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Cooperative mean-frequency absorption: A two-beam two-photon process

David L. Andrews and Kevin P. Hopkins

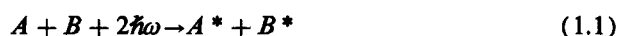
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England

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It is shown that by a cooperative process involving virtual photon coupling between molecules, pairwise two-photon absorption can lead to molecular transitions associated with the mean of the laser frequencies in a two-beam experiment. The process is represented by $A + A + \hbar\omega_1 + \hbar\omega_2 \rightarrow A^* + A^*$, and the selection rules are those normally applicable to two-photon absorption. The interaction may involve the excitation of chromophore pairs in polyatomic molecules, van der Waals molecules, or more usually discrete molecules in a gas or liquid. In the former case, however, dissymmetric juxtaposition of the chromophores produces a chirality which is manifest in a circular dichroism associated with the absorption process. The appropriate absorption rates are calculated using the methods of quantum electrodynamics, and the dependence on the separation of the interacting pair is examined in detail. Methods for observing the mean-frequency interaction are also outlined, and attention is drawn to a resonance condition which should appreciably enhance the absorption rate.

I. INTRODUCTION

In two previous papers,^{1,2} the methods of quantum electrodynamics (QED) have been applied to a nonlinear optical process in which two chemical centers, which may be either distinct chromophores in a single molecule, or separate molecules, undergo cooperative excitation through two-photon absorption from an intense laser beam. The interaction between the two centers, mediated by virtual photon coupling, provides the mechanism for energy exchange such that the overall process



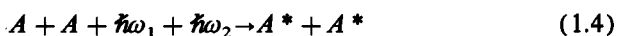
can take place even when the individual transitions $A \rightarrow A^*$ and $B \rightarrow B^*$ are forbidden on energy grounds, as illustrated in Fig. 1(a). For this cooperative process to be experimentally observable, ω must be chosen to lie in a region where neither A nor B display absorption, and we thus have

$$\hbar\omega = \frac{1}{2}(E_{\alpha 0} + E_{\beta 0}), \quad (1.2)$$

$$\hbar\omega \neq E_{\alpha 0}, E_{\beta 0}. \quad (1.3)$$

A number of other theoretical and experimental studies of this type of process have been made, most of which deal with atomic, rather than molecular excitations.³⁻⁵

In the present paper, we consider the converse case in which the two centers have identical chemical composition, and are cooperatively excited by two-photon absorption at the intersection of *two* laser beams with differing frequencies ω_1 and ω_2 . Hence, the process to be discussed can be represented by the equation



for which the energetics are shown in Fig. 1(b). Again, we specify that the frequencies ω_1 and ω_2 are chosen in a region where single-photon absorption cannot lead to the direct excitation of either center; we also specify that the final state is accessible through a two-photon, but not a one-photon electric dipole interaction (cf. Ref. 1). Thus we have

$$\frac{1}{2}(\hbar\omega_1 + \hbar\omega_2) = E_{\alpha 0}, \quad (1.5)$$

$$\hbar\omega_1, \hbar\omega_2 \neq E_{\alpha 0}. \quad (1.6)$$

The former relation (1.5) illustrates the fact that from a phenomenological point of view, this cooperative process has the characteristics of *mean frequency absorption*.

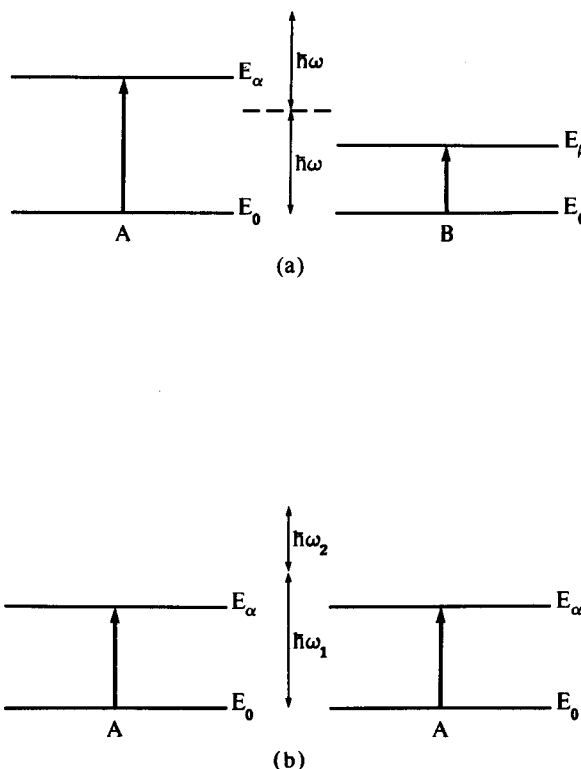


FIG. 1. Cooperative two-photon absorption processes; (a) with single-frequency excitation of a chemically inequivalent pair, and (b) with two-frequency excitation of a chemically equivalent pair.

II. QUANTUM ELECTRODYNAMICAL CALCULATIONS

The quantum electrodynamical methods on which our calculations are based have recently been reviewed in the book by Craig and Thirunamachandran.⁶ This text has established the rigorous use of SI units in molecular QED, and we have adopted the same conventions in the present paper. This represents a departure from the two earlier papers^{1,2} in which equations were cast in Gaussian units. For this reason, we include salient SI definitions in our derivation below.

Results are calculated within the electric dipole approximation for each molecular center ξ , which is equivalent to the inclusion of higher order multipole terms for the pair. Hence, the interaction operator is given by

$$H_{\text{int}}(\xi) = -\epsilon_0^{-1} \mu(\xi) \cdot \mathbf{d}^\perp(\mathbf{R}_\xi), \quad (2.1)$$

where $\mu(\xi)$ is the electric dipole moment operator for molecule ξ at position \mathbf{R}_ξ , and \mathbf{d}^\perp is the transverse electric displacement operator, which has the mode expansion;

$$\mathbf{d}^\perp(\mathbf{r}) = i \sum_{\mathbf{k}, \lambda} \left(\frac{\hbar c \epsilon_0}{2V} \right)^{1/2} \{ \mathbf{e}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} - \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) a^{\dagger(\lambda)}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{r}} \}, \quad (2.2)$$

in which other symbols have their usual meaning. The initial state $|i\rangle$ and the final state $|f\rangle$ for the cooperative absorption process defined by Eq. (1.4) can be represented by

$$|i\rangle = |0; 0; n_1; n_2; 0\rangle, \quad (2.3)$$

$$|f\rangle = |\alpha; \alpha; (n_1 - 1); (n_2 - 1); 0\rangle. \quad (2.4)$$

Here the sequence in each ket denotes: the state of A_1 ; the state of A_2 ; the number of photons in beam 1, the number of photons in beam 2; the number of virtual photons s , and the two A species are differentiated by labeling them A_1 and A_2 . Beam 1 is characterized by polarization vector \mathbf{e}_1 , wave vector \mathbf{k}_1 , and frequency $\omega_1 = c|\mathbf{k}_1|$; beam 2 is similarly characterized by \mathbf{e}_2 , \mathbf{k}_2 , and ω_2 .

$$\begin{aligned} M_{fi}^{(1)} = & \sum_r \sum_s \sum_{\mathbf{k}} \sum_{\epsilon} \langle \alpha; \alpha; (n_1 - 1); (n_2 - 1); 0 | H_{\text{int}} | \alpha; s; (n_1 - 1); n_2; 0 \rangle \\ & \times \langle \alpha; s; (n_1 - 1); n_2; 0 | H_{\text{int}} | \alpha; 0; (n_1 - 1); n_2; 1 \rangle \\ & \times \langle \alpha; 0; (n_1 - 1); n_2; 1 | H_{\text{int}} | r; 0; (n_1 - 1); n_2; 0 \rangle \langle r; 0; (n_1 - 1); n_2; 0 | H_{\text{int}} | 0; 0; n_1; n_2; 0 \rangle \\ & \times \{ (E_{0\alpha} + E_{0s} + \hbar\omega_1)(E_{0\alpha} + \hbar\omega_1 - \hbar c\kappa)(E_{0r} + \hbar\omega_1) \}^{-1}. \end{aligned} \quad (2.5)$$

Summing all 48 such contributions leads to the following result:

$$\begin{aligned} M_{fi} = & - \left(\frac{\hbar c}{2V\epsilon_0} \right)^2 (n_1 n_2 k_1 k_2)^{1/2} \sum_{\kappa, \epsilon} \bar{\epsilon}_\kappa \epsilon_\kappa \\ & \times \left[e_{1i} e_{2j} e^{i(\mathbf{k}_1 \cdot \mathbf{R}_{A_1} + \mathbf{k}_1 \cdot \mathbf{R}_{A_2})} S_{ik}^{\alpha 0}(\omega_1) S_{jl}^{\alpha 0}(\omega_2) \left[\frac{e^{i\mathbf{k} \cdot \mathbf{R}}}{(E_{\alpha 0} - \hbar c k_1 - \hbar c \kappa)} - \frac{e^{-i\mathbf{k} \cdot \mathbf{R}}}{(E_{\alpha 0} - \hbar c k_1 + \hbar c \kappa)} \right] \right. \\ & \left. + e_{1j} e_{2i} e^{i(\mathbf{k}_1 \cdot \mathbf{R}_{A_1} + \mathbf{k}_2 \cdot \mathbf{R}_{A_2})} S_{ik}^{\alpha 0}(\omega_2) S_{jl}^{\alpha 0}(\omega_1) \left[\frac{e^{i\mathbf{k} \cdot \mathbf{R}}}{(E_{\alpha 0} - \hbar c k_2 - \hbar c \kappa)} - \frac{e^{-i\mathbf{k} \cdot \mathbf{R}}}{(E_{\alpha 0} - \hbar c k_2 + \hbar c \kappa)} \right] \right], \end{aligned} \quad (2.6)$$

using the implied summation convention for repeated tensor indices; the molecular tensors $S^{\alpha 0}(\omega_1)$, $S^{\alpha 0}(\omega_2)$ are to be understood as generalizations of the tensor defined by Eq. (2.12) of Ref. 1, i.e.,

$$S_{ij}^{\alpha 0}(\omega_1) = \sum_r \left[\frac{\mu_i^{\alpha r} \mu_j^{r 0}}{(E_{\alpha r} - \hbar\omega_1)} - \frac{\mu_j^{\alpha r} \mu_i^{r 0}}{(E_{r 0} - \hbar\omega_1)} \right] \quad (2.7)$$

with a similar expression for $S_{ij}^{\alpha 0}(\omega_2)$.

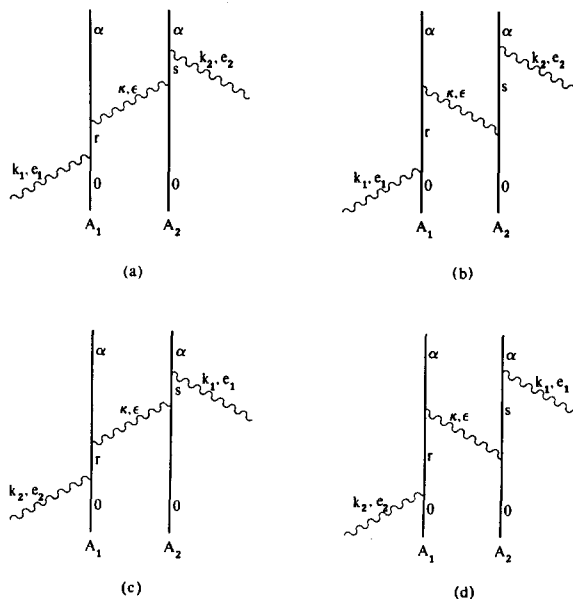


FIG. 2. Four typical time-ordered diagrams for two-beam two-photon cooperative absorption.

The rate of cooperative excitation is determined from the Fermi Rule using fourth-order time-dependent perturbation theory. The appropriate matrix element M_{fi} can be constructed in the usual way with the aid of time-ordered diagrams. Only diagrams in which each of the two real photons is absorbed at a different center contribute; the possibility of both real photons being absorbed at the same center would necessitate excitation of its partner by a single virtual photon interaction, which we have specified is electric-dipole forbidden. There remain 48 diagrams to be taken into consideration; Fig. 2 illustrates four typical cases. The matrix element contribution corresponding to Fig. 2(a), for example, is as follows:

The sum over the virtual photon wave vector κ and polarization ϵ in equation (2.6) is effected by a method described in detail elsewhere.⁷ The result is as follows:

$$M_{fi} = - \left(\frac{\hbar c}{2V\epsilon_0^2} \right) (n_1 n_2 k_1 k_2)^{1/2} e^{i(\mathbf{k}_2 \cdot \mathbf{R}_{A_1} + \mathbf{k}_1 \cdot \mathbf{R}_{A_2})} \\ \times [e_{1i} e_{2j} S_{ik}^{\alpha 0}(\omega_1) S_{jl}^{\alpha 0}(\omega_2) V_{kl}(\gamma_1, \mathbf{R}) \\ + e_{1j} e_{2i} S_{ik}^{\alpha 0}(\omega_2) S_{jl}^{\alpha 0}(\omega_1) V_{kl}(\gamma_2, \mathbf{R}) e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}}], \quad (2.8)$$

where the vector \mathbf{R} defines the location of A_2 relative to A_1 , i.e., $\mathbf{R} = \mathbf{R}_{A_2} - \mathbf{R}_{A_1}$. The two parameters γ_1 and γ_2 are defined by

$$\hbar c \gamma_1 = E_{\alpha 0} - \hbar \omega_1; \quad (2.9)$$

$$\hbar c \gamma_2 = E_{\alpha 0} - \hbar \omega_2 \quad (2.10)$$

and thereby effectively denote the energy transferred between the two centers by the virtual photon; $V_{kl}(\gamma, \mathbf{R})$ is the complex retarded resonance electric dipole-electric dipole interaction^{7,8};

$$V_{kl}(\gamma, \mathbf{R}) = \frac{1}{4\pi\epsilon_0 R^3} [(\delta_{kl} - 3\hat{R}_k \hat{R}_l) \\ \times (\cos \gamma R + \gamma R \sin \gamma R) \\ - (\delta_{kl} - \hat{R}_k \hat{R}_l) \gamma^2 R^2 \cos \gamma R \\ + i\{(\delta_{kl} - 3\hat{R}_k \hat{R}_l)(\sin \gamma R - \gamma R \cos \gamma R) \\ - (\delta_{kl} - \hat{R}_k \hat{R}_l) \gamma^2 R^2 \sin \gamma R\}]. \quad (2.11)$$

Thus from Eq. (2.8) the Fermi Rule gives the following result for the cooperative absorption rate;

$$\Gamma = K e_{1i} e_{2j} \bar{e}_{1m} \bar{e}_{2n} S_{ik}^{\alpha 0}(\omega_1) S_{jl}^{\alpha 0}(\omega_2) \bar{S}_{mo}^{\alpha 0}(\omega_1) \bar{S}_{np}^{\alpha 0}(\omega_2) \\ \times [V_{kl}(\gamma_1, \mathbf{R}) \bar{V}_{op}(\gamma_1, \mathbf{R}) + V_{kl}(\gamma_2, \mathbf{R}) \bar{V}_{op}(\gamma_2, \mathbf{R}) \\ + V_{kl}(\gamma_1, \mathbf{R}) \bar{V}_{op}(\gamma_2, \mathbf{R}) e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}} \\ + V_{kl}(\gamma_2, \mathbf{R}) \bar{V}_{op}(\gamma_1, \mathbf{R}) e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}}], \quad (2.12)$$

where

$$K = \frac{\pi \rho_f I_1 I_2}{2\hbar c^2 \epsilon_0^4} \quad (2.13)$$

and in which the density of final states for the system is given by the autocorrelation function

$$\rho_f = \int \rho_\alpha(\epsilon) \rho_\alpha(\hbar \omega_1 + \hbar \omega_2 - \epsilon) d\epsilon. \quad (2.14)$$

The general result of Eq. (2.12) is applicable to two molecules in a fixed orientation with respect to each other and to the two laser beams. In contrast to the corresponding theory of the single-beam two-photon allowed cooperative process,¹ the interference terms in Eq. (2.12) carry phase factors which complicate the usual procedure of rotational averaging required to derive the corresponding result for a fluid sample. This introduces various novel features which are described in detail in the following sections.

III. GENERAL RESULTS FOR FLUID MEDIA

In order to obtain a rate equation appropriate to fluid media, a rotational average of Eq. (2.12) has to be per-

formed to account for the random orientation of the A_1 - A_2 system. The methodology for this calculation has been described in detail previously^{1,2}; we therefore simply note that while the first and second terms in Eq. (2.12) require only a straightforward fourth-rank tensor average,⁹ the third and fourth terms require a *phased* fourth-rank tensor average, the result for which has only recently been calculated.¹⁰

The result of this rotational averaging is a rate equation which is most concisely expressed in matrix form, and is cast in terms of polarization parameters denoted by $A^{(j,p)}$ and molecular invariants denoted by $T^{(j,q)}(\gamma_1, \gamma_2)$.

These are defined as follows:

$$A^{(j,p)} = e_{1i} e_{2j} \bar{e}_{1k} \bar{e}_{2l} U_{ijkl}^{(4;j,p)}(\hat{\mathbf{u}}), \quad (3.1)$$

$$T^{(j,q)}(\gamma_1, \gamma_2) = S_{\lambda\pi}^{\alpha 0}(\omega_1) S_{\mu\rho}^{\alpha 0}(\omega_2) \bar{S}_{\nu\sigma}^{\alpha 0}(\omega_1) \bar{S}_{\tau\theta}^{\alpha 0}(\omega_2) \\ \times V_{\pi\rho}(\gamma_1, \mathbf{R}) \bar{V}_{\sigma\theta}(\gamma_2, \mathbf{R}) W_{\lambda\mu\nu\sigma}^{(4;j,q)}(\hat{\mathbf{R}}), \quad (3.2)$$

where $\mathbf{u} = (\mathbf{k}_2 - \mathbf{k}_1)$ and $U_{ijkl}^{(4;j,p)}$, $W_{\lambda\mu\nu\sigma}^{(4;j,q)}$ are tensor projections given explicitly in Ref. 10. The explicit forms of the polarization parameters, which are experimentally variable, are listed in Table I. For example, $A^{(0,1)}$ is obtained from the tensor contraction of $e_{1i} e_{2j} \bar{e}_{1k} \bar{e}_{2l}$ with $U_{ijkl}^{(4;0,1)} = \delta_{ij} \delta_{kl}$, giving $(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_1 \cdot \mathbf{e}_2)$. Equally, $A^{(1;1)}$ results from the contraction of $e_{1i} e_{2j} \bar{e}_{1k} \bar{e}_{2l}$ with $U_{ijkl}^{(4;1,1)}(\hat{\mathbf{u}}) = \epsilon_{ijm} \hat{u}_m \delta_{kl}$ giving $(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_1 \times \mathbf{e}_2) \cdot \hat{\mathbf{u}}$. The molecular tensor invariants $T^{(j,q)}(\gamma_1, \gamma_2)$ are constructed in an exactly similar way, and are listed in Table II.

TABLE I. Explicit form of the polarization parameters $A^{(j,p)}$.

j	p	$A^{(j,p)}$
0	1	$(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)$
0	2	1
0	3	$(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)$
1	1	$(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_1 \times \mathbf{e}_2) \cdot \hat{\mathbf{u}}$
1	2	$(\mathbf{e}_1 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}$
1	3	$(\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)(\mathbf{e}_1 \times \bar{\mathbf{e}}_2) \cdot \hat{\mathbf{u}}$
1	4	$(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_2 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}$
1	5	$(\mathbf{e}_2 \times \bar{\mathbf{e}}_2) \cdot \hat{\mathbf{u}}$
1	6	$(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \times \bar{\mathbf{e}}_2) \cdot \hat{\mathbf{u}}$
2	1	$(\mathbf{e}_1 \cdot \mathbf{e}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)$
2	2	$(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}$
2	3	$(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)$
2	4	$(\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}(\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)$
2	5	$(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1) - \frac{1}{3}$
2	6	$(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_1 \cdot \mathbf{e}_2)$
3	1	$(\mathbf{e}_1 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}[(\mathbf{e}_1 \times \bar{\mathbf{e}}_1) \cdot \mathbf{e}_2(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) \\ + (\mathbf{e}_1 \times \bar{\mathbf{e}}_1) \cdot \bar{\mathbf{e}}_2(\hat{\mathbf{u}} \cdot \mathbf{e}_2) + (\mathbf{e}_1 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}]$
3	2	$(\mathbf{e}_2 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}[(\mathbf{e}_2 \times \bar{\mathbf{e}}_1) \cdot \mathbf{e}_1(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) \\ + (\mathbf{e}_2 \times \bar{\mathbf{e}}_1) \cdot \bar{\mathbf{e}}_2(\hat{\mathbf{u}} \cdot \mathbf{e}_1) + (\mathbf{e}_2 \times \bar{\mathbf{e}}_1) \cdot \hat{\mathbf{u}}(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)]$
3	3	$(\bar{\mathbf{e}}_1 \times \bar{\mathbf{e}}_2) \cdot \hat{\mathbf{u}}(\hat{\mathbf{u}} \cdot \mathbf{e}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}[(\bar{\mathbf{e}}_1 \times \bar{\mathbf{e}}_2) \cdot \mathbf{e}_1(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) \\ + (\bar{\mathbf{e}}_1 \times \bar{\mathbf{e}}_2) \cdot \mathbf{e}_2(\hat{\mathbf{u}} \cdot \mathbf{e}_1) + (\bar{\mathbf{e}}_1 \times \bar{\mathbf{e}}_2) \cdot \hat{\mathbf{u}}(\mathbf{e}_1 \cdot \mathbf{e}_2)]$
4	1	$(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) - \frac{1}{3}[(\mathbf{e}_1 \cdot \mathbf{e}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) \\ + (\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) + (\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) \\ + (\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2) + (\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1) \\ + (\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_1)(\hat{\mathbf{u}} \cdot \bar{\mathbf{e}}_2)] + \frac{1}{33}[(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) \\ + 1 + (\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\mathbf{e}_2 \cdot \bar{\mathbf{e}}_1)]$

TABLE II. Explicit form of the molecular tensor invariants, $T^{(jq)} = Z_{\sigma\mu\sigma\tau}^{(jq)} \times V_{\sigma\mu}(\gamma_1, \mathbf{R}) \bar{V}_{\sigma\tau}(\gamma_2, \mathbf{R})$.

j	q	$Z_{\sigma\mu\sigma\tau}^{(jq)}$
0	1	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\lambda\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
0	2	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\lambda\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
0	3	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\lambda\tau}^{\sigma\sigma}(\omega_2)$
1	1	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
1	2	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
1	3	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
1	4	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
1	5	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
1	6	$\epsilon_{\lambda\mu\nu} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	1	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	2	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	3	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	4	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	5	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
2	6	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $- \frac{1}{2} S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$
3	1	$\frac{1}{2} \epsilon_{\lambda\mu\nu} \{ S_{\lambda\pi}^{\sigma\sigma} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \}$
3	2	$\frac{1}{2} \epsilon_{\lambda\mu\nu} \{ S_{\lambda\pi}^{\sigma\sigma} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \}$
3	3	$\frac{1}{2} \epsilon_{\lambda\mu\nu} \{ S_{\lambda\pi}^{\sigma\sigma} \hat{R}_\nu S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\sigma S_{\mu\mu}^{\sigma\sigma}(\omega_1) S_{\lambda\pi}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $- \hat{R}_\nu S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \}$
4	1	$S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu \hat{R}_\sigma$ $- \frac{1}{2} \{ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \hat{R}_\mu \hat{R}_\nu$ $+ \frac{1}{2} \{ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2)$ $+ S_{\lambda\pi}^{\sigma\sigma}(\omega_1) S_{\mu\mu}^{\sigma\sigma}(\omega_2) \bar{S}_{\mu\sigma}^{\sigma\sigma}(\omega_1) \bar{S}_{\mu\tau}^{\sigma\sigma}(\omega_2) \}$

The rotationally averaged rate can be concisely expressed by the following equation:

$$\Gamma = K \left\{ \sum_{p,q} g_{(4,0)}^{pq} A^{(0;p)} T^{(0;q)}(\gamma_1, \gamma_1) + \sum_{j=0}^4 \sum_{p,q} \frac{(2j)!}{2^j(j!)^2} i^j j_j(\alpha) g_{(4,j)}^{pq} A^{(j;p)} T^{(j;q)}(\gamma_1, \gamma_2) \right\} + \{\gamma_1 \leftrightarrow \gamma_2\}. \quad (3.3)$$

Here $j_j(\alpha)$ denote spherical Bessel functions of order j , where $\alpha = |\mathbf{k}_2 - \mathbf{k}_1|R$ and $g_{(4,j)}^{pq}$ are numerical coefficients which may be found tabulated in the literature. (Refer to the

right-hand column of Table I in Ref. 11, where the heading should read $g_{(4,j)}^{pq}$ rather than g^{pq}).

The above result (3.3) is directly applicable to the situation in which the centers A_1 and A_2 are held in a fixed mutual orientation, but where the pair is free to rotate. This could, for example, correspond to cases where A_1 and A_2 represent chromophores of the same chemical composition in a relatively large molecule, or else a van der Waals dimer. For the situation in which the two centers are additionally free to rotate with respect to each other, as for example where they represent individual molecules in a gas, or molecules separated by more than the extent of short-range order in a liquid, then the same equation (3.3) can be utilized if each $T^{(jq)}$ is replaced by its rotational average $\langle T^{(jq)} \rangle$. This is obtained by first averaging over the orientation of A_2 with respect to A_1 , and then averaging over the orientation of the displacement vector \mathbf{R} with respect to A_1 . This procedure has been discussed in detail in Refs. 1 and 2.

Perhaps the most important difference in the result for a pair of free molecules is the absence of the $j=1$ and $j=3$ terms in the counterpart to Eq. (3.3). The reason for this is more clearly evident by obtaining the result through an alternative, but equivalent, series of rotational averages in which first A_1 and A_2 are averaged with respect to \mathbf{R} , and then \mathbf{R} is averaged with respect to the laboratory frame. This final average carries the phase factor, and the $j=1, 3$ contributions to the result disappear since they are associated with the contraction of a Levi-Civita antisymmetric tensor with a string of \hat{R} vectors. The significance of this feature is pointed out in Sec. V.

IV. DEPENDENCE ON THE PAIR SEPARATION

While the results of the last section are applicable to an unrestricted range of distances between the two centers, it is instructive to examine the limiting form of the short- and long-range behavior. First, we consider the near-zone, where the following conditions are satisfied;

$$|\gamma_1|R, |\gamma_2|R \ll 1 \quad (4.1)$$

and

$$|\mathbf{k}_2 - \mathbf{k}_1|R \ll 1. \quad (4.2)$$

Equation (4.1) places a lower limit on R of the order $\lambda_{\sigma\sigma}/2\pi$, where $\lambda_{\sigma\sigma}$ is the wavelength corresponding to the excitation energy $E_{\sigma\sigma}$, i.e., $\lambda_{\sigma\sigma} = hc/E_{\sigma\sigma}$. Equation (4.2) however, which essentially allows the phase factors in the rate equation to be approximated by unity, places a more stringent condition upon the range of R , and has a lower limit $\lambda_{\sigma\sigma}/4\pi$. Thus, for example, if the excitation energy corresponds to a wavelength of 600 nm in the visible range, the near-zone approximation will be applicable for separations $R \ll 50$ nm. The results will therefore be valid for most cases of fixed chromophore pairs or van der Waals dimers.

Since in the short-range limit, the spherical Bessel functions $j_j(\alpha)$ fall off as α^{-j} , all contributions to the sum over j in the second part of Eq. (3.3) can be neglected, except for the $j=0$ term. Also the appropriate form of the retarded resonance electric dipole-electric dipole interaction is the limiting near-zone (static) result;

$$\lim_{\gamma R \ll 1} V_{kl}(\gamma, \mathbf{R}) = V_{kl}(0, \mathbf{R}) = \frac{1}{4\pi\epsilon_0 R^3} (\delta_{kl} - 3\hat{R}_k\hat{R}_l) \quad (4.3)$$

which we note is traceless. Since the limit has R^{-3} dependence, the corresponding near-zone rate expressions vary as

R^{-6} and thus cooperative absorption involving pairs of *free* molecules will also mostly occur within the near-zone. The general result (3.3) reduces to a particularly simple form under these conditions, and is explicitly expressed by the following equations:

(a) Chromophore pair (near-zone)

$$\begin{aligned} \Gamma = \frac{K}{120\pi^2\epsilon_0^2 R^6} [& \{4(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - 1 - (\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2)\} S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\sigma\pi}^{\alpha 0}(\omega_1) S_{\lambda\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\rho}^{\alpha 0}(\omega_2) \\ & + \{ - (\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) + 4 - (\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\lambda\pi}^{\alpha 0}(\omega_1) S_{\sigma\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\rho}^{\alpha 0}(\omega_2) \\ & + \{ - (\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - 1 + 4(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\sigma\pi}^{\alpha 0}(\omega_1) S_{\sigma\nu}^{\alpha 0}(\omega_2) \bar{S}_{\lambda\rho}^{\alpha 0}(\omega_2)] \\ & \times (\delta_{\mu\nu} - 3\hat{R}_\mu\hat{R}_\nu)(\delta_{\pi\rho} - 3\hat{R}_\pi\hat{R}_\rho). \end{aligned} \quad (4.4)$$

(b) Free molecules (near-zone)

$$\begin{aligned} \Gamma = \frac{K}{18000\pi^2\epsilon_0^2 R^6} [& -58(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - 3 + 67(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} \\ & \times \{ S_{\lambda\lambda}^{\alpha 0}(\omega_1) \bar{S}_{\mu\mu}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\sigma}^{\alpha 0}(\omega_2) + S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\mu\lambda}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2) \} \\ & + \{ -3(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) + 2 - 3(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} \{ S_{\lambda\lambda}^{\alpha 0}(\omega_1) \bar{S}_{\mu\mu}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2) \\ & + S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\lambda\mu}^{\alpha 0}(\omega_1) (S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\sigma}^{\alpha 0}(\omega_2) + S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\lambda\mu}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2) \\ & + S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\mu\lambda}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2) \} + \{ 67(\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) - 3 - 58(\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} \\ & \times \{ S_{\lambda\lambda}^{\alpha 0}(\omega_1) \bar{S}_{\mu\mu}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2) + S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\mu\lambda}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\sigma}^{\alpha 0}(\omega_2) \} \\ & + 2\{ (\mathbf{e}_1 \cdot \mathbf{e}_2)(\bar{\mathbf{e}}_1 \cdot \bar{\mathbf{e}}_2) + 166 + (\mathbf{e}_1 \cdot \bar{\mathbf{e}}_2)(\bar{\mathbf{e}}_1 \cdot \mathbf{e}_2) \} S_{\lambda\mu}^{\alpha 0}(\omega_1) \bar{S}_{\lambda\mu}^{\alpha 0}(\omega_1) S_{\nu\nu}^{\alpha 0}(\omega_2) \bar{S}_{\sigma\nu}^{\alpha 0}(\omega_2)]. \end{aligned} \quad (4.5)$$

Finally, we note that for free molecules separated by large distances where $(|\gamma_1|R, |\gamma_2|R, |\mathbf{k}_2 - \mathbf{k}_1|R) \gg 1$, all of the spherical Bessel functions contribute to the result and the long-range behavior is determined by the limit

$$\lim_{\gamma R \gg 1} V_{kl}(\gamma, \mathbf{R}) = \frac{\gamma^2}{4\pi\epsilon_0 R} (\hat{R}_k\hat{R}_l - \delta_{kl}) e^{i\gamma R} \quad (4.6)$$

which is purely transverse with respect to the intermolecular vector \mathbf{R} . The phase factor disappears in the rate equation and the result thus has a simple limiting inverse-square dependence on the molecular separation. The explicit form of the result for a chromophore pair follows directly from Eq. (3.3). For the case of two free molecules, the explicit long-range result has a very lengthy expression, and is available as a supplementary publication for this paper.¹⁸

V. POLARIZATION DEPENDENCE

As mentioned earlier, the 19 polarization parameters $A^{(j,p)}$ listed in Table I are experimentally variable. For any particular laser beam and polarization geometry, their values can be directly calculated and inserted into Eqs. (3.3), (4.4), and (4.5) to give the corresponding rates. In this section we consider a number of polarization combinations in which the two laser beams are collinear. This represents the experimentally most useful case since it maximizes the volume of a sample traversed by both beams. The values of $A^{(j,p)}$ for seven particular combinations of plane and circular polarizations are listed in Table III.

Where both laser beams are plane polarized, the result is worth considering both for parallel and for perpendicular

TABLE III. Values of the polarization parameters $A^{(j,p)}$ for seven polarization combinations with copropagating beams.

j	p	$e_1^p \ e_2^p$	$e_1^p \perp e_2^p$	$e_1^p; e_2^p$	$e_1^p; e_2^p$	$e_1^p; e_2^p$	$e_1^p; e_2^p$	$e_1^p; e_2^p$
0	1	1	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	1
0	2	1	1	1	1	1	1	1
0	3	1	0	$\frac{1}{2}$	$\frac{1}{2}$	1	1	0
1	1	0	0	$i/2$	$-i/2$	0	0	$-i$
1	2	0	0	0	0	$-i$	i	$-i$
1	3	0	0	$-i/2$	$i/2$	$-i$	i	0
1	4	0	0	$-i/2$	$i/2$	$-i$	i	0
1	5	0	0	$-i$	i	$-i$	i	i
1	6	0	0	$-i/2$	$i/2$	0	0	i
2	1	$-\frac{1}{2}$	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	0	$-\frac{1}{2}$
2	2	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
2	3	$-\frac{1}{2}$	0	$-\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0
2	4	$-\frac{1}{2}$	0	$-\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0
2	5	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
2	6	$-\frac{1}{2}$	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	0	$-\frac{1}{2}$
3	1	0	0	0	0	$i/5$	$-i/5$	$-i/5$
3	2	0	0	$-i/2$	$i/2$	$i/5$	$-i/5$	0
3	3	0	0	$-i/2$	$i/2$	0	0	$i/5$
4	1	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$

polarizations, and the appropriate parameters are listed in columns 1 and 2 of Table III. The first point to notice is that the odd- j parameters vanish, so that the leading j_0 terms are a particularly good approximation in the near-zone. Secondly, we note that the differences in the values of $A^{(jp)}$ for the two cases indicates a linear dichroism which is a known characteristic of two-photon absorption.¹²

In each of the remaining polarization conditions, in general there are contributions from all values of j , and the rate expressions are accordingly somewhat more complicated. The most interesting feature of these results is the appearance of circular dichroism. Columns 3 and 4 of Table III give the results for the case where beam 1 is plane polarized and beam 2 is circularly polarized with either left- or right-handed helicity. While the even- j values of $A^{(jp)}$ are the same for either handedness, the odd- j values change sign when the helicity is reversed. Hence, chiral discrimination is manifest; obviously the same remarks apply to the case where beam 1 is circularly polarized and beam 2 plane polarized. Equally,

comparing columns 5 and 6 of Table III illustrates the circular dichroism associated with two circularly polarized beams of the same handedness; once again reversing the helicity of the entire radiation field changes the sign of the odd- j polarization parameters. These manifestations of chirality are only observed for the case where the two centers A_1 and A_2 have a fixed mutual orientation; it is also true that the corresponding molecular properties $T^{(1;q)}$ and $T^{(3;q)}$ disappear unless the two centers are dissymmetrically juxtaposed. The result is therefore a circular dichroism associated with the well-known coupled-oscillator model of a chiral system (see, for example, Ref. 13). Not surprisingly, the chirality disappears when A_1 and A_2 are free to rotate independently, since as noted earlier the odd- j terms then vanish.

Since the circular dichroism is generally associated with coupled groups in the near-zone range of distances, the explicit results for the Kuhn dissymmetry factors can be obtained from the leading j_1/j_0 terms in the rate expressions, and are as follows:

$$g_1 \equiv \frac{\Gamma(p,L) - \Gamma(p,R)}{\frac{1}{2}[\Gamma(p,L) + \Gamma(p,R)]} \quad (5.1)$$

$$= \frac{(\omega_1 - \omega_2)R(T^{(1;1)} - T^{(1;3)} - T^{(1;4)} - 2T^{(1;5)} - T^{(1;6)})}{c(T^{(0;1)} + 6T^{(0;2)} + T^{(0;3)})}, \quad (5.2)$$

$$g_2 \equiv \frac{\Gamma(L,L) - \Gamma(R,R)}{\frac{1}{2}[\Gamma(L,L) + \Gamma(R,R)]} \quad (5.3)$$

$$= \frac{(\omega_1 - \omega_2)R(T^{(1;2)} + T^{(1;3)} + T^{(1;4)} + T^{(1;5)})}{c(2T^{(0;1)} - 3T^{(0;2)} - 3T^{(0;3)})}, \quad (5.4)$$

where the molecular parameters can be read off from Table II, with the limiting short-range form of the interaction potential given by Eq. (4.3). Here $\Gamma(p,L)$ refers to the rate of absorption with beam 1 plane polarized and beam 2 left-handedly polarized, and so forth. It is interesting to note the linear dependence on the group separation in Eqs. (5.2) and (5.4); this near-zone behavior has been noted previously, for example in connection with circular differential Rayleigh and Raman scattering¹⁴ and optical rotation.¹⁵

Finally, returning to Table III, we note the results given in column 7, which apply to the situation in which the two laser beams have circular polarization of opposite handedness. The results here differ from those in either columns 5 or 6 in *each* value of j . This represents the fact that changing the helicity of one beam produces a dichroism associated with a discrimination of the handedness of A_1 - A_2 pair dressed by the chirality of the other circularly polarized beam. This again is a known feature of two-photon absorption,¹⁶ and one which persists even when the pair is not held in a fixed mutual orientation. In this case the dissymmetry factor has both numerator and denominator given by the leading j_0 terms, and the explicit result is as follows:

$$g_3 \equiv \frac{\Gamma(L,L) - \Gamma(L,R)}{\frac{1}{2}[\Gamma(L,L) + \Gamma(L,R)]} \quad (5.5)$$

$$= \frac{5(T^{(0;3)} - T^{(0;1)})}{(T^{(0;1)} + 6T^{(0;2)} + T^{(0;3)})}. \quad (5.6)$$

VI. DISCUSSION

In this paper we have presented the theory of a two-beam two-photon absorption process which can only occur through the simultaneous excitation of two chemically equivalent species. It is important to note that although the effect is one which is predominantly effective over short distances, it is nonetheless one which is induced by *proximity* rather than either collision, in the case of free molecules, or orbital overlap in the case of a chromophore pair. This much is made clear by the fact that irrespective of any energy shifts or selection rule weakening which collisions or orbital overlap might induce, the absorption processes which occur at each center A_1 and A_2 are *separately* forbidden on energy grounds [see Figure 1(b)]. The role of such proximity effects in low-temperature matrices has also recently been noted.¹⁷

Many of the remarks which were made in earlier work on cooperative two-photon absorption equally apply to the process described in this paper. We shall therefore concentrate on features which are unique to the two-beam case. First, we note that there is a great deal more experimental flexibility with two beams, since the frequency, polarization, and direction of propagation of each absorbed photon is independently variable. It is also interesting to note that for this process, the two beams in principle need not intersect, in other words neither A_1 nor A_2 need be irradiated by both

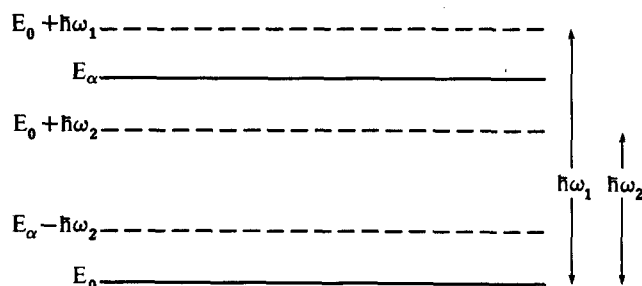


FIG. 3. Resonance energy levels (indicated by dotted lines) for mean-frequency absorption.

beams. However, the requirement for close molecular proximity, coupled with the fact that a laser beam tends to have a smooth Gaussian intensity profile, makes this point more of academic than of practical importance.

The effect should be most easily detected by measurement of fluorescence associated with the decay channel of the excited state $|\alpha\rangle$. Radiationless decay within the vibrational manifold of the initially populated electronic state will generally mean that the fluorescence will be Stokes shifted in frequency away from $E_{\alpha 0}/\hbar$. Nevertheless, since the same excited state $|\alpha\rangle$ is also accessible through single-beam two-photon absorption at a frequency $E_{\alpha 0}/2\hbar$, its decay characteristics can be ascertained in a separate single-beam experiment and then used to monitor the cooperative two-beam effect. In passing we note that a four-wave mixing process at a single center ($\omega_1 + \omega_2 \rightarrow \omega + \omega$), followed by absorption of the frequency ω , could in principle contribute to the effect we have described here. However, the four-wave interaction will be relatively ineffectual unless the emission at frequency ω is stimulated by an additional source.

There are three distinct possibilities for resonance enhancement of mean-frequency absorption, as shown in Fig. 3. If the molecules possess energy levels close to $(E_0 + \hbar\omega_1)$ or $(E_0 + \hbar\omega_2)$, then although the molecular tensors $S^{\alpha 0}(\omega_1)$ or $S^{\alpha 0}(\omega_2)$ are resonantly enhanced, direct competition from single-photon absorption will undoubtedly swamp the cooperative process. However, in the third reso-

nance condition, where a molecular energy level exists close to $E_\alpha - \hbar\omega_2$ (assuming that ω_2 is the lower of the laser frequencies), then the first term of $S^{\alpha 0}(\omega_2)$, as given by the ω_2 analog of Eq. (2.7), becomes resonantly enhanced and thus leads to an increased cooperative absorption rate. In this case, provided the resonant level lies sufficiently far above the ground state not to be appreciably thermally populated, then there is no possibility of competition from one-photon absorption. This feature could therefore prove significant in selecting laser frequencies to optimize the prospects for observing the phenomenon we have described.

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