_{\nu\lambda\nu}$	$T_{\lambda\mu\nu}^{(2-\alpha)} \bar{T}_{\lambda\mu\nu}^{(2-\alpha)}$
12	$T_{\lambda\mu\nu} \bar{T}_{\nu\lambda\mu}$	$T_{\lambda\mu\nu}^{(2-\alpha)} \bar{T}_{\lambda\mu\nu}^{(2-\beta)}$
13	$T_{\lambda\mu\mu} \bar{T}_{\nu\mu\lambda}$	$T_{\lambda\mu\nu}^{(2-\beta)} \bar{T}_{\lambda\mu\nu}^{(2-\alpha)}$
14	$T_{\lambda\mu\nu} \bar{T}_{\mu\nu\lambda}$	$T_{\lambda\mu\nu}^{(2-\beta)} \bar{T}_{\lambda\mu\nu}^{(2-\beta)}$
15	$T_{\lambda\mu\nu} \bar{T}_{\nu\mu\lambda}$	$T_{\lambda\mu\nu}^{(3-)} \bar{T}_{\lambda\mu\nu}^{(3-)}$

$$T_{\lambda\mu\nu}^{(2\beta-)} = \frac{1}{6}\epsilon_{\mu\nu\tau}(2\epsilon_{\rho\sigma\tau}T_{\lambda\rho\sigma} + 2\epsilon_{\rho\sigma\lambda}T_{\tau\rho\sigma} + \epsilon_{\rho\sigma\tau}T_{\rho\sigma\lambda} + \epsilon_{\rho\sigma\lambda}T_{\rho\sigma\tau} - 2\delta_{\lambda\tau}\epsilon_{\rho\sigma\tau}T_{\rho\sigma\lambda}), \quad (4.11)$$

$$T_{\lambda\mu\nu}^{(3-)} = \frac{1}{6}(T_{\lambda\mu\nu} + T_{\lambda\nu\mu} + T_{\mu\lambda\nu} + T_{\mu\nu\lambda} + T_{\nu\lambda\mu} + T_{\nu\mu\lambda}) - \frac{1}{15}[\delta_{\lambda\mu}(T_{\rho\rho\nu} + T_{\rho\nu\rho} + T_{\nu\rho\rho}) + \delta_{\lambda\nu}(T_{\rho\rho\mu} + T_{\rho\mu\rho} + T_{\mu\rho\rho}) + \delta_{\mu\nu}(T_{\rho\rho\lambda} + T_{\rho\lambda\rho} + T_{\lambda\rho\rho})], \quad (4.12)$$

where $\epsilon_{\lambda\mu\nu}$ is the Levi-Civita tensor, and where each component has odd parity. A number of new features arise in connection with this third rank tensor which we detail below.

The molecular parameters t_q in Eq. (3.14), which are all tensor products, e.g., $T_{\lambda\lambda\mu}\bar{T}_{\mu\nu\nu}$ (see Table II), can be reexpressed in terms of irreducible tensor products t_r^i by using the relation given in Eq. (4.5). Because of index symmetry properties, the inner product of tensors with unequal weights is zero. Hence there are 15 nonvanishing products, which are also listed in Table II. The reducible parameters can be expressed in terms of the irreducible parameters by means of the relation

$$t_q = \sum_{r=1}^{15} (j^{-1})_{qr} t_r^i, \quad (4.13)$$

where j represents a matrix whose numerical components are given in Ref. 10. By introducing the matrix

$$w_{pr} = m_{pq}^{(6)} (j^{-1})_{qr} \quad (4.14)$$

the rate can be reexpressed as

$$\Gamma = L \sum_{p,r} a_p w_{pr} t_r^i. \quad (4.15)$$

However, because one of the field interactions is with the static field for which the direction unit vector has to be real (in contrast to the complex polarization vectors which arise for circularly polarized radiation, for example), the 15 polarization parameters a_p are not all linearly independent. This condition reduces the number of linearly independent polarization parameters to nine, and thus we can write

$$\Gamma = L \sum_p \sum_r^{15} a_p w_{pr} t_r^i. \quad (4.16)$$

The explicit result is given by Eq. (4.17);

$$\Gamma = \frac{L|E|^2}{840} \begin{bmatrix} (\mathbf{e}_1 \cdot \mathbf{e}'_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{E})(\bar{\mathbf{e}}'_2 \cdot \mathbf{E}) \\ |\mathbf{e}_1 \cdot \mathbf{e}'_2|^2 \\ (\bar{\mathbf{e}}_1 \cdot \mathbf{e}'_2)(\mathbf{e}_1 \cdot \mathbf{E})(\bar{\mathbf{e}}'_2 \cdot \mathbf{E}) \\ |\mathbf{e}_1 \cdot \mathbf{E}|^2 \\ (\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}'_2)(\mathbf{e}_1 \cdot \mathbf{E})(\mathbf{e}'_2 \cdot \mathbf{E}) \\ |\mathbf{e}'_2 \cdot \mathbf{E}|^2 \\ 1 \\ (\mathbf{e}_1 \cdot \bar{\mathbf{e}}'_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{E})(\mathbf{e}'_2 \cdot \mathbf{E}) \\ |\mathbf{e}_1 \cdot \bar{\mathbf{e}}'_2|^2 \end{bmatrix}^T \begin{bmatrix} 0 & -56 & -336 & -336 & -56 & -21 & 84 \\ 0 & 112 & 112 & 112 & 112 & 7 & -28 \\ 140 & 7 & -28 & 112 & 112 & -28 & -448 \\ -140 & 7 & 112 & -28 & 112 & 112 & 112 \\ 0 & -56 & -56 & -56 & -336 & -21 & 84 \\ -140 & 7 & -28 & 112 & -28 & 7 & 112 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 140 & 7 & 112 & -28 & -28 & -28 & -28 \\ -140 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} -56 & 84 & -21 & 0 & 0 & 0 & 42 & -16 \\ 112 & -28 & 7 & 0 & 0 & 0 & -42 & -8 \\ -28 & -28 & -28 & 14 & 56 & -28 & -28 & 12 \\ -28 & 112 & 7 & -14 & 28 & 28 & -14 & 12 \\ -336 & 84 & -21 & 0 & 0 & 0 & 42 & -16 \\ 112 & 112 & 112 & -14 & -56 & -56 & -56 & 12 \\ 0 & 0 & 0 & 56 & 56 & 56 & 56 & 20 \\ 112 & -448 & -28 & 14 & -28 & 56 & -28 & 12 \\ 0 & 0 & 0 & -56 & -56 & -56 & 28 & 20 \end{bmatrix} \begin{bmatrix} T_{\lambda\mu\nu}^{(0-)} \bar{T}_{\lambda\mu\nu}^{(0-)} \\ T_{\lambda\mu\nu}^{(1\alpha-)} \bar{T}_{\lambda\mu\nu}^{(1\alpha-)} \\ T_{\lambda\mu\nu}^{(1\alpha-)} \bar{T}_{\lambda\mu\nu}^{(1\beta-)} \\ T_{\lambda\mu\nu}^{(1\alpha-)} \bar{T}_{\lambda\mu\nu}^{(1\gamma-)} \\ T_{\lambda\mu\nu}^{(1\beta-)} \bar{T}_{\lambda\mu\nu}^{(1\alpha-)} \\ T_{\lambda\mu\nu}^{(1\beta-)} \bar{T}_{\lambda\mu\nu}^{(1\beta-)} \\ T_{\lambda\mu\nu}^{(1\beta-)} \bar{T}_{\lambda\mu\nu}^{(1\gamma-)} \\ T_{\lambda\mu\nu}^{(1\gamma-)} \bar{T}_{\lambda\mu\nu}^{(1\alpha-)} \\ T_{\lambda\mu\nu}^{(1\gamma-)} \bar{T}_{\lambda\mu\nu}^{(1\beta-)} \\ T_{\lambda\mu\nu}^{(1\gamma-)} \bar{T}_{\lambda\mu\nu}^{(1\gamma-)} \\ T_{\lambda\mu\nu}^{(2\alpha-)} \bar{T}_{\lambda\mu\nu}^{(2\alpha-)} \\ T_{\lambda\mu\nu}^{(2\alpha-)} \bar{T}_{\lambda\mu\nu}^{(2\beta-)} \\ T_{\lambda\mu\nu}^{(2\beta-)} \bar{T}_{\lambda\mu\nu}^{(2\alpha-)} \\ T_{\lambda\mu\nu}^{(2\beta-)} \bar{T}_{\lambda\mu\nu}^{(2\beta-)} \\ T_{\lambda\mu\nu}^{(3-)} \bar{T}_{\lambda\mu\nu}^{(3-)} \end{bmatrix} \quad (4.17)$$

Equation (4.17) applies in the general case where the molecular parameters t_r^i are formed from a tensor $T_{\lambda\mu\nu}$ which does not have index symmetry. In the application to field-induced Raman scattering however, detailed analysis of the tensor³ reveals index symmetry in the first two indices. The electro-optical two-photon absorption tensor can also possess index symmetry if the two excitation beams are of the same frequency.² When the molecular tensor has pair index symmetry the weight-0 component vanishes, and only two of the three weight-1 tensors and one of the two weight-2 tensors are linearly independent (see the Appendix). The appropriate transition rate can still be derived from Eq. (4.17), since the molecular parameters for the two cases are related by a nonunique mapping x ,

$$t_{(3,\text{nis})r}^i = \sum_s^6 x_{rs} t_{(3,\text{is})s}^i \quad (4.18)$$

Here the subscript 3 indicates the rank of the tensor, and the subscripts nis and is indicate no index symmetry and index symmetry, respectively. There are 15 linearly independent $t_{(3,\text{nis})r}^i$ terms and 6 linearly independent $t_{(3,\text{is})s}^i$ terms, and consequently the mapping x is described by a 15×6 matrix. The explicit form of x and its derivation are given in the Appendix. Inserting Eq. (4.18) into Eq. (4.16) then gives the rate equation for the case where T_{ijk} has pair index symmetry

$$\Gamma = L \sum_p^9 \sum_r^{15} \sum_s^6 a_p w_{pr} x_{rs} t_{(3,\text{is})s}^i \quad (4.19)$$

V. DERIVATION OF THE SELECTION RULES

The $(E1 \times E1)$ -optically allowed channel, and the $(E1 \times E1 \times E1)$ -electro-optically allowed channel are each associated with a distinct set of selection rules. In each case, as the detailed analysis of the molecular response tensors reveals, the general principle is that the product of the irreducible representations of the initial and final states of the molecule must be spanned by one or more components of the appropriate tensor. In the common case of a totally symmetric ground state, this reduces to a requirement that one of the irreducible parts of the tensor transforms under the same representation as the excited state. The optically allowed channel involves the concerted action of two photons at one molecular center, and the selection rules are thus governed by how the direct product of the two dipole operators, (one for each photon), transforms. This can be expressed as

$$S_{\lambda\mu} \Leftrightarrow \mu_\lambda \otimes \mu_\mu \Leftrightarrow D^{(1-)} \otimes D^{(1-)} \\ \Leftrightarrow D^{(0+)} \oplus D^{(1+)} \oplus D^{(2+)}, \quad (5.1)$$

where the symbol \Leftrightarrow means transforms as. Consequently, the irreducible components of the tensor $S_{\lambda\mu}$ may transform as either the scalar, $x^2 + y^2 + z^2$, the rotations, $R_{x,y,z}$, or as the components of an index-symmetric traceless weight-2 tensor in the case of $S_{\lambda\mu}^{(2+)}$. Here the sole effect of the electric field is to bring about some degree of order to the molecular orientations, producing an anisotropic distribution within the sample. Although this causes an associated change of line intensities within the spectra, conventional two-photon selection rules still apply and will therefore not be discussed further here.

For the electro-optical channel a completely different set of selection rules is applicable. The interaction of the electric field with the absorbing species may be viewed as a radiation-molecule interaction in the limit where the radiation is of zero frequency. Hence, electro-optically allowed electric field induced two-photon processes proceed via *three* photon-molecule events. Consequently the selection rules are governed by how the direct product of the *three* dipole operators transforms,

$$T_{\lambda\mu\nu} \Leftrightarrow \mu_\lambda \otimes \mu_\mu \otimes \mu_\nu \Leftrightarrow D^{(1-)} \otimes D^{(1-)} \otimes D^{(1-)} \\ \Leftrightarrow D^{(0-)} \oplus 3D^{(1-)} \oplus 2D^{(2-)} \oplus D^{(3-)} \quad (5.2)$$

The seven resultant irreducible representations are all of odd parity. This highlights one of the very important distinctions between the electro-optical and the optical channels in centrosymmetric molecules. The electro-optical channel leads to Laporte-type selection rules, ($g \leftrightarrow u$), whereas the optically allowed channel results in parity-preserving selection rules of the type $g \leftrightarrow g$ and $u \leftrightarrow u$. Thus, *field-induced* two-photon absorption transitions have the characteristics of three-photon absorption,¹⁰ and *field-induced* Raman transitions obey selection rules characteristic of hyper-Raman scattering.^{11,12}

The symmetry properties of $T_{\lambda\mu\nu}$ are governed by Eq. (5.2), and the irreducible components of Eqs. (4.6)–(4.12) have the following transformation properties under the operations of the full rotation group:

- (i) $T_{\lambda\mu\nu}^{(3-)}$ transforms as a traceless, fully index-symmetric third rank polar tensor, which is odd with respect to spatial inversion.
- (ii) $T_{\lambda\mu\nu}^{(2-)}$ transforms as a traceless rank two tensor, odd with respect to spatial inversion.
- (iii) $T_{\lambda\mu\nu}^{(1-)}$ transforms as a polar vector.
- (iv) $T_{\lambda\mu\nu}^{(0-)}$ transforms as a pseudoscalar, again odd with respect to spatial inversion.

There are 11 distinct classes of electro-optical transition determined by the particular combination of irreducible weights allowed, as shown in Table III. The classification scheme adopted here is a development of that used in earlier work.¹⁰ Table IV presents an analysis of the classes of transition allowed in a double-beam electric-field-induced two-photon absorption, (EFITPA), and electric-field-induced

TABLE III. Allowed classes for EFITPA and EFIRS: Each weight is associated with components of the third rank polar tensor $T_{\lambda\mu\nu}$ and thus has odd parity.

Weights	Single beam EFITPA,EFIRS	Double beam EFITPA,EFIRRS
3,2,1,0		IA'
3,2,1	IA	IA
3,1	IB	IB
3,2,0		IIA'
3,2	IIA	IIA
3,0		IIB'
3	IIB	IIB
1	III	III
2,0		IV'
2	IV	IV
0		V

TABLE IV. Representations spanned by the irreducible components of the tensor $T_{\lambda\mu\nu}$ for selected molecular point groups.

Point group	Weight 0	Weight 1	Weight 2	Weight 3	Class	
C_{6h}	A_u	A_u	A_u	A_u	IA'	
				$2B_u$	IIB	
	E_{1u}	E_{1u}	E_{1u}	E_{1u}	IA	
				E_{2u}	IIA	
				A_{2u}	A_{2u}	IV'
					A_{2u}	IB
D_{6h}	A_{1u}	A_{2u}	A_{1u}	A_{2u}	IIB	
				B_{1u}	IIB	
	E_{1u}	E_{1u}	E_{2u}	E_{1u}	IA	
				E_{2u}	IIA	
				A_u	A_u	IIA'
					A_u	IV
T_h	A_u	F_u	E_u	IA		
			$2F_u$	IA		
			V	V	V	
				V	IIB	
O_h	A_{1u}	F_{1u}	E_u	A_{2u}	IIB	
				E_u	IV	
	F_{1u}	F_{2u}	F_{2u}	F_{1u}	IB	
				F_{2u}	IIA	
				V	V	V
					V	III
I_h	A_u	F_{1u}	F_{2u}	G_u	IIB	
				G_u	IIB	
	$D_{\infty h}$	A_{1u}	A_{2u}	A_{2u}	A_{2u}	IV
					A_{2u}	III
					E_{1u}	IA
					E_{2u}	IIA
			E_{3u}	IIB		

resonance-Raman scattering, (EFIRRS). The same classes are allowed for single-beam EFITPA and off-resonance electric-field-induced Raman scattering, (EFIRS), with the exception of class V (weight-0 alone) which is forbidden by virtue of the index symmetry of the molecular tensor. However, as Table IV shows, only molecules of octahedral, icosahedral, (or T_d) symmetry possess states of this type.

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APPENDIX: ANALYSIS OF THE INDEX-SYMMETRIC FORMS OF THE IRREDUCIBLE WEIGHTS OF THE MOLECULAR RESPONSE TENSOR $T_{\lambda\mu\nu}$

In order to derive the mapping x_{pq} it is necessary to consider the index-symmetric form of each of the irreducible weights of the molecular response tensor in turn. From Eq. (4.6) the index-symmetric form of the weight-0 component is given by

$$T_{(\lambda\mu)\nu}^{(0-)} = (1/6)\epsilon_{\lambda\mu\nu}\epsilon_{\rho\sigma\tau}T_{(\rho\sigma)\tau}. \quad (A1)$$

However, the molecular tensor is symmetric in its first two indices, as indicated by the bracketed subscripts and therefore interchanging the first two indices must give the same result, i.e.,

$$T_{(\lambda\mu)\nu}^{(0-)} = T_{(\mu\lambda)\nu}^{(0-)} = (1/6)\epsilon_{\mu\lambda\nu}\epsilon_{\rho\sigma\tau}T_{(\rho\sigma)\tau} \\ = - (1/6)\epsilon_{\lambda\mu\nu}\epsilon_{\rho\sigma\tau}T_{(\rho\sigma)\tau} = -T_{(\lambda\mu)\nu}^{(0-)}, \quad (A2)$$

where the third equality follows from the fact that $\epsilon_{\lambda\mu\nu} = -\epsilon_{\mu\lambda\nu}$. Clearly Eq. (A2) can only be valid if the weight-0 tensor is identically zero.

Imposing index symmetry on β and γ weight-1 components of Eqs. (4.8) and (4.9) leads to

$$T_{(\lambda\mu)\nu}^{(1\beta-)} = (1/10)(-\delta_{\lambda\mu}T_{(\rho\nu)\rho} \\ + 4\delta_{\lambda\nu}T_{(\rho\mu)\rho} - \delta_{\mu\nu}T_{(\rho\lambda)\rho}), \quad (A3)$$

$$T_{(\lambda\mu)\nu}^{(1\gamma-)} = (1/10)(-\delta_{\lambda\mu}T_{(\rho\nu)\rho} \\ - \delta_{\lambda\nu}T_{(\rho\mu)\rho} + 4\delta_{\mu\nu}T_{(\rho\lambda)\rho}). \quad (A4)$$

Explicit calculation of the triply-contracted tensor products $T_{(\lambda\mu)\nu}^{(1\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(1\beta-)}$, $T_{(\lambda\mu)\nu}^{(1\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)}$, $T_{(\lambda\mu)\nu}^{(1\gamma-)}\bar{T}_{(\lambda\mu)\nu}^{(1\beta-)}$, and $T_{(\lambda\mu)\nu}^{(1\gamma-)}\bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)}$ reveals the following linear dependence;

$$T_{(\lambda\mu)\nu}^{(1\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(1\beta-)} = -4T_{(\lambda\mu)\nu}^{(1\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)} \\ = -4T_{(\lambda\mu)\nu}^{(1\gamma-)}\bar{T}_{(\lambda\mu)\nu}^{(1\beta-)} = T_{(\lambda\mu)\nu}^{(1\gamma-)}\bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)}. \quad (A5)$$

It is therefore preferable to introduce a new weight-1 component of the form

$$T_{(\lambda\mu)\nu}^{(1\beta-,1\gamma-)} = T_{(\lambda\mu)\nu}^{(1\beta-)} + T_{(\lambda\mu)\nu}^{(1\gamma-)}. \quad (A6)$$

The fact that the two weight-2 tensors of Eqs. (4.10) and (4.11) are linearly dependent is not so obvious. Consider

$$T_{(\lambda\mu)\nu}^{(2\alpha-)} = (1/6)\epsilon_{\lambda\mu\tau}(2\epsilon_{\rho\sigma\tau}T_{(\rho\sigma)\nu} + 2\epsilon_{\rho\sigma\nu}T_{(\rho\sigma)\tau} \\ + \epsilon_{\rho\sigma\tau}T_{(\nu\rho)\sigma} + \epsilon_{\rho\sigma\nu}T_{(\tau\rho)\sigma} - 2\delta_{\nu\tau}\epsilon_{\pi\rho\sigma}T_{(\pi\rho)\sigma}). \quad (A7)$$

The first, second, and fifth terms in Eq. (A7) vanish because of the antisymmetric properties of the Levi-Civita tensor ϵ and we thus have

$$T_{(\lambda\mu)\nu}^{(2\alpha-)} = (1/6)\epsilon_{\lambda\mu\tau}(\epsilon_{\rho\sigma\tau}T_{(\nu\rho)\sigma} + \epsilon_{\rho\sigma\nu}T_{(\tau\rho)\sigma}). \quad (A8)$$

Similarly from Eq. (4.11) we have

$$T_{(\lambda\mu)\nu}^{(2\beta-)} = (1/6)\epsilon_{\mu\nu\tau}(2\epsilon_{\rho\sigma\tau}T_{(\lambda\rho)\sigma} + 2\epsilon_{\rho\sigma\lambda}T_{(\tau\rho)\sigma} \\ + \epsilon_{\rho\sigma\tau}T_{(\rho\sigma)\lambda} + \epsilon_{\rho\sigma\lambda}T_{(\rho\sigma)\tau} - 2\delta_{\lambda\tau}\epsilon_{\pi\rho\sigma}T_{(\pi\rho)\sigma}), \quad (A9)$$

giving

$$T_{(\lambda\mu)\nu}^{(2\beta-)} = (1/3)\epsilon_{\mu\nu\tau}(\epsilon_{\rho\sigma\tau}T_{(\lambda\rho)\sigma} + \epsilon_{\rho\sigma\lambda}T_{(\tau\rho)\sigma}). \quad (A10)$$

The linear dependence of Eqs. (A8) and (A10) is only apparent when all possible tensor products of these tensors are taken, when it is again found that they are related by simple numerical factors

$$T_{(\lambda\mu)\nu}^{(2\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(2\beta-)} = 4T_{(\lambda\mu)\nu}^{(2\alpha-)}\bar{T}_{(\lambda\mu)\nu}^{(2\alpha-)} = -4T_{(\lambda\mu)\nu}^{(2\beta-)}\bar{T}_{(\lambda\mu)\nu}^{(2\alpha-)} \\ = -4T_{(\lambda\mu)\nu}^{(2\alpha-)}\bar{T}_{(\lambda\mu)\nu}^{(2\beta-)}. \quad (A11)$$

Hence it is appropriate to combine the $(2\alpha-)$ and $(2\beta-)$ components as

$$T_{(\lambda\mu)\nu}^{(2-)} = T_{(\lambda\mu)\nu}^{(2\alpha-)} + T_{(\lambda\mu)\nu}^{(2\beta-)}. \quad (A12)$$

The explicit form of Eq. (4.11) now follows directly from Eqs. (A1)–(A12), and is given by

$$\begin{bmatrix} T_{(\lambda\mu)\nu}^{(0-)} \bar{T}_{(\lambda\mu)\nu}^{(0-)} \\ T_{(\lambda\mu)\nu}^{(1\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(1\alpha-)} \\ T_{(\lambda\mu)\nu}^{(1\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(1\beta-)} \\ T_{(\lambda\mu)\nu}^{(1\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)} \\ T_{(\lambda\mu)\nu}^{(1\beta-)} \bar{T}_{(\lambda\mu)\nu}^{(1\alpha-)} \\ T_{(\lambda\mu)\nu}^{(1\beta-)} \bar{T}_{(\lambda\mu)\nu}^{(1\beta-)} \\ T_{(\lambda\mu)\nu}^{(1\beta-)} \bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)} \\ T_{(\lambda\mu)\nu}^{(1\gamma-)} \bar{T}_{(\lambda\mu)\nu}^{(1\alpha-)} \\ T_{(\lambda\mu)\nu}^{(1\gamma-)} \bar{T}_{(\lambda\mu)\nu}^{(1\beta-)} \\ T_{(\lambda\mu)\nu}^{(1\gamma-)} \bar{T}_{(\lambda\mu)\nu}^{(1\gamma-)} \\ T_{(\lambda\mu)\nu}^{(2\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(2\alpha-)} \\ T_{(\lambda\mu)\nu}^{(2\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(2\beta-)} \\ T_{(\lambda\mu)\nu}^{(2\beta-)} \bar{T}_{(\lambda\mu)\nu}^{(2\alpha-)} \\ T_{(\lambda\mu)\nu}^{(2\beta-)} \bar{T}_{(\lambda\mu)\nu}^{(2\beta-)} \\ T_{(\lambda\mu)\nu}^{(3-)} \bar{T}_{(\lambda\mu)\nu}^{(3-)} \end{bmatrix} = \frac{1}{12} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 8 & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 8 & 0 & 0 \\ 0 & 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 0 & -3 & 0 \\ 0 & 0 & 0 & 0 & 12 & 0 \\ 0 & 0 & 0 & 0 & 0 & 12 \end{bmatrix} \begin{bmatrix} T_{(\lambda\mu)\nu}^{(1\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(1\alpha-)} \\ T_{(\lambda\mu)\nu}^{(1\alpha-)} \bar{T}_{(\lambda\mu)\nu}^{(1\beta-,1\gamma-)} \\ T_{(\lambda\mu)\nu}^{(1\beta-,1\gamma-)} \bar{T}_{(\lambda\mu)\nu}^{(1\alpha-)} \\ T_{(\lambda\mu)\nu}^{(1\beta-,1\gamma-)} \bar{T}_{(\lambda\mu)\nu}^{(1\beta-,1\gamma-)} \\ T_{(\lambda\mu)\nu}^{(2-)} \bar{T}_{(\lambda\mu)\nu}^{(2-)} \\ T_{(\lambda\mu)\nu}^{(3-)} \bar{T}_{(\lambda\mu)\nu}^{(3-)} \end{bmatrix} \quad (\text{A13})$$

where the matrix of numerical coefficients represents x_{pq} .

¹J. Wilson and J. F. B. Hawkes, *Optoelectronics: An Introduction* (Prentice-Hall, Englewood Cliffs, 1983).

²D. L. Andrews and K. P. Hopkins, *J. Chem. Phys.* **88**, 6030 (1988).

³D. L. Andrews and N. P. Blake, *J. Chem. Phys.* **88**, 6039 (1988).

⁴D. L. Andrews and B. S. Sherborne, *Chem. Phys.* **88**, 1 (1984).

⁵D. L. Andrews and B. S. Sherborne, *Chem. Phys.* **108**, 357 (1986).

⁶D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, London, 1984).

⁷T. L. Mazely and W. M. Hetherington III, *J. Chem. Phys.* **86**, 3640 (1987).

⁸D. L. Andrews and M. J. Harlow, *Phys. Rev. A* **29**, 2796 (1984).

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

¹⁰D. L. Andrews and P. J. Wilkes, *J. Chem. Phys.* **83**, 2009 (1985).

¹¹C. D. Churcher, *Mol. Phys.* **46**, 621 (1982).

¹²D. L. Andrews and M. J. Harlow, *Mol. Phys.* **49**, 937 (1983).