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Electric-field-induced two-photon absorption

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This paper provides a theoretical treatment of the electrochromic effect of a static electric field on molecular two-photon absorption, based on a full quantum electrodynamical formulation of the interactions. The results include a description of changes in the spectrum resulting both from electro-optical interactions and, in the case of polar fluids, from the anisotropy associated with energetically favored molecular orientations. A detailed consideration of the effect of varying laser polarization and field direction is included in the analysis. The results demonstrate that on application of the field, weak but potentially detectable new lines should appear in the two-photon spectrum. These lines are associated with transitions to vibronic states which would normally require three-photon excitation. The application of the static electric field also results in the selective enhancement of other lines normally present in the two-photon spectrum. The effect may thus offer scope for the accurate determination of the frequency and symmetry character of weak vibronic transitions when they occur under the wing of strongly allowed transitions.

I. INTRODUCTION

As noted in the previous paper,[1] hereinafter referred to as paper I, electric-field-induced two-photon processes underlie several phenomena of major importance in the field of electro-optics. However, in comparison with such processes, electric-field-induced two-photon absorption (EFITPA) has received little attention. The effects of an electric field on *multiphoton dissociation* rates have been studied in some depth: Gozel and van den Bergh[2] reported, in 1981, a significant enhancement of the rate of infrared multiphoton dissociation of CF_2HCl caused by the aplication of a static electric field. This enhancement, which was seen under essentially collision-free conditions, was attributed to a breakdown in the angular momentum selection rules caused by mixing of states in the applied field. Later van den Bergh and co-workers[3] extended this work and applied it to CF_3D. An overview covering electric field enhancement of multiphoton absorption processes in samples aligned by an applied static electric field has been given by Thomas,[4] and the dressing effect of the electric fields of the laser beams in two-photon ionization has been considered by Cardimona.[5]

A treatment of the selection rules for optical transitions induced in free molecules by an electric field, which was initially simplified by considering an isotropic distribution of molecules, was reported in 1984.[6] This was subsequently developed to consider orientational effects[7] caused by the external field, employing specially developed techniques[8] to account for the induced anisotropy of the sample. This work has been further developed in this series of three papers, on electric-field-induced two-photon processes. Paper I has covered much of the general theory, while this paper is concerned specifically with EFITPA, and the subsequent paper deals with electric-field-induced Raman spectroscopy. All the work is conducted within the framework of quantum electrodynamics with interactions considered in the electric-dipole approximation.

This paper deals with the effects of the application of a static electric field on two-photon absorption (TPA). There are two distinct mechanisms by which the external field can influence this process, referred to as (i) the electrically polarized channel and (ii) the electro-optical channel.

The electrically polarized channel, which is dealt with in Sec. III, relates specifically to fluids containing polar molecules. Here, application of the static field produces macroscopic anisotropy by introducing a degree of molecular alignment. This results in a relaxation of the normal symmetry restrictions on the allowed transitions, leading to distinctive changes of intensity in the various lines of the spectrum. Moreover, suitable choice of beam configuration enables other lines which are usually absent from the spectrum to appear.

The second channel, which is discussed in Sec. IV, is of more universal application, and is one in which molecular transitions proceed through an electro-optical interaction normally absent. Here the static field perturbs and partially mixes the molecular wave functions, thereby allowing some transitions to take place which would otherwise be forbidden. This can give rise to a novel effect wherein application of the field enables certain lines to be "switched into" the spectra.

II. THEORY

The matrix element for EFITPA results from the summation of contributions from two apparently distinct absorption routes, which can be calculated using the time-ordered diagrams[9] of Fig. 1. Here, Fig. 1(a) applies to the case where the sole effect of the applied electric field is to bring about a rearrangement of any polar molecules in the sample, i.e., the optically $(E1 \times E1)$-allowed channel. This diagram is the same as that which is used to represent conventional TPA, showing two radiation-molecule interactions. Time-ordered diagrams (such as those of Fig. 1) are a schematic representation of a particular process, employed to aid the derivation of the matrix element for that process. In the case of optically allowed (electrically polarized) EFITPA the matrix element is the same as that for conventional TPA,
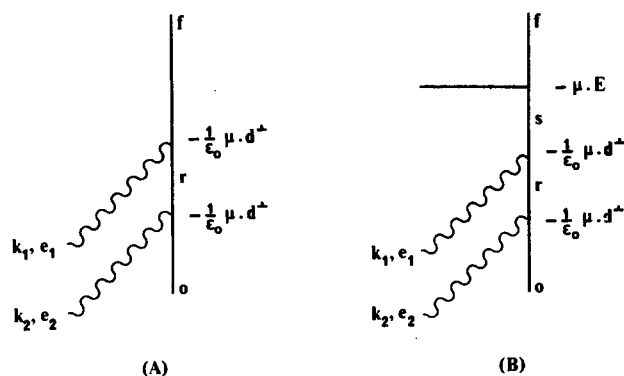
FIG. 1. Typical time-ordered diagrams for two-photon absorption in the presence of a static electric field. Time increases vertically; the wavy lines denote photons and the horizontal line the static field.

and hence the time-ordered diagrams are the same. There is no interaction between the molecule and the static field represented in the diagram because the static field is not involved in the actual transition. The bulk anisotropy introduced into the sample by the field is accounted for in the theory at the later, ensemble averaging stage. Conversely, in Fig. 1(b), which represents the electro-optically $(E1 \times E1 \times E1)$-allowed channel, the electric field is explicitly included. Here the field produces a *transition* electric-dipole interaction with the molecule, and it is necessary to include this in the matrix element represented by the time-ordered diagram. There are two time-ordered diagrams of the type (1a), which sum to produce a matrix element contribution which we shall denote as $M_{fi}(a)$. Similarly, there are six diagrams of the type (1b), which sum to give $M_{fi}(b)$. These two distinct absorption routes relate to the electrically polarized, and electro-optical channels, respectively, and represent the second and third terms of Eq. (2.6) in paper I.

The matrix element for electric field induced two-photon absorption (EFITPA) is thus given by

$$M_{fi} = M_{fi}(a) + M_{fi}(b) \qquad (2.1)$$

[identifiable with the first and second terms of Eq. (2.7) in paper I], and application of the Fermi Golden Rule gives

$$\Gamma \propto |M_{fi}(a)|^2 + 2\,\text{Re}\{M_{fi}(a)\,\overline{M_{fi}(b)}\} + |M_{fi}(b)|^2. \qquad (2.2)$$

If the molecules of the sample possess a nonzero static dipole moment, ($\mu^{00} \neq 0$), the electric field produces a preferred orientation of these molecules, and a Boltzmann-weighted averaging process is required to determine the overall rate expression. For any optically allowed transition, the first term of Eq. (2.2) is finite and greatly more significant than the higher-order terms, so explicit treatment of the first term alone is sufficient. This, the electrically polarized channel, is considered in Sec. III.

Now, if the molecular transition $|f\rangle \leftarrow |0\rangle$ is forbidden for the second-order route, then $M_{fi}(a)$ is zero, and the first two terms of Eq. (2.2) disappear leaving only the third term. For molecules with a zero dipole moment the orientational average of this term is calculated using isotropic sixth-rank averaging. This electro-optical channel is considered in Sec. IV.

From an examination of molecular point group character tables, it is clear that several transitions observed in polar molecules (which belong to one of the axial point groups) are allowed by $M_{fi}(b)$ but not by $M_{fi}(a)$. For instance, transitions of B symmetry under the operations of the point group C_6 have transformation properties characteristic of a third rank tensor, and are therefore forbidden by $M_{fi}(a)$ but allowed for $M_{fi}(b)$. In this case the leading term in the rate equation is the isotropic result of Sec. IV.

The electrically polarized and electro-optical channels can, in many cases, be distinguished by differences arising in the selection rules for the two absorption routes. For centrosymmetric molecules two-photon absorption via the electrically orientated channel obeys the normal selection rules of simple two-photon absorption, producing a vibronically excited state of *gerade* symmetry if the transition originates from a totally symmetric ground state. In contrast, absorption through the electro-optical channel proceeds via three radiation–molecule interaction events, leading to an excited state of ungerade symmetry. Additionally, as will be shown later in this paper, the rate for the electro-optical route contains irreducible components of weights 0–3, whereas the rate for the electrically polarized route has only components of weights 0–2.

III. ABSORPTION BY POLAR MOLECULES ORIENTATED BY THE ELECTRIC FIELD

A. Absorption rate

For molecules with a nonzero static electric-dipole moment ($\mu^{00} \neq 0$), an electric field produces the adoption of preferential orientations and necessitates a Boltzmann-weighted averaging procedure to correctly account for the possible molecular orientations.

For simple two-photon absorption the rate is given by

$$\Gamma = L_{\text{TPA}}\,e_{1_i}e_{2_j}\bar{e}_{1_k}\bar{e}_{2_l}S_{ij}\overline{S}_{kl}, \qquad (3.1)$$

where e_1 is the polarization vector of photon 1, e_2 that of photon 2, and the constant labeled L_{TPA} is defined as

$$L_{\text{TPA}} = \frac{2\pi}{\hbar}\rho_f\left(\frac{\hbar c}{2V\epsilon_0}\right)^2 n_1 n_2 k_1 k_2, = \frac{\pi \rho_f I_1 I_2}{2c^2 \hbar \epsilon_0^2}. \qquad (3.2)$$

Here n_1 denotes the number of photons to type 1 (frequency $\omega_1 = ck_1$) and n_2 the number of photons of type 2 (frequency $\omega_2 = ck_2$) within the quantization volume V. The second equality in Eq. (3.2) follows from use of the relationship $I = nhc^2k/V$ for the irradiance I of each beam. The molecular response tensor S_{ij} can be written down using the time-ordered diagrams of Fig. 2, and is explicitly given by

$$S_{ij} = \sum_r \left[\frac{\mu_i^{fr}\mu_j^{r0}}{(E_{r0} - \hbar\omega_1)} + \frac{\mu_j^{fr}\mu_i^{r0}}{(E_{r0} - \hbar\omega_2)} \right]. \qquad (3.3)$$

In the case of an isotropic fluid, the rotationally averaged absorption rate is

$$\langle\Gamma\rangle = L_{\text{TPA}}\,e_{1_i}e_{2_j}\bar{e}_{1_k}\bar{e}_{2_l}S_{\lambda\mu}\overline{S}_{\nu o}\langle l_{i\lambda}l_{j\mu}l_{k\nu}l_{lo}\rangle. \qquad (3.4)$$

Two Cartesian coordinate systems are employed in this equation; a laboratory-fixed frame denoted by latin indices, in which the laser polarizations are fixed, and a molecule-fixed frame denoted by greek indices to which the molecular
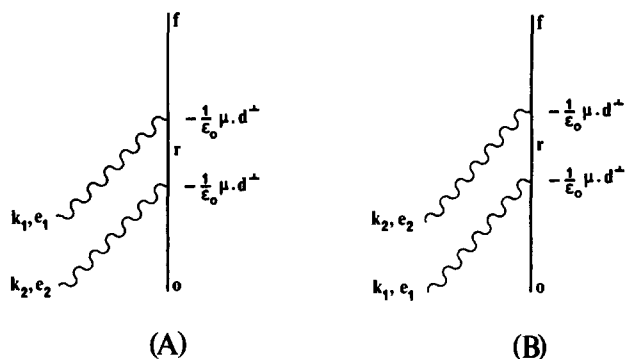
(A)   (B)

FIG. 2. The two time-ordered diagrams for the optically allowed channel of two-photon absorption.

response tensors are referred. The direction cosine between the $\hat{i}$ and $\hat{\lambda}$ directions, denoted by $l_{i\lambda}$, refers to the (i,λ) element of the Euler angle matrix. However, for a polar liquid subjected to a static electric field, a Boltzmann-weighting factor $(\exp \mu^{00} \cdot E / kT)$ has to be incorporated into the evaluation of any rotationally averaged result. Hence, the average over direction cosines in Eq. (3.4) is replaced by

$$\langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} \exp(i\alpha \hat{\mu}^{00} \cdot \hat{E}) \rangle / \langle \exp(i\alpha \hat{\mu}^{00} \cdot \hat{E}) \rangle \quad (3.5)$$

with

$$\alpha = - i\mu^{00} E / kT = - i\gamma \quad (3.6)$$

[compare Eqs. (3.4)–(3.6) with Eq. (3.8) of paper I]. Evaluation of the average is then conducted by means of the method described in Ref. 8, making use of the identity

$$\langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} \exp(i\alpha \hat{\mu}^{00} \cdot \hat{E}) \rangle$$
$$= I'^{(4)\phi}_{ijkl;\lambda\mu\nu o} (- i\gamma, \hat{E}, \hat{\mu}^{00})$$
$$= \sum_{j=0}^{4} I'^{(4;j)\phi}_{ijkl;\lambda\mu\nu o} (- i\gamma, \hat{E}, \hat{\mu}^{00}), \quad (3.7)$$

where $I'^{(n;j)\phi}$ has been defined in Eq. (3.10) of paper I. The five parts of the expansion can then be expressed in terms of the reduced spherical Bessel functions, (see Table I of paper I) defined by

$$j'_n (- i\gamma) = \frac{j_n(- i\gamma)}{j_0(- i\gamma)}. \quad (3.8)$$

Hence the result takes the general form

$$\Gamma = L_{\text{TPA}} [a + b j'_1 (- i\gamma) + c j'_2 (- i\gamma)$$
$$+ d j'_3 (- i\gamma) + e j'_4 (- i\gamma)] \quad (3.9)$$

with the explicit expression given in Appendix A. However, in the low-field (high-temperature) limit the reduced Bessel functions, $j'_n (- i\gamma)$ become proportional to γ^n, i.e., $j'_n (- i\gamma) \approx (- i\gamma)^n / (2n + 1)!!$. In this limit, the result for electric field orientated two-photon absorption can be written as a fourth degree polynomial in γ, i.e.,

$$\Gamma = L_{\text{TPA}} \left[a - \frac{bi\gamma}{3} - \frac{c\gamma^2}{15} + \frac{di\gamma^3}{105} + \frac{e\gamma^4}{945} \right]. \quad (3.10)$$

It is interesting to note that the first term of each expansion (3.9) and (3.10), i.e., the term independent of γ, is the orientationally averaged result for an isotropic medium. Therefore, the result for electric field oriented two-photon

absorption can essentially be regarded as the isotropic result with a series of additional correction terms, each increasing in the power of γ. The higher order terms will only become significantly where γ approaches unity. Hence, a detailed study of the isotropic result is appropriate, and much of the ground work has been done on this in previous papers. The isotropic result can be written as[10]

$$\Gamma = \frac{L_{\text{TPA}}}{30} [FS_{\lambda\lambda}\overline{S}_{\mu\mu} + GS_{\lambda\mu}\overline{S}_{\lambda\mu} + HS_{\lambda\mu}\overline{S}_{\mu\lambda}], \quad (3.11)$$

where

$$F = 4|e_1 \cdot e_2|^2 - 1 - |e_1 \cdot \bar{e}_2|^2, \quad (3.12)$$
$$G = - |e_1 \cdot e_2|^2 + 4 - |e_1 \cdot \bar{e}_2|^2, \quad (3.13)$$

and

$$H = - |e_1 \cdot e_2|^2 - 1 + 4|e_1 \cdot \bar{e}_2|^2. \quad (3.14)$$

The three molecular tensor products in Eq. (3.11) may more conveniently be expressed in terms of three irreducible tensor products using Eqs. (4.1)–(4.4) of paper I:

$$S_{\lambda\lambda}\overline{S}_{\mu\mu} = 3S_{\lambda\mu}^{(0+)}\overline{S}_{\lambda\mu}^{(0+)}, \quad (3.15)$$
$$S_{\lambda\mu}\overline{S}_{\lambda\mu} = S_{\lambda\mu}^{(0+)}\overline{S}_{\lambda\mu}^{(0+)} + S_{\lambda\mu}^{(1+)}\overline{S}_{\lambda\mu}^{(1+)} + S_{\lambda\mu}^{(2+)}\overline{S}_{\lambda\mu}^{(2+)}, \quad (3.16)$$
$$S_{\lambda\mu}\overline{S}_{\mu\lambda} = S_{\lambda\mu}^{(0+)}\overline{S}_{\lambda\mu}^{(0+)} - S_{\lambda\mu}^{(1+)}\overline{S}_{\lambda\mu}^{(1+)} + S_{\lambda\mu}^{(2+)}\overline{S}_{\lambda\mu}^{(2+)}. \quad (3.17)$$

Irreducible tensors are introduced into the theory here in order to facilitate a study of selection rules. (The plus signs in the superscripts, which denote even parity under spatial inversion, are dropped in subsequent equations since even parity is invariably associated with the S tensor.) Equation (3.11) now becomes

$$\Gamma = \frac{L_{\text{TPA}}}{30} [(3F + G + H)S_{\lambda\mu}^{(0)}\overline{S}_{\lambda\mu}^{(0)}$$
$$+ (G - H)S_{\lambda\mu}^{(1)}\overline{S}_{\lambda\mu}^{(1)} + (G + H)S_{\lambda\mu}^{(2)}\overline{S}_{\lambda\mu}^{(2)}], \quad (3.18)$$

and from Eqs. (3.12)–(3.14),

$$(3F + G + H) = 10|e_1 \cdot e_2|^2, \quad (3.19)$$
$$(G - H) = 5(1 - |e_1 \cdot \bar{e}_2|^2), \quad (3.20)$$
$$(G + H) = - 2|e_1 \cdot e_2|^2 + 3 + 3|e_1 \cdot \bar{e}_2|^2. \quad (3.21)$$

By examining Eqs. (3.19)–(3.21) it is clear that for any experimental configuration with beam polarizations conforming to the condition $e_1 \cdot e_2 = 0$, there can be no contribution to the absorption rate from the weight-0 component. It is also evident that for parallel linear polarizations, or corotating circular polarizations (where $e_1 \cdot \bar{e}_2 = 1$ for either case), there is no contribution from the weight-1 component. Obviously, then, there can be no weight-1 contribution for any single-beam two-photon absorption experiment (in the absence of any external perturbation). Further, a brief examination of the expression for $(G + H)$ reveals that the weight-2 contribution cannot be removed by any choice of beam polarizations.

The fully general rate expression for the electrically polarized channel nonetheless contains contributions from irreducible tensors of all three weights, although experimental configurations can be selected to eliminate contributions

from particular weights (see below). This suggests that it should be possible through a considered choice of polarization parameters, to switch a transition into a two-photon absorption spectrum, through the application of an electric field.

For example, if the beam polarizations are chosen to be parallel to one another, there is no weight-1 contribution to the rate in the absence of a field. Therefore, any transition which is of pure weight-1 character will not be seen in the spectrum. However, application of an electric field to the same experiment leads to the addition of weight-1 components to the overall rate expression. Hence, a pure weight-1 transition is only seen in the presence of the field, and is said to have been "switched into" the spectrum, although the signal may be difficult to detect since it is of the order of γ^2 times smaller than normal two-photon absorption signals. This results from the fact that any choice of polarization configuration that eliminates weight-1 contributions from the first term of Eq. (3.9) also removes the leading $j_1'(-i\gamma)$ correction term, by reducing b to zero.

B. Polarization analysis

1. Case A: beam polarizations and electric field parallel

In the absence of the electric field, the rate expression in terms of irreducible tensor products is

$$\Gamma = \frac{L_{\text{TPA}}}{15} \{5S_{\lambda\mu}^{(0)}\overline{S}_{\lambda\mu}^{(0)} + 2S_{\lambda\mu}^{(2)}\overline{S}_{\lambda\mu}^{(2)}\}, \tag{3.22}$$

which is the isotropic (fourth rank average) result. As can be seen, this configuration produces a result containing components of weight-0 and weight-2, but none of weight-1. Therefore, any molecular transitions of pure weight-1 character, e.g., F_1 in I or F_{1g} in I_h molecules, will not be observed in the spectrum.

On application of the field, (see Fig. 3) the Boltzmann-weighted average leads to the addition of higher order terms:

$$\langle\Gamma\rangle = L_{\text{TPA}} \{1/15 [5S_{\lambda\mu}^{(0)}\overline{S}_{\lambda\mu}^{(0)} + 2S_{\lambda\mu}^{(2)}\overline{S}_{\lambda\mu}^{(2)}],$$

$$+ \frac{j_2'(-i\gamma)}{21} [3S_2 - 2S_0]$$

$$+ \frac{j_4'(-i\gamma)}{35} [35S_4 - 5S_2 + S_0]\}. \tag{3.23}$$

The S_2 and S_4 terms, which are defined in Appendix B, contain components of all three weights, so the pure weight-1 transitions not seen in the absence of the field may be seen in its presence. A proof that S_2 and S_4 contain weights 0, 1, and 2 is detailed in Appendix C. However, the electrically polarized contributions to the rate [$j_n'(-i\gamma)$ terms with $n \geqslant 1$] are smaller than the optical contributions by a factor of γ^2, since $j_2'(-i\gamma) \propto \gamma^2$ in the low-field limit.

2. Case B: perpendicular linear polarizations, one parallel to the field

The result with the field "off" is

$$\langle\Gamma\rangle = \frac{L_{\text{TPA}}}{30} [5S_{\lambda\mu}^{(1)}\overline{S}_{\lambda\mu}^{(1)} + 3S_{\lambda\mu}^{(2)}\overline{S}_{\lambda\mu}^{(2)}]. \tag{3.24}$$

Here, there are contributions from weights-1 and -2, but not from weight-0, so any molecular transition of pure weight-0 character will not be seen. With the field "on" (see Fig. 3)
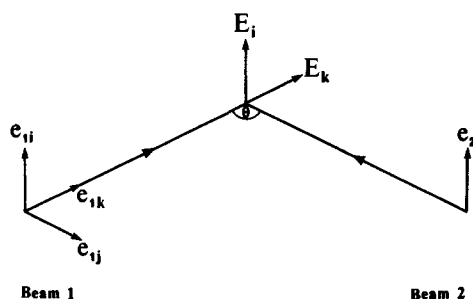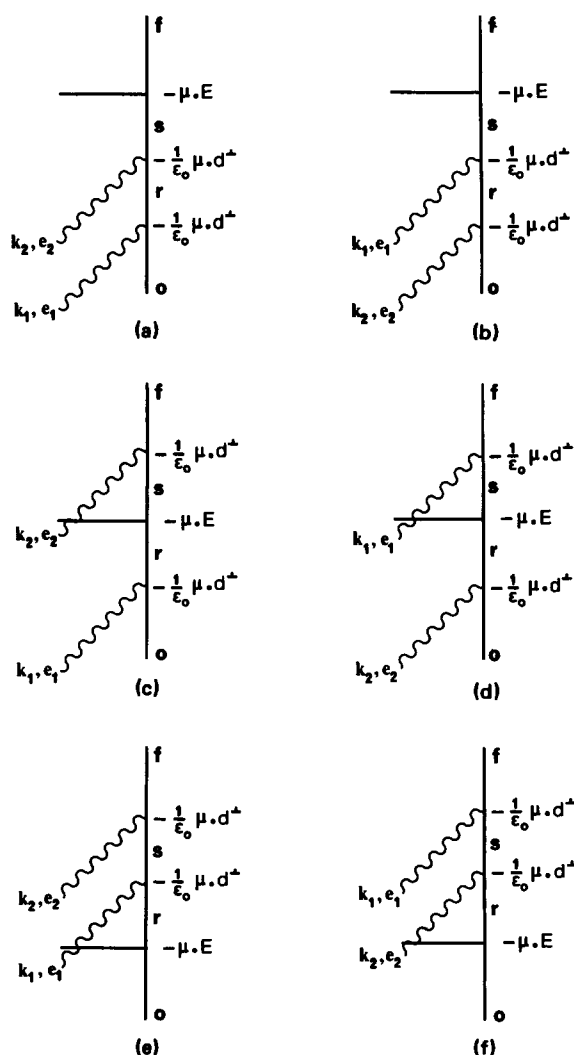

FIG. 3. Beam polarizations and electric field orientations employed in the polarization analysis. Case A: $e_{1\parallel}, e_2, E_\parallel$. Case B: $e_{1\perp}, e_2, E_\parallel$. Case C: $e_{1\parallel}, e_2, E_k$. Case D: $e_{1\perp}, e_2, E_k$.

FIG. 4. The six time-ordered diagrams for the electro-optically allowed channel of two-photon absorption.

the result becomes

$$\langle \Gamma \rangle = L_{\text{TPA}} \{ 1/30 [5S_{\lambda\mu}^{(1)} \overline{S}_{\lambda\mu}^{(1)} + 3S_{\lambda\mu}^{(2)} \overline{S}_{\lambda\mu}^{(2)}]$$

$$+ \frac{j_2'(-i\gamma)}{42} [2S_0 - 7S_{\lambda\mu}\overline{S}_{\lambda\mu} - 3S_2$$

$$+ 21\hat{\mu}_\lambda\hat{\mu}_\nu S_{\lambda\nu}\overline{S}_{\nu\mu}]$$

$$+ \frac{j_4'(-i\gamma)}{70} [-35S_4 - 10S_2 - 2S_0] \}, \qquad (3.25)$$

which does contain weight-0 components. This is not of great physical interest, however, since only in highly symmetric molecules belonging to one of the cubic point groups do we find totally symmetric transitions of pure weight-0 character. In all the axial point groups to which polar molecules must belong, both weight-0 and weight-2 tensor components transform together under the totally symmetric representation. In this case, the inclusion of weight-0 components in the above rate equation should not, therefore, result in the appearance of new lines in the spectrum.

IV. THE ELECTRO-OPTICAL CHANNEL

A. Absorption rate

The rate of EFITPA transitions, for the electro-optical channel, is determined using third-order time-dependent perturbation theory. The appropriate matrix element can be constructed in the usual manner, with the aid of time-ordered diagrams. There are six of these to be taken into consideration, as illustrated in Fig. 4. The contribution arising from Fig. 4(a) is, for example,

$$M_{fi}^{(1)} = \left(\frac{n_1 \hbar c k_1}{2V\epsilon_0} \right)^{1/2} \left(\frac{n_2 \hbar c k_2}{2V\epsilon_0} \right)^{1/2} e_{1i} e_{2j} E_k$$

$$\times \sum_{rs} \left[\frac{\mu_k^{fs} \mu_j^{sr} \mu_i^{r0}}{(E_{s0} - \hbar\omega_1 - \hbar\omega_2)(E_{r0} - \hbar\omega_1)} \right]. \qquad (4.1)$$

Summing all six such contributions leads to the following result:

$$M_{fi} = \frac{\hbar c}{2V\epsilon_0} (n_1 n_2 k_1 k_2)^{1/2} e_{1i} e_{2j} E_k T_{ijk}. \qquad (4.2)$$

The molecular response tensor, T_{ijk}, of Eq. (4.2) is given by

$$T_{ijk} = \sum_{r,s} \left[\frac{\mu_k^{fs}\mu_j^{sr}\mu_i^{r0}}{(E_{s0}-\hbar\omega_1-\hbar\omega_2)(E_{r0}-\hbar\omega_1)} + \frac{\mu_j^{fs}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}-\hbar\omega_1)(E_{r0}-\hbar\omega_1)} + \frac{\mu_k^{fs}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}-\hbar\omega_1-\hbar\omega_2)(E_{r_0}-\hbar\omega_2)} \right.$$

$$\left. + \frac{\mu_i^{fs}\mu_k^{sr}\mu_j^{r0}}{(E_{s0}-\hbar\omega_2)(E_{r0}-\hbar\omega_2)} + \frac{\mu_j^{fs}\mu_i^{sr}\mu_k^{r0}}{(E_{s0}-\hbar\omega_1)(E_{r0})} + \frac{\mu_i^{fs}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-\hbar\omega_2)(E_{r0})} \right]. \qquad (4.3)$$

It is perhaps worth observing at this point that the tensor T_{ijk} of this paper is a particular case of the more general molecular response tensor given in a recent paper by Andrews and Wilkes.[11] Tensors of this general form arise wherever there are three photon events at one center. For example, in the case currently under review the static electric field can be represented by a photon of zero frequency. Thus, by setting ω_3 to zero in the formula of Andrews and Wilkes we achieve the above result (4.3). The selection rules are therefore directly similar; in other words electro-optically allowed two-photon absorption has the same selection rules as three-photon absorption.[11,12]

The rate can now be written as

$$\Gamma = L_{\text{TPA}} e_{1i} e_{2j} E_k \bar{e}_{1l} \bar{e}_{2m} E_n T_{ijk} \overline{T}_{lmn}, \qquad (4.4)$$

leading to the rotationally averaged rate

$$\Gamma = L_{\text{TPA}} \langle e_{1i} e_{2j} E_k \bar{e}_{1l} \bar{e}_{2m} E_n T_{ijk} \overline{T}_{lmn} \rangle. \qquad (4.5)$$

B. Polarization analysis

The general rate expression for the electro-optical channel is given as Eq. (4.17) of paper I. The nine linearly independent polarization parameters therein are experimentally variable. For any particular laser beam and polarization geometry, their values can be calculated and inserted directly into the general rate expression to give the corresponding rate. The choices of configurations are numerous, and it would in principle be possible to construct 15 experimentally different setups in order to arrive at 15 rate expressions. These could in turn be treated as 15 simultaneous equations, and be solved to elucidate the values of all 15 molecular tensor products. However, this would appear to be of purely academic interest, as an experimentalist confronted with the need for so many experiments and experimental measurements is unlikely to undertake such a task unless convinced that such efforts will produce fruitful results. We shall, therefore, contain our discussions to a number of specific configurations displaying points of particular interest.

1. Case C: parallel linear polarizations perpendicular to the field

In two-beam two-photon absorption, arranging two linearly polarized beams parallel to one another leads to a result composed of tensors of even weights-0 and 2, i.e., there is no weight-1 contribution to the rate. However, application of an electric field (see Fig. 3) leads to a rate:

$$\Gamma = \frac{L_{\text{TPA}} E^2}{840} \{ 112 [T_{\lambda\mu\nu}^{(1\alpha)} \overline{T}_{\lambda\mu\nu}^{(1\alpha)} + T_{\lambda\mu\nu}^{(1\alpha)} \overline{T}_{\lambda\mu\nu}^{(1\beta)} + T_{\lambda\mu\nu}^{(1\alpha)} \overline{T}_{\lambda\mu\nu}^{(1\gamma)} + T_{\lambda\mu\nu}^{(1\beta)} \overline{T}_{\lambda\mu\nu}^{(1\alpha)}] + 7T_{\lambda\mu\nu}^{(1\beta)} \overline{T}_{\lambda\mu\nu}^{(1\beta)} - 28T_{\lambda\mu\nu}^{(1\beta)} \overline{T}_{\lambda\mu\nu}^{(1\gamma)}$$

$$+ 112T_{\lambda\mu\nu}^{(1\gamma)} \overline{T}_{\lambda\mu\nu}^{(1\alpha)} - 28T_{\lambda\mu\nu}^{(1\gamma)} \overline{T}_{\lambda\mu\nu}^{(1\beta)} + 7T_{\lambda\mu\nu}^{(1\gamma)} \overline{T}_{\lambda\mu\nu}^{(1\gamma)} + 42T_{\lambda\mu\nu}^{(2\beta)} \overline{T}_{\lambda\mu\nu}^{(2\beta)} + 32T_{\lambda\mu\nu}^{(3)} \overline{T}_{\lambda\mu\nu}^{(3)} \}. \qquad (4.6)$$

Hence, the electric field can be employed to switch a pure (odd) weight-1 transition into the two-photon absorption spectrum.

2. Case D. linear polarizations and electric field mutually perpendicular

This is, perhaps, the easiest configuration for which to calculate the rate since all but one of the nine polarization parameters in the rate expression are reduced to zero, and hence:

$$\Gamma = \frac{L_{TPA}E^2}{840} \left[140 T^{(0)}_{\lambda\mu\nu} \overline{T}^{(0)}_{\lambda\mu\nu} + 56\{ T^{(2\alpha)}_{\lambda\mu\nu} \overline{T}^{(2\alpha)}_{\lambda\mu\nu} \right.$$
$$+ T^{(2\alpha)}_{\lambda\mu\nu} \overline{T}^{(2\beta)}_{\lambda\mu\nu} + T^{(2\beta)}_{\lambda\mu\nu} \overline{T}^{(2\alpha)}_{\lambda\mu\nu} + T^{(2\beta)}_{\lambda\mu\nu} \overline{T}^{(2\beta)}_{\lambda\mu\nu} \}$$
$$\left. + 20 T^{(3)}_{\lambda\mu\nu} \overline{T}^{(3)}_{\lambda\mu\nu} \right]. \tag{4.7}$$

Here the irreducible parts of the term T are as given by Eqs. (4.5)–(4.12) of paper I, with the minus signs denoting odd parity left implicit. In the absence of an electric field, two mutually perpendicularly polarized beams produce a rate comprising of contributions from even weights 1 and 2. However, as can be seen from Eq. (4.17) of paper I, in the presence of the field contributions arise from odd weights 0, 2, and 3. Therefore, any transition to a state of pure (odd) weight-0 character, pure (odd) weight-3, (or a combination

of these weights), will not be present in the spectrum in the absence of the field. Such a transition can, thus, be switched into two-photon absorption spectra by applying the electric field.

C. Incident beams of identical frequency

The rate expression derived in paper I, and given there as Eq. (4.17), is the general expression for the rate of EFITPA with arbitrary beam directions, frequencies, and polarizations. This result is considerably simplified if we consider the case where the frequencies of the two absorbed photons are the same, i.e., $\omega_1 = \omega_2$; $|\mathbf{k}_1| = |\mathbf{k}_2|$. Although this places no restriction on the direction of the two propagation vectors, it does allow a contraction of the molecular tensor parameters, as a direct consequence of the symmetry imposed on the molecular response tensor by energy considerations.

By examining Eq. (4.3), and setting $\omega_1 = \omega_2$ in the energy denominators, it is easily seen that the molecular response tensor $T_{\lambda\mu\nu}$ becomes index symmetric in its first two indices. This index symmetry in $T_{\lambda\mu\nu}$ causes the $T^{(0)}_{\lambda\mu\nu}$ irreducible component to vanish and removes the linear independence of the weight-1, and weight-2, sets of components [see Eq. (A13) in the Appendix to paper I]. The 15 molecular tensor products can then be reduced to six terms, leading to

$$\Gamma = \frac{L_{TPA}}{5040} \begin{bmatrix} (\mathbf{e}_1\cdot\mathbf{e}_2)(\mathbf{E}\cdot\overline{\mathbf{e}}_1)(\mathbf{E}\cdot\overline{\mathbf{e}}_2) \\ |\mathbf{e}_1\cdot\mathbf{e}_2|^2 E^2 \\ (\overline{\mathbf{e}}_1\cdot\mathbf{e}_2)(\mathbf{E}\cdot\mathbf{e}_1)(\mathbf{E}\cdot\overline{\mathbf{e}}_2) \\ |\mathbf{e}_1\cdot\mathbf{E}|^2 \\ (\overline{\mathbf{e}}_1\cdot\overline{\mathbf{e}}_2)(\mathbf{E}\cdot\mathbf{e}_1)(\mathbf{E}\cdot\mathbf{e}_2) \\ |\mathbf{e}_2\cdot\mathbf{E}|^2 \\ E^2 \\ (\mathbf{e}_1\cdot\overline{\mathbf{e}}_2)(\mathbf{E}\cdot\overline{\mathbf{e}}_1)(\mathbf{E}\cdot\mathbf{e}_2) \\ |\mathbf{e}_1\cdot\overline{\mathbf{e}}_2|^2 E^2 \end{bmatrix}^T \begin{bmatrix} -336 & -2016 & -336 & -336 & 252 & -96 \\ 672 & 672 & 672 & 112 & -252 & -48 \\ 42 & 252 & 252 & 252 & -189 & 72 \\ 42 & 252 & 252 & 252 & -189 & 72 \\ -336 & -336 & -2016 & -336 & 252 & -96 \\ 42 & 252 & 252 & 252 & -189 & 72 \\ 0 & 0 & 0 & 0 & 252 & 120 \\ 42 & 252 & 252 & 252 & -189 & 72 \\ 0 & 0 & 0 & 0 & 252 & 120 \end{bmatrix} \begin{bmatrix} T^{(1\alpha)}_{(\lambda\mu)\nu} & \overline{T}^{(1\alpha)}_{(\lambda\mu)\nu} \\ T^{(1\alpha)}_{(\lambda\mu)\nu} & \overline{T}^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} \\ T^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} & \overline{T}^{(1\alpha)}_{(\lambda\mu)\nu} \\ T^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} & \overline{T}^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} \\ T^{(2\beta)}_{(\lambda\mu)\nu} & \overline{T}^{(2\beta)}_{(\lambda\mu)\nu} \\ T^{(3)}_{(\lambda\mu)\nu} & \overline{T}^{(3)}_{(\lambda\mu)\nu} \end{bmatrix}. \tag{4.8}$$

At first, it appears that this case is again of academic interest since matching the frequencies, and thereby the energies, of the two laser beams means that two-beam two-photon absorption cannot be distinguished from single-beam two-photon absorption. Therefore, the values of the polarization parameters in any experiment with $\omega_1 = \omega_2$ cannot be separately determined, unless it is specified to be a single-beam experiment, in which case the symmetry imposed on the nine polarization parameters of Eq. (4.8) (i.e., $\mathbf{e}_1 = \mathbf{e}_2$) reduces them to five independent parameters. The purely electro-optical rate expression then becomes

$$\Gamma = \frac{L_{TPA}}{1260} \begin{bmatrix} (\mathbf{e}\cdot\mathbf{e})(\mathbf{E}\cdot\overline{\mathbf{e}})^2 \\ |\mathbf{e}\cdot\mathbf{e}|^2 E^2 \\ |\mathbf{e}\cdot\mathbf{E}|^2 \\ (\overline{\mathbf{e}}\cdot\overline{\mathbf{e}})(\mathbf{E}\cdot\mathbf{e})^2 \\ E^2 \end{bmatrix}^T \begin{bmatrix} -84 & -504 & -84 & -84 & 63 & -24 \\ 168 & 168 & 168 & 28 & -63 & -12 \\ 42 & 252 & 252 & 252 & -189 & 72 \\ -84 & -84 & -504 & -84 & 63 & -24 \\ 0 & 0 & 0 & 0 & 126 & 60 \end{bmatrix} \begin{bmatrix} T^{(1\alpha)}_{(\lambda\mu)\nu} & \overline{T}^{(1\alpha)}_{(\lambda\mu)\nu} \\ T^{(1\alpha)}_{(\lambda\mu)\nu} & \overline{T}^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} \\ T^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} & \overline{T}^{(1\alpha)}_{(\lambda\mu)\nu} \\ T^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} & \overline{T}^{(1\beta,1\gamma)}_{(\lambda\mu)\nu} \\ T^{(2\beta)}_{(\lambda\mu)\nu} & \overline{T}^{(2\beta)}_{(\lambda\mu)\nu} \\ T^{(3)}_{(\lambda\mu)\nu} & \overline{T}^{(3)}_{(\lambda\mu)\nu} \end{bmatrix}. \tag{4.9}$$

However if counterpropagating laser beams are employed, the signal associated with absorption of one photon from each beam does not suffer the Doppler-broadening associated with absorption of two photons from either beam. The

Doppler-free signal is a well-established experimental feature of the two-photon spectrum in this configuration,[13] and may thus still facilitate the type of analysis outlined above.

If optically allowed transitions are considered, then the

result of Eq. (4.9) represents only one part of a more complex expression applicable to the totally general rate of single-beam EFITPA. The leading term of that expression comes from the $|M_{fi}(a)|^2$ part of the rate expression Eq. (1.2). The first correction term is then $2 \, \text{Re}\{M_{fi}(a) \, \overline{M_{fi}(b)}\}$, with $|M_{fi}(b)|^2$, now given above as Eq. (4.9), representing a second, additional correction term. For an unperturbed single-beam two-photon absorption experiment, the absorption rate contains components of only the even weights-0 and -2 (as demonstrated in Sec. III A). Hence, $M_{fi}(a)$ can, in the single-beam case, only contain these components while $M_{fi}(b)$ contains the odd weights 1–3. Equation (4.9) is therefore the leading correction for weight-1 components and the second order correction term for weight-2 components. It is of course necessary to calculate the cross-term $2 \, \text{Re}\{M_{fi}(a) \, \overline{M_{fi}(b)}\}$ in order to obtain the full rate expression, but attention is drawn to the $|M_{fi}|(b)|^2$ term because it provides the only means of observing a pure weight-3 transition.

V. DISCUSSION

For the electrically polarized channel, the overall rate is a sum of contributions from five terms [Eq. (3.10)]. This represents the isotropic (fourth rank average) result, with a series of additional correction terms to account for the alignment of the absorbing species induced by the electric field. Each successive term increases by one in the power of γ, where $\gamma = \mu^{00} \, E/kT$. By using a plausible electric field strength of 10^8 V m^{-1},[14] and taking a typical value for a transition dipole moment as 1 D ($\equiv 3.3 \times 10^{-30}$ C m), the magnitude of γ at STP is 0.08. The $j_1'(-i\gamma)$ term would thereby provide a contribution to the overall rate that is approximately 8% of the isotropic result. Subsequent terms become increasingly smaller as the power of γ increases, but are obviously far more sensitive to any increase in the electric field strength. The higher-order terms such as $j_2'(-i\gamma)$ may thus still prove significant in cases where the $j_1'(-i\gamma)$ term is zero.

Turning now to the electro-optical channel, the overall rate from Eq. (4.5), is smaller than the rate of two-photon absorption (TPA) by a factor roughly of the order $(\mu^{rs} \cdot E/\Delta E)^2$, where μ^{rs} is a typical transition dipole moment and ΔE is a typical detuning from one-photon resonances. Using the figures given previously, and 5×10^{13} Hz as a typical detuning from resonance, we can estimate that the rate of EFITPA is smaller than the rate of TPA by a factor of 0.004. While the effect is therefore obviously weak, it helps to keep a perspective by noting that it is nonetheless a great deal stronger than three-photon absorption, for which numerous spectra of good resolution have already successfully been obtained.

While the rate of EFITPA (by either channel) is somewhat smaller than that for TPA, the process has been shown to allow access to vibronically excited states totally inaccessible through TPA. The fact that EFITPA can lead to transitions formally forbidden by selection rules in TPA produces the concept of utilizing an external perturbation (in this case

the applied static electric field) to switch transitions into spectra. This concept has been reported before,[6,7] and is perhaps seen here most clearly in the case of a nonpolar centrosymmetric molecule, where only transitions of *gerade* symmetry are allowed under TPA selection rules, whereas in electro-optical EFITPA only *ungerade* transitions are seen. Another significant feature concerns weak two-photon vibronic transitions which occur under the wing of strongly allowed transitions, and are thus difficult to deconvolute from the spectrum. The use of EFITPA techniques to change the relative intensities of different vibronic bands might thus prove valuable in accurately determining the frequency and symmetry character of such weak transitions.

One of the most sensitive detection techniques is the detection of fluorescence after two-photon excitation. The initial absorption of two photons in EFITPA is often likely to be followed by fluorescence from the excited state so formed. The emitted photons can be detected with a high degree of sensitivity using a high-gain photomultiplier. Because there is likely to be a large frequency difference between the incident and emitted photons, filters can be employed to remove the intense light of the laser beams used to excite the molecules, leaving only the fluorescence photons. (The frequency of these emitted photons is generally Stokes shifted from the sum of the two excitation frequencies.) The fluorescence detection method becomes difficult to employ where molecules have a low quantum yield of fluorescence, and in such cases it may be useful to consider resonance-enhanced multiphoton ionization techniques,[14] which offer the additional facility of conjunction with mass spectrometric detection.[15]

In studying the effects of an applied external electric field on the infrared multiphoton dissociation of CF_2HCl, Gozel and van den Bergh[2] recorded an apparent linear relationship between the reaction yield and the square of the field, for field strengths between 0 and 4×10^5 V m^{-1}. This linear dependence of the yield on the square of the field is entirely compatible with our theoretical results if the reaction proceeds via an electro-optical pathway. The matrix element for the electro-optical pathway is linear in the applied field and, thus, the quantum electrodynamical rate for an electro-optical multiphoton absorption process is in general proportional to the square of the field [cf. Eq. (4.5)]. Hence, this observation of Gozel and van den Bergh can be accounted for by ascribing the process to an electro-optical mechanism. However, these authors also noted that, for field strengths in excess of 4×10^5 V/m^{-1}, the observed yield proved to be independent of the field. This may result from appreciable population of excited states, which thereby causes saturation effects to ensure.

The time-dependent perturbation theory employed in this paper produces results which are directly applicable to the system only shortly after application of any intense perturbation, i.e., where the excited states are not appreciably populated, and the majority of the molecules remain in their ground states. The theory is therefore lacking in that it takes no account of the possibility of saturation effects. For instance, if a vibronic state populated through EFITPA is subject to a slow deactivation route, then a population inversion

may result. In cases where this type of effect occurs, additional kinetic constraints have to be incorporated into the theory and methods similar to those which apply to the two-photon laser[16] would be better employed.

ACKNOWLEDGMENT

APPENDIX A: THE GENERAL (AVERAGED) RATE EXPRESSION FOR THE ELECTRO-OPTICAL CHANNEL

The orientationally averaged rate of EFITPA, for the electro-optical channel, is most concisely represented by

$$\langle \Gamma \rangle = K \left[a + b j_1'' (- i\gamma) + c j_2'' (- i\gamma) + d j_3'' (- i\gamma) + e j_4'' (- i\gamma) \right], \tag{A1}$$

where

$$a = \frac{1}{30} \begin{bmatrix} (e_1 \cdot e_2)(\bar{e}_1 \cdot \bar{e}_2) \\ 1 \\ (e_1 \cdot \bar{e}_2)(e_2 \cdot \bar{e}_1) \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} S_{\lambda\lambda}\bar{S}_{\mu\mu} \\ S_{\lambda\mu}\bar{S}_{\lambda\mu} \\ S_{\lambda\mu}\bar{S}_{\mu\lambda} \end{bmatrix}, \tag{A2}$$

$$b = \frac{i}{10} \begin{bmatrix} (e_1 \times e_2)\cdot\hat{E}(\bar{e}_1 \cdot \bar{e}_2) \\ (e_1 \times \bar{e}_1)\cdot\hat{E} \\ (e_1 \times \bar{e}_2)\cdot\hat{E}(e_2 \cdot \bar{e}_1) \\ (e_2 \times \bar{e}_1)\cdot\hat{E}(e_1 \cdot \bar{e}_2) \\ (e_2 \times \bar{e}_2)\cdot\hat{E} \\ (\bar{e}_1 \times \bar{e}_2)\cdot\hat{E}(e_1 \cdot e_2) \end{bmatrix}^T \begin{bmatrix} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{bmatrix} \begin{bmatrix} \epsilon_{\lambda\mu\nu}\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{oo} \\ \epsilon_{\lambda vo}\hat{\mu}_o S_{\lambda\mu}\bar{S}_{\nu\mu} \\ \epsilon_{\lambda ov}\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\mu o} \\ \epsilon_{\mu vo}\hat{\mu}_o S_{\lambda\mu}\bar{S}_{\nu\lambda} \\ \epsilon_{\lambda vo}\hat{\mu}_o S_{\lambda\mu}\bar{S}_{\lambda\nu} \\ \epsilon_{v\mu o}\hat{\mu}_o S_{\lambda\lambda}\bar{S}_{\nu\mu} \end{bmatrix}, \tag{A3}$$

$$c \equiv \frac{i}{14} \begin{bmatrix} (e_1 \cdot e_2)(\hat{E} \cdot \bar{e}_1)(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_1 \cdot e_2)(\bar{e}_1 \cdot \bar{e}_2) \\ (\hat{E} \cdot \bar{e}_2)(\hat{E} \cdot \bar{e}_2) - \frac{1}{3} \\ (e_1 \cdot \bar{e}_2)(E_1 \cdot e_2)(E_2 \cdot \bar{e}_1) - \frac{1}{3}(e \cdot \bar{e}_2)(e_2 \cdot \bar{e}_1) \\ (e_2 \cdot \bar{e}_1)(\hat{E} \cdot \bar{e}_1)(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_2 \cdot \bar{e}_1)(e_1 \cdot \bar{e}_2) \\ (E \cdot e_1)(\hat{E} \cdot \bar{e}_1) - \frac{1}{3} \\ (\bar{e}_1 \cdot \bar{e}_2)(\hat{E} \cdot e_1)(\hat{E} \cdot e_2) - \frac{1}{3}(\bar{e}_1 \cdot \bar{e}_2)(e_1 \cdot e_2) \end{bmatrix}^T$$

$$\times \begin{bmatrix} 11 & -3 & -3 & -3 & -3 & 4 \\ -3 & 11 & -3 & -3 & 4 & -3 \\ -3 & -3 & 11 & 4 & -3 & -3 \\ -3 & -3 & 4 & 11 & -3 & -3 \\ -3 & 4 & -3 & -3 & 11 & -3 \\ 4 & -3 & -3 & -3 & -3 & 11 \end{bmatrix} \begin{bmatrix} \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\lambda}\bar{S}_{\mu\nu} - \frac{1}{3}S_{\lambda\lambda}\bar{S}_{\mu\mu} \\ \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\lambda\nu} - \frac{1}{3}S_{\lambda\mu}\bar{S}_{\lambda\mu} \\ \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\nu\lambda} - \frac{1}{3}S_{\lambda\mu}\bar{S}_{\mu\lambda} \\ \hat{\mu}_\lambda\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\mu\nu} - \frac{1}{3}S_{\lambda\mu}\bar{S}_{\mu\lambda} \\ \hat{\mu}_\lambda\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\nu\mu} - \frac{1}{3}S_{\lambda\mu}\bar{S}_{\lambda\mu} \\ \hat{\mu}_\lambda\hat{\mu}_\mu S_{\lambda\mu}\bar{S}_{\nu\nu} - \frac{1}{3}S_{\lambda\lambda}\bar{S}_{\mu\mu} \end{bmatrix}, \tag{A4}$$

$$d = \frac{-5i}{8} \begin{bmatrix} (e_1 \times \bar{e}_1)\cdot\hat{E}(\hat{E} \cdot e_2)(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_1 \times \bar{e}_1)\cdot e_2(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_1 \times \bar{e}_1)\cdot\bar{e}_2(\hat{E} \cdot e_2) - \frac{1}{3}(e_1 \times \bar{e}_1)\cdot\hat{E} \\ (e_2 \times \bar{e}_1)\cdot\hat{E}(\hat{E} \cdot e_1)(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_2 \times \bar{e}_1)\cdot e_1(\hat{E} \cdot \bar{e}_2) - \frac{1}{3}(e_2 \times \bar{e}_1)\cdot\bar{e}_2(\hat{E} \cdot e_1) - \frac{1}{3}(e_2 \times \bar{e}_1)\cdot\hat{E}(e_1 \cdot \bar{e}_2) \\ (\bar{e}_1 \times \bar{e}_2)\cdot\hat{E}(\hat{E} \cdot e_1)(\hat{E} \cdot e_2) - \frac{1}{3}(\bar{e}_1 \times \bar{e}_2)\cdot e_1(\hat{E} \cdot e_2) - \frac{1}{3}(\bar{e}_1 \times \bar{e}_2)\cdot e_2(\hat{E} \cdot e_1) - \frac{1}{3}(\bar{e}_1 \times \bar{e}_2)\cdot\hat{E}(e_1 \cdot e_2) \end{bmatrix}^T$$

$$\times \begin{bmatrix} 3 & -1 & 1 \\ -1 & 3 & 1 \\ 1 & 1 & 3 \end{bmatrix} \begin{bmatrix} \epsilon_{\lambda vo}\hat{\mu}_\mu\hat{\mu}_\epsilon\hat{\mu}_o - \frac{1}{5}\epsilon_{\lambda v\mu}\hat{\mu}_\epsilon - \frac{1}{5}\epsilon_{\lambda v\epsilon}\hat{\mu}_\mu - \frac{1}{5}\epsilon_{\lambda vo}\hat{\mu}_o\delta_{\mu\epsilon} \\ \epsilon_{\mu vo}\hat{\mu}_\lambda\hat{\mu}_\epsilon\hat{\mu}_o - \frac{1}{5}\epsilon_{\mu v\lambda}\hat{\mu}_\epsilon - \frac{1}{5}\epsilon_{\mu v\epsilon}\hat{\mu}_\lambda - \frac{1}{5}\epsilon_{\mu vo}\hat{\mu}_o\delta_{\lambda\epsilon} \\ \epsilon_{veo}\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_o - \frac{1}{5}\epsilon_{ve\lambda}\hat{\mu}_\mu - \frac{1}{5}\epsilon_{ve\mu}\hat{\mu}_\lambda - \frac{1}{5}\epsilon_{veo}\hat{\mu}_o\delta_{\lambda\mu} \end{bmatrix} S_{\lambda\mu}\bar{S}_{v\epsilon}, \tag{A5}$$

$$e = \frac{35}{8} \left[(\hat{E} \cdot e_1)(\hat{E} \cdot e_2)(\hat{E} \cdot \bar{e}_1)(\hat{E} \cdot \bar{e}_2) - \frac{1}{7}\{(e_1 \cdot e_2)(\hat{E} \cdot \bar{e}_1)(\hat{E} \cdot \bar{e}_2) \right.$$

$$+ (\hat{E} \cdot e_2)(\hat{E} \cdot \bar{e}_2) + (e_2 \cdot \bar{e}_1)(\hat{E} \cdot e_1)(\hat{E} \cdot \bar{e}_2) + (\hat{E} \cdot e_1)(\hat{E} \cdot \bar{e}_2)$$

$$+ (e_1 \cdot \bar{e}_2)(\hat{E} \cdot \bar{e}_1)(\hat{E} \cdot e_2) + (\bar{e}_2 \cdot \bar{e}_1)(\hat{E} \cdot e_1)(\hat{E} \cdot e_2)\}$$

$$+ \frac{1}{35}\{(e_1 \cdot e_2)(\bar{e}_1 \cdot \bar{e}_2) + 1 + (e_1 \cdot \bar{e}_2)(e_2 \cdot \bar{e}_1)\} \left] \left[\hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu\hat{\mu}_o - \frac{1}{7}\{\delta_{\lambda\mu}\hat{\mu}_\nu\hat{\mu}_o + \delta_{\lambda\nu}\hat{\mu}_\mu\hat{\mu}_o \right.\right.$$

$$+ \delta_{\lambda o}\hat{\mu}_\mu\hat{\mu}_\nu + \delta_{\mu\nu}\hat{\mu}_\lambda\hat{\mu}_o + \delta_{\mu o}\hat{\mu}_\lambda\hat{\mu}_\nu + \delta_{vo}\hat{\mu}_\lambda\hat{\mu}_\mu\}$$

$$+ \frac{1}{35}\{\delta_{\lambda\mu}\delta_{vo} + \delta_{\lambda\nu}\delta_{\mu o} + \delta_{\lambda o}\delta_{\mu\nu}\} \left] S_{\lambda\mu}\bar{S}_{vo}. \tag{A6}$$

APPENDIX B

The quantities S_0, S_2, and S_4 appearing in Sec. III are defined as follows:

$$S_0 = S_{\lambda\mu}\bar{S}_{\lambda\mu} + S_{\lambda\mu}\bar{S}_{\mu\lambda} + S_{\lambda\lambda}\bar{S}_{\mu\mu}, \tag{B1}$$

$$S_2 = \hat{\mu}_\lambda\hat{\mu}_\mu S_{\lambda\mu}\bar{S}_{\nu\nu} + \hat{\mu}_\lambda\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\nu\mu} \tag{B2}$$

$$+ \hat{\mu}_\lambda\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\mu\nu} + \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\nu\lambda}$$

$$+ \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\mu}\bar{S}_{\lambda\nu} = \hat{\mu}_\mu\hat{\mu}_\nu S_{\lambda\lambda}\bar{S}_{\mu\nu},$$

$$S_4 = \hat{\mu}_\lambda\hat{\mu}_\mu\hat{\mu}_\nu\hat{\mu}_o S_{\lambda\mu}\bar{S}_{\nu o}. \tag{B3}$$

APPENDIX C: PROOF THAT S_2 AND S_4 CONTAIN COMPONENTS OF WEIGHTS 0, 1, AND 2

The molecular tensor $S_{\lambda\mu}$ has components of weights 0, 1, and 2 and the possible weights produced by the contraction of $S_{\lambda\mu}$ and $\bar{S}_{\nu o}$ can be tabulated as follows

$S_{\lambda\mu}\bar{S}_{\nu o}$		$\bar{S}_{\nu o}$ allowed weights		
		0	1	2
$S_{\mu\nu}$	0	0	1	2
allowed weights	1	1	012	123
	2	2	123	01234

However, the product $S_{\lambda\mu}\bar{S}_{\lambda\nu}$ can have only weights 0, 1, and 2 (since it has one pair of common indices and two hanging indices), and contraction of this product with $\hat{\mu}_\lambda$ can be represented by

$S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu$		$\hat{\mu}_\mu$ allowed weight
		1
$S_{\lambda\mu}\bar{S}_{\lambda\nu}$	0	1
allowed weights	1	012
	2	123

Since $S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu$ has only one hanging index it can have only weight 1. Contraction with $\hat{\mu}_\nu$ produces $S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu\hat{\mu}_\nu$ which,

since all indices are summed in pairs, must have an overall character of weight-0, i.e., a scalar.

$S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu\hat{\mu}_\nu$		$\hat{\mu}_\nu$ allowed weight
		1
$S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu$	1	012
allowed weights		

Now, since $S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu\hat{\mu}_\nu$ must be of purely weight-0 character, it can be seen from above that it must arise from a contraction involving the weight-1 component of $S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu$. This can in turn arise from any of weights 0, 1, and 2 of $S_{\lambda\mu}\bar{S}_{\lambda\nu}$ (see above). Since $S_{\lambda\mu}\bar{S}_{\lambda\nu}$ can be any of weights 0, 1, and 2, the result can evidently originate from the combination of any weight of $S_{\lambda\mu}$ with any weight of $\bar{S}_{\lambda\nu}$.

Thus it has been shown that the terms contributing to $S_{\lambda\mu}\bar{S}_{\lambda\nu}\hat{\mu}_\mu\hat{\mu}_\nu$ contain molecular tensors of weights 0, 1, and 2. A similar argument to that developed above may be employed to demonstrate that every component of S_2 and S_4 involves tensors of weight 0, 1, and 2 character.

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