Cooperative two-photon absorption

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It is well known that irradiation with intense laser light can lead to nonlinear absorption processes by individual molecules. However, the mutual interaction between two molecules can lead to cooperative nonlinear processes which result in entirely new features in the absorption spectrum. In this paper, the theory of cooperative two-photon absorption is developed using the principles of quantum electrodynamics, and expressions are derived for the rate of cooperative absorption for transitions which are forbidden in the absence of any such interaction. Several different cases are examined in detail, including crystalline or matrix-isolated species, gaseous and liquid mixtures, and van der Waals molecules. It is shown that the cooperative absorption rate can be substantially increased by choosing materials with suitable energy levels where one of several resonance enhancement mechanisms can be exploited. Finally, methods of observation are discussed, and a specific photochemical example is given for the case of a mixture of formaldehyde and deuterioformaldehyde.

I. INTRODUCTION

It has long been known that the interaction between two atoms or molecules can result in their simultaneous excitation when irradiated with light of a suitable frequency. The first observations of this effect were made over 30 years ago in infrared studies on compressed gases; a comprehensive review of the work in this period is given by Ketelaar.[1] More recently this effect has been proposed as an explanation for some of the features in the spectra of planetary atmospheres where high pressures of gaseous mixtures naturally occur.[2] Recent experimental studies have focused on interaction-induced atomic transitions.[3-6] For a comprehensive review of laser-stimulated molecular dynamics the reader is referred to the recent article by George.[17]

Despite the fact that each of these processes involves a pair of atoms or molecules, the absorption process involves only a single photon. With light of sufficient intensity, however, it should be possible to observe nonlinear effects in which two or more photons are absorbed by each pair. White has recently reported the first observation of such an effect in a mixture of barium and thallium vapor.[7] In his experiment both barium and thallium atoms were simultaneously promoted to excited states by a cooperative absorption process involving two laser photons.

In this paper we present a detailed examination of the theory of cooperative two-photon absorption in molecules. Our results are applied to two types of chemical systems; (a) van der Waals molecules, or other large molecules in which there are two identifiable groups which become excited; and (b) any other fluid system in which two independently oriented molecules participate in the process.

The underlying physics is identical in each case, and for this reason we adopt the general term "cooperative two-photon absorption." The physically most interesting case is where the transitions in both species are forbidden as single-photon processes, but allowed under two-photon selection rules, and we concentrate our attention specifically on this case.

The theory developed below is based on a fully quantum electrodynamical treatment of the system, allowing results to be obtained which are valid over an unrestricted range of intermolecular distances. The retardation effects which become apparent at large separation are shown to be highly significant in modifying the form of the results, such that the contributions to the effect from molecules separated by large distances are by no means negligible. The results are shown to deviate markedly from those which would be predicted using a semiclassical approach.

In the Discussion section, we consider a number of features connected with observation of the process, e.g., the sensitivity to pressure in the case of gaseous mixtures, and the dependence on the guest/host ratio in crystalline or matrix-isolated systems. We also discuss in detail the possibilities of obtaining resonance enhancement of the process by choice of compounds with suitable sets of energy levels. Finally, we consider possible techniques of observation including photochemical methods, and we provide a specific example in the case of formaldehyde.

II. THEORY

We begin by writing down the quantum electrodynamical Hamiltonian for the system comprising the radiation and the two molecules A and B. We adopt the Hamiltonian given by the Power–Zienau–Woolley transformation, which is as follows[8,9]:

$$H = H_{rad} + \sum_{\xi = A, B} H_{mol}(\xi) + \sum_{\xi = A, B} H_{int}(\xi) . \qquad (2.1)$$

Here H_{rad} is the radiation field Hamiltonian given by

$$H_{rad} = \frac{1}{8\pi} \int \{ d^{\perp 2}(r) + b^2(r) \} d^3r , \qquad (2.2)$$

where $d^{\perp}$ and b are the transverse electric field and magnetic field operators, respectively; $H_{mol}(\xi)$ is the nonrelativistic Schrödinger operator for the molecule ξ, and $H_{int}(\xi)$ is the Hamiltonian representing the molecular interaction with the radiation. It is important to note that there is no intermolecular Coulomb

potential in Eq. (2.1); in the Power–Zienau–Woolley formalism all intermolecular interactions are mediated by a coupling to the radiation field. The Casimir–Polder or van der Waals interaction, e.g., is calculated on the basis of an exchange of virtual photons between the molecules. The quantum electrodynamical method automatically incorporates the retardation effects which modify the R^{-6} dependence of this interaction to R^{-7} at large distances.[10] Since Casimir and Polder's work, the incorporation of retardation effects has been shown to be important in many systems; see, e.g., Milonni and Knight's work on atomic interaction.[18]

The explicit form of the interaction Hamiltonian $H_{int}(\xi)$ consists of a series of multipolar terms, but for our purposes we need only consider the leading electric dipole term

$$H_{int}(\xi) = - \mu(\xi) \cdot d^{\perp}(R_{\xi}) . \qquad (2.3)$$

The electric field operator can be written in the usual way in terms of a summation over radiation modes as follows:

$$d^{\perp}(r) = \sum_{k,\lambda} \left(\frac{2\pi\hbar ck}{V} \right)^{1/2}$$
$$\times i[e^{(\lambda)}(k)a^{(\lambda)}(k) e^{ik\cdot r} - \bar{e}^{(\lambda)}(k)a^{(\lambda)\dagger}(k)e^{-ik\cdot r}] . \qquad (2.4)$$

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

Our basis for calculation of the cooperative absorption rate Γ is time-dependent perturbation theory using the equation

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

where the transition matrix element is given by

$$M_{fi} = \langle f|H_{int}|i\rangle + \sum_{I}{}' \frac{\langle f|H_{int}|I\rangle \langle I|H_{int}|i\rangle}{(E_i - E_I)} + \sum_{I}{}'\sum_{II}{}' \frac{\langle f|H_{int}|II\rangle\langle II|H_{int}|I\rangle \langle I|H_{int}|i\rangle}{(E_i - E_{II})(E_i - E_I)}$$
$$+ \sum_{I}{}' \sum_{II}{}' \sum_{III}{}' \frac{\langle f|H_{int}|III\rangle\langle III|H_{int}|II\rangle\langle II|H_{int}|I\rangle\langle I|H_{int}|i\rangle}{(E_i - E_{III})(E_i - E_{II})(E_i - E_I)} \cdots . \qquad (2.6)$$

All states appearing in this expression are states of the *system* comprising the radiation plus the two molecules A and B, and the primes denote omission of the initial and final states of the system from each summation.

Explicitly, we may represent the state vector of the system at any stage of the interaction by $|a;b;n_r;n_v\rangle$, where $|a\rangle$ is the state vector for molecule A, $|b\rangle$ refers to molecule B, and n_r and n_v denote the number of real (incident) photons and virtual photons, respectively. If the cooperative absorption of two photons with frequency ω results in the excitation of molecule A to an excited state $|\alpha\rangle$, and B to an excited state $|\beta\rangle$, then we have

$$2\hbar\omega = E_{\alpha 0} + E_{\beta 0} , \qquad (2.7)$$

and the state vectors for the initial and final states of the system are

$$|i\rangle = |0; 0; n; 0\rangle , \qquad (2.8)$$

$$|f\rangle = |\alpha;\beta; n-2; 0\rangle . \qquad (2.9)$$

It is then readily apparent that the first nonzero contribution from Eq. (2.6) is the fourth order term, corresponding to four separate photon creation and annihilation events; these comprise the two annihilations of real photons from the incident light, and the creation and annihilation of one virtual photon which couples the two molecules.

We are interested in the case where each molecular transition is two photon allowed, but one photon forbidden; the case of two photon forbidden cooperative transitions in atoms has recently been examined by Nayfeh and Hillard,[11] and we intend to deal with the molecular case in a later publication. The complete set of interaction sequences incorporated in the fourth-order term for M_{fi} are conveniently represented by time-ordered diagrams, typified by those shown in Figs. 1a and b. In Fig. 1a, e.g., molecule A first absorbs a real photon of wave vector k and polarization
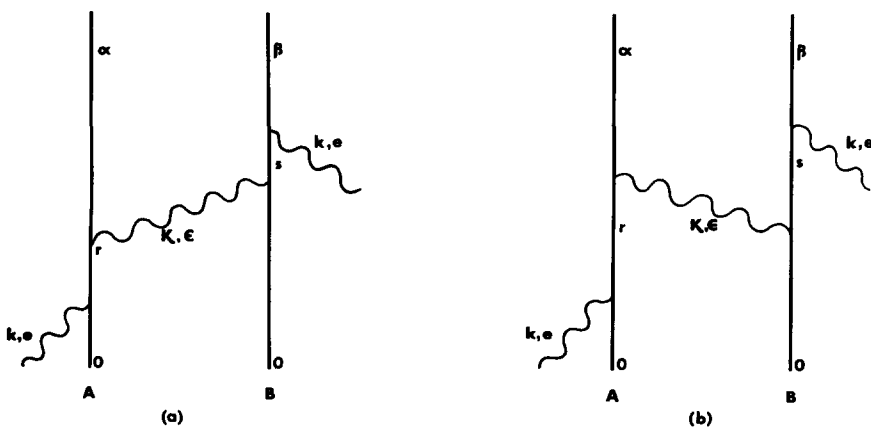

FIG. 1. Typical time-ordered diagrams for cooperative two-photon absorption.

vector $\mathbf{e}$, and thereby undergoes a virtual transition to an excited state $|r\rangle$; a virtual photon of wave vector $\boldsymbol{\kappa}$, and polarization $\boldsymbol{\epsilon}$ is then created and A goes into its final state $|\alpha\rangle$. The virtual photon then propagates to molecule B when it is annihilated, resulting in the pro-

motion of B to an excited state $|s\rangle$, and finally B absorbs a second real photon, and thereby reaches its final state $|\beta\rangle$. The matrix element contribution corresponding to this diagram is evaluated using Eq. (2.6), and is thus as follows;

$$\sum_r \sum_s \sum_{\kappa,\epsilon} \langle \alpha;\beta;n-2;0|H_{1\text{nt}}|\alpha;s;n-1;0\rangle\langle\alpha;s;n-1;0|H_{1\text{nt}}|\alpha;0;n-1;1\rangle\langle\alpha;0;n-1;1|H_{1\text{nt}}|r;0;n-1;0\rangle$$

$$\times\langle r;0;n-1;0|H_{1\text{nt}}|0;0;n;0\rangle\{(E_{0\alpha}+E_{0s}+\hbar\omega)(E_{0\alpha}+\hbar\omega-\hbar c\kappa)(E_{0r}+\hbar\omega)\}^{-1} \quad . \tag{2.10}$$

There are twelve different contributions of this class to be calculated, corresponding to the 12 different orderings of the radiative interactions in Fig. 1a; 12 others of the kind shown in Fig. 1b also arise, where the virtual photon propagates from B to A. Notice that only one "virtual collision" is necessary for the cooperative absorption process to occur.

By summing the contributions from all 24 time-ordered diagrams using Eqs. (2.3) and (2.4), we obtain the following result:

$$M_{fi} = -\left(\frac{2\pi\hbar}{V}\right)^2 c\omega n^{1/2}(n-1)^{1/2}S_{ji}^{\alpha 0}S_{ik}^{\beta 0} e_i e_j e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$\times\sum_{\kappa,\epsilon}\kappa\epsilon_k\bar{\epsilon}_l\left[\frac{e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}}{(E_{\beta 0}-\hbar\omega-\hbar c\kappa)}-\frac{e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}}{(E_{\beta 0}-\hbar\omega+\hbar c\kappa)}\right] , \tag{2.11}$$

where we adopt the implied summation convention for repeated tensor indices, and it is understood that tensors labeled with α or β refer to molecules A and B, respectively; R is the vector **AB**. The explicit form of the tensor S^{f0} is as follows:

$$S_{ij}^{f0} = \sum_r \left[\frac{\mu_i^{fr}\mu_j^{r0}}{(E_{fr}-\hbar\omega)}-\frac{\mu_j^{fr}\mu_i^{r0}}{(E_{r0}-\hbar\omega)}\right] . \tag{2.12}$$

It is readily shown that this is identically equal to the electronic Raman scattering tensor for the Raman transition $|f\rangle \leftarrow |0\rangle$. Note that the first term in Eq. (2.12) dominates if there exists a state $|r\rangle$ such that $E_{fr}\approx\hbar\omega$; the second term dominates if there is a state such that $E_{r0}\approx\hbar\omega$. We consider these cases of resonance enhancement in more detail later.

In order to perform the summation over the virtual photon wave vectors and polarizations in Eq. (2.11) we make use of the identity

$$\frac{1}{2V}\sum_{\mathbf{k},\mathbf{s}}\kappa\epsilon_k\bar{\epsilon}_l\left[\frac{e^{i\boldsymbol{\kappa}\cdot\mathbf{R}}}{(\gamma-\kappa)}-\frac{e^{-i\boldsymbol{\kappa}\cdot\mathbf{R}}}{(\gamma+\kappa)}\right] = V_{kl}(\gamma,\mathbf{R}) , \tag{2.13}$$

where $V_{kl}(\gamma,\mathbf{R})$ is the retarded resonance electric dipole–electric dipole interaction[12] given by

$$V_{kl}(\gamma,\mathbf{R}) = \frac{1}{4\pi R^3}\{F(\gamma,R)\delta_{kl}+G(\gamma,R)\hat{R}_k\hat{R}_l\} , \tag{2.14}$$

where

$$F(\gamma,R) = \cos\gamma R + \gamma R \sin\gamma R - \gamma^2 R^2 \cos\gamma R , \tag{2.15}$$

$$G(\gamma,R) = -3\cos\gamma R - 3\gamma R \sin\gamma R + \gamma^2 R^2 \cos\gamma R . \tag{2.16}$$

Hence we obtain

$$M_{fi} = -\frac{8\pi^2\hbar\omega}{V} n^{1/2}(n-1)^{1/2}S_{ji}^{\alpha 0}S_{ik}^{\beta 0} V_{kl}(\gamma,\mathbf{R}) e_i e_j e^{i\mathbf{k}\cdot\mathbf{R}} , \tag{2.17}$$

where $\hbar c\gamma$, given by

$$\hbar c\gamma = E_{\beta 0} - \hbar\omega , \tag{2.18}$$

may be understood as the energy transferred from molecule A to molecule B in the course of the interaction.

We can now calculate the rate of cooperative absorption from Eq. (2.5) with a density of final states for the A–B system given by

$$\rho_f = \int \rho_A^\alpha(\epsilon)\,\rho_B^\beta(2\hbar\omega-\epsilon)\,d\epsilon . \tag{2.19}$$

The result, expressed in terms of the mean irradiance I and the degree of second order coherence $g^{(2)}$ of the incident light is as follows:

$$\Gamma = \frac{128\pi^5 I^2 g^{(2)}\rho_f}{\hbar c^2} S_{ji}^{\alpha 0}S_{ik}^{\beta 0}\bar{S}_{np}^{\alpha 0}\bar{S}_{mo}^{\beta 0}$$

$$\times V_{kl}(\gamma,\mathbf{R})V_{op}(\gamma,\mathbf{R}) e_i e_j \bar{e}_m\bar{e}_n . \tag{2.20}$$

It is important to note that the phase factor $e^{i\mathbf{k}\cdot\mathbf{R}}$ of Eq. (2.17) drops out of the rate Eq. (2.20). This is in contrast to the situation in the two photon forbidden cooperative process mentioned earlier, which takes place through the absorption of two real photons by one molecule, with virtual photon coupling to the second.[11] In that case the persistence of phase factors in the rate equation leads to additional retardation effects.

As it stands, the above result is directly applicable to any system where the two molecules taking part in the cooperative absorption process are rigidly held in a fixed orientation with respect to the laser beam and with respect to each other; however, we are principally interested in deriving results for fluid systems. There are several different cases to consider, and these are discussed in detail in the following sections.

Before leaving this section, we note that a simple expression for M_{fi} in terms of the irradiance can be obtained from Eq. (2.17) if we assume that the radiation is plane polarized, and coherence effects are ignored; the result is

$$M_{fi} = -\frac{8\pi^2}{c} IS_{ji}^{\alpha 0}S_{ik}^{\beta 0} V_{kl}(\gamma,\mathbf{R}) e_i e_j e^{i\mathbf{k}\cdot\mathbf{R}} \tag{2.21}$$

From this off-diagonal term, we can by simple manipulation obtain the field-induced dispersion energy which results from the coupling of absorption and stimulated

emission between the two molecules. The result is

$$\Delta E = \frac{16\pi^2}{c} \, I^A S_{jl}^{00\,B} S_{lk}^{00} V_{kl}\left(\frac{\omega}{c}, \mathbf{R}\right) e_i e_j \cos \mathbf{k} \cdot \mathbf{R} \, ,$$

(2.22)

where we note that each S^{00} is simply a polarizability tensor. Retardation effects in this energy shift have recently been examined by Thirunamachandran.[19]

III. TWO MOLECULES IN A FIXED MUTUAL ORIENTATION

We first consider the case where the mutual orientation of A and B is fixed, but the A–B system may freely rotate with respect to the laser beam. The results we derive here are then applicable to van der Waals molecules, or to other large molecules in which A and B represent chromophores.

In order to obtain a rate equation which is appropriate to such a situation we need to perform a rotational aver-

age of Eq. (2.20) to account for the random orientation of the A–B system. To accomplish this, we first specify two Cartesian coordinate systems; a laboratory-fixed frame denoted by $\mathbf{p}$, in which the laser polarization vectors are fixed, and a frame for the A–B system denoted by $\mathbf{s}$, in which the molecular tensors and the vector R are fixed. Hence Eq. (2.20) may be written:

$$\Gamma = K S_{s_j s_i}^{\alpha 0} S_{s_i s_k}^{\beta 0} \bar{S}_{s_n s_p}^{\alpha 0} \bar{S}_{s_m s_o}^{\beta 0} V_{s_k s_l}(\gamma, \mathbf{R}) V_{s_o s_p}(\gamma, \mathbf{R})$$

$$\times e_{p_i} e_{p_j} \bar{e}_{p_m} \bar{e}_{p_n} l_{p_i s_i} l_{p_j s_j} l_{p_m s_m} l_{p_n s_n} \, ,$$

(3.1)

where

$$K = \frac{128\pi^5 I^2 g^{(2)} \rho_f}{\hbar c^2}$$

(3.2)

and $l_{p_\alpha s_\alpha}$ is the direction cosine between the $\hat{\mathbf{p}}_\alpha$ and $\hat{\mathbf{s}}_\alpha$ directions, given by the (p_α, s_α) element of the Euler angle matrix.[13]

The requisite rotational average of Eq. (3.1) is now obtained using the result[14];

$$\langle l_{i_1\lambda_1} l_{i_2\lambda_2} l_{i_3\lambda_3} l_{i_4\lambda_4}\rangle = \frac{1}{30}\begin{bmatrix}\delta_{i_1 i_2}\delta_{i_3 i_4} \\ \delta_{i_1 i_3}\delta_{i_2 i_4} \\ \delta_{i_1 i_4}\delta_{i_2 i_3}\end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix}\begin{bmatrix}\delta_{\lambda_1\lambda_2}\delta_{\lambda_3\lambda_4} \\ \delta_{\lambda_1\lambda_3}\delta_{\lambda_2\lambda_4} \\ \delta_{\lambda_1\lambda_4}\delta_{\lambda_2\lambda_3}\end{bmatrix} \, .$$

(3.3)

Application of this result in Eq. (3.1) thus gives:

$$\Gamma = \frac{K}{480\pi^2 R^6}\left[\{F^2(\gamma,R)S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{ij}^{\beta 0}\bar{S}_{kl}^{\beta 0} + 2F(\gamma,R)G(\gamma,R)\,\mathrm{Re}\,S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{lm}^{\beta 0}\bar{S}_{kl}^{\beta 0}\hat{R}_j\hat{R}_m + G^2(\gamma,R)S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{lm}^{\beta 0}\bar{S}_{kn}^{\beta 0}\hat{R}_j\hat{R}_l\hat{R}_m\hat{R}_n\}(4\eta - 2)\right.$$

$$+ \{F^2(\gamma,R)(S_{ij}^{\alpha 0}\bar{S}_{ik}^{\alpha 0}S_{ij}^{\beta 0}\bar{S}_{ik}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{kj}^{\beta 0}\bar{S}_{il}^{\beta 0}) + 2F(\gamma,R)G(\gamma,R)\,\mathrm{Re}(S_{ij}^{\alpha 0}\bar{S}_{ik}^{\alpha 0}S_{lm}^{\beta 0}\bar{S}_{lk}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{km}^{\beta 0}\bar{S}_{il}^{\beta 0})\hat{R}_j\hat{R}_m$$

$$+ G^2(\gamma,R)(S_{ij}^{\alpha 0}\bar{S}_{il}^{\alpha 0}S_{km}^{\beta 0}\bar{S}_{kn}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{kl}^{\alpha 0}S_{km}^{\beta 0}\bar{S}_{in}^{\beta 0})\hat{R}_j\hat{R}_l\hat{R}_m\hat{R}_n\}(3 - \eta) \, ,$$

(3.4)

where

$$\eta = (\mathbf{e}\cdot\mathbf{e})(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}) \, .$$

(3.5)

In Eq. (3.4) we have written $S_{s_i s_j}^{\alpha 0}$ as $S_{ij}^{\alpha 0}$, e.g., since now all indices are related to the system frame. It is worth noting the value of η for two particular polarization states: $\eta = 1$ for plane polarized light, and $\eta = 0$ for circularly polarized light.

The R^{-6} dependence of Eq. (3.4) is complicated by the R dependence of $F(\gamma,R)$ and $G(\gamma,R)$ as given by Eqs. (2.15) and (2.16). However for the particular case we are examining in this section where the two centers A and B are held in a fixed relative orientation, R is unlikely to exceed 1 nm, and the product γR will always be such that $\gamma R \ll 1$. In this case we can use the limiting near-zone results for $F(\gamma,R)$ and $G(\gamma,R)$ which are as follows:

$$\lim_{\gamma R \to 0} F(\gamma,R) = 1 \, ,$$

(3.6)

$$\lim_{\gamma R \to 0} G(\gamma,R) = -3 \, ;$$

(3.7)

hence there is a simple overall R^{-6} dependence of the cooperative absorption rate.

IV. TWO RANDOMLY ORIENTED MOLECULES

We now consider the case where A and B assume random orientations with respect to the laser beam, and also with respect to each other. In this case the result will be applicable to gaseous or liquid mixtures, and also to solutions where A and B represent the solvent and solute species. For simplicity we assume that there is no angular correlation between molecules in the liquid phase.

In order to account for the random orientation of A and B it is necessary to perform three successive rotational averages on the rate expression given by Eq. (2.20). A similar averaging procedure which arises in the theory of dispersion-induced circular dichroism has recently been discussed by Schipper.[15] The first step involves referring all the molecular tensors and the R vector to a frame attached to molecule A, denoted by $\mathbf{a}$, followed by an orientational average of $\mathbf{a}$ with respect to the laboratory-fixed frame $\mathbf{p}$ in which the laser polarization vectors are fixed. Secondly the molecular tensors relating to molecule B are reexpressed in terms of a reference frame $\mathbf{b}$ attached to B, and a rotational average is performed over the mutual orientations of the frames $\mathbf{a}$ and $\mathbf{b}$.

Finally the vector R is reexpressed in terms of a system frame **s** which is then rotationally averaged with respect to **a**. The three stages in the averaging method are illustrated schematically in Table I.

After performing the full rotational average, the result from Eq. (2.20) is as follows:

$$\Gamma = \frac{K}{432\,000\,\pi^2 R^6} \left[p(S_{ij}^{\alpha 0}\bar{S}_{ij}^{\alpha 0}S_{kk}^{\beta 0}\bar{S}_{ll}^{\beta 0} + S_{ii}^{\alpha 0}\bar{S}_{jj}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{kl}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{ji}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{kl}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{ji}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{lk}^{\beta 0}) + q(S_{ii}^{\alpha 0}\bar{S}_{jj}^{\alpha 0}S_{kk}^{\beta 0}\bar{S}_{ll}^{\beta 0} + S_{ij}^{\alpha 0}\bar{S}_{ji}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{lk}^{\beta 0}) \right.$$

$$\left. + r(S_{ij}^{\alpha 0}\bar{S}_{ji}^{\alpha 0}S_{kk}^{\beta 0}\bar{S}_{ll}^{\beta 0} + S_{ii}^{\alpha 0}\bar{S}_{jj}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{lk}^{\beta 0}) + sS_{ij}^{\alpha 0}\bar{S}_{ij}^{\alpha 0}S_{kl}^{\beta 0}\bar{S}_{kl}^{\beta 0} \right] , \tag{4.1}$$

where

$$p = -\{30F^2(\gamma, R) + 20F(\gamma, R)G(\gamma, R) + 4G^2(\gamma, R)\}(3\eta + 1) , \tag{4.2}$$

$$q = 4\{60F^2(\gamma, R) + 40F(\gamma, R)G(\gamma, R) + 3G^2(\gamma, R)\}(2\eta - 1) - \{30F^2(\gamma, R) + 20F(\gamma, R)G(\gamma, R) - 6G^2(\gamma, R)\}(3 - \eta) , \tag{4.3}$$

$$r = -4\{15F^2(\gamma, R) + 10F(\gamma, R)G(\gamma, R) - 3G^2(\gamma, R)\}(2\eta - 1) + 2\{60F^2(\gamma, R) + 40F(\gamma, R)G(\gamma, R) + 3G^2(\gamma, R)\}(3 - \eta) , \tag{4.4}$$

$$s = 4\{30F^2(\gamma, R) + 20F(\gamma, R)G(\gamma, R) + 9G^2(\gamma, R)\}(3\eta + 1) + 100\{3F^2(\gamma, R) + 2F(\gamma, R)G(\gamma, R) + G^2(\gamma, R)\})(3 - \eta) . \tag{4.5}$$

We draw attention to the fact that the coefficients p, q, r, and s are functions not only of the polarization expressed in terms of the parameter η discussed in the last section, but also of γ and R. It is therefore these functions together with the R^{-6} factor in Eq. (4.1) which determine the overall dependence of the cooperative absorption rate on the intermolecular distance R. Two particular cases where the overall R dependence is more transparent are worth examining in more detail.

A. $\gamma R \ll 1$

First we may examine the near-zone case where $\gamma R \ll 1$. Since $\hbar c\gamma$ can be expressed from Eqs. (2.7) and (2.18) as

$$\hbar c\gamma = \tfrac{1}{2}(E_{\beta 0} - E_{\alpha 0}) , \tag{4.6}$$

which represents half the difference between the energy absorbed by A and B, we generally satisfy the condition $\gamma R \ll 1$ if R is comparable with molecular dimensions. In cases where the two-photon transitions at A and B are very close in energy, the condition will be satisfied over a much greater range. The corresponding expression for the cooperative absorption rates then follows from Eq. (4.1) using the limiting results of Eqs. (3.6) and (3.7) for $F(\gamma, R)$ and $G(\gamma, R)$; the result is a straightforward R^{-6} rate dependence.

B. $\gamma R \gg 1$

Secondly we have the far-zone case where $\gamma R \gg 1$; this generally will apply to intermolecular distances

TABLE I. Rotational averaging scheme for the case of two randomly oriented molecules.

Vector and tensor quantities	e	$\mathbf{S}^{\alpha 0}$	$\mathbf{S}^{\beta 0}$	$\mathbf{V}(\gamma, R)$
Result prior to rotational averaging	p	p	p	p
	↓	↕	↕	↕
1st rotational average; $a \leftrightarrow p$	p	a	a	a
	↓	↓	↕	↓
2nd rotational average; $b \leftrightarrow a$	p	a	b	a
	↓	↓	↓	↕
3rd rotational average; $s \leftrightarrow a$	p	a	b	s

which are large compared to optical wavelengths. Here the dominant terms in $F(\gamma, R)$ and $G(\gamma, R)$ are those which are quadratic in γR, i.e.,

$$\lim_{\gamma R \gg 1} F(\gamma, R) = -\gamma^2 R^2 \cos \gamma R , \tag{4.7}$$

$$\lim_{\gamma R \gg 1} G(\gamma, R) = \gamma^2 R^2 \cos \gamma R . \tag{4.8}$$

Substitution of these results into Eq. (4.1) shows that, apart from a modulating factor of $\cos^2 \gamma R$, the overall behavior is an *inverse square* dependence on the intermolecular distance R. This result is important since it shows that the cooperative absorption rate does not fall off with distance anywhere near as fast as the initial R^{-6} behavior would indicate. Since by far the greatest majority of molecules will lie in the far-zone region, their contribution should evidently not be neglected. However, the number of molecular pairs which can participate in the cooperative process is limited by the requirement that both lie within the small volume irradiated by the laser beam.

In general, the total rate of cooperative absorption will be given by a sum over all pairs of molecules in the volume irradiated by the laser. Since the form of the intermolecular potential energy curve governs the statistical distribution of intermolecular distances, it is not possible to provide an analytic expression for the overall absorption rate in a general case. Although even the long-range contributions are significant, since the number of molecules separated by distance R then increases roughly as R^2 and compensates for the R^{-2} dependence of the rate equation, it is nevertheless readily shown that the molecules in the near zone still make by far the largest contribution to the process. For this reason the phenomenon should be very sensitive to pressure, and large enhancements can be expected at high pressures.

V. DISCUSSION

The theory which has been developed in this paper has a range of applications. Firstly, we note that the molecular excitation may be either electronic or vibrational, according to the wavelength of the light used.
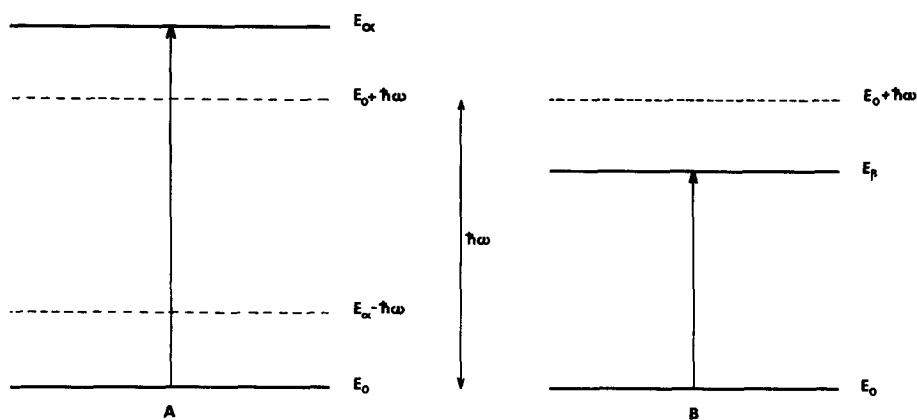
FIG. 2. Energy level diagram.

In the case of vibrational excitation, i.e., where $E_{\alpha0}/\hbar$ and $E_{\beta0}/\hbar$ are vibrational frequencies of A and B, then the irradiation frequency for the cooperative two-photon process is the mean of these two vibrational frequencies. Vibrational modes which can participate in this process must be Raman allowed by virtue of the two-photon selection rules; also in this case the limiting near-zone behavior applies up to distances comparable to infrared wavelengths.

We have concentrated on cases where the sample is in either a gaseous or a liquid state, and it may be argued that here the cooperative process is essentially a collisional phenomenon, since it is greatly enhanced for pairs of molecules which are separated by small distances, and it is certainly a very pressure-sensitive effect. However, we would wish to draw attention again to the contributions from molecules in the far-zone region, which we have demonstrated to be significant; hence we prefer the general term "cooperative." Also, this name applies to the case of solid-state samples where the same process should be observed; it is molecular proximity rather than motion which is important.

If A and B were identical species, and $|\alpha\rangle$ and $|\beta\rangle$ equivalent excited states, then it would be difficult to experimentally distinguish the cooperative process from single-photon absorption, except where there was a difference in the selection rules. For this reason we have concentrated on the case where A and B differ, even if only by isotopic constitution. However, the theory can also apply to the case where A and B are identical, but the excited states $|\alpha\rangle$ and $|\beta\rangle$ differ. For a single component phase, the effect should be observable as the absorption of two photons with energy halfway between that of the two excited states; this applies equally to free molecules or loosely associated van der Waals dimers. For a two component phase containing a mixture of A and B molecules, the effect should be seen for A–A, B–B, and A–B interactions, and hence several new bands should appear in the two-photon absorption spectrum.

Solid-state applications may also be found, where A and B assume the roles of guest species in a host lattice; the theory is then applicable to the study of crystalline impurities and matrix-isolated species. Since the

R dependence of our results shows a crucial dependence on the radial distribution of species B about a given molecule A, the cooperative two-photon process is clearly highly sensitive to the ratio of concentrations of A and B, and study of this dependence should provide useful information.

The magnitude of the effect is difficult to estimate since typical values of the electronic Raman scattering tensors are not readily available. However, by assuming that all transition dipole moments are of the order ea_0, and the electronic transition energies are of the order e^2/a_0, we can show that the rate associated with the cooperative process should be smaller than a normal two-photon absorption rate by a factor of the order $(a_0/R)^6$ in the near zone. Hence if A and B are separated only by typical chemical bond distances, then the cooperative absorption rate should be equally as large as the single-center two-photon absorption rate; the size of the effect then diminishes with $(a_0/R)^6$ as A and B are moved further apart. We may conclude then that observation of the cooperative process should be possible under similar conditions to conventional two-photon absorption. Hence it should not be necessary to utilize exceptionally intense laser sources, where it would be necessary to incorporate higher order effects into the theory.

One important aspect of the process is the possibility of obtaining a resonance enhancement of the absorption rate. Because of the structure of the S tensors, there are two possible resonance mechanisms to consider, as indicated earlier. For the tensor $S^{\alpha0}$, we obtain a resonance amplification under conditions where there exists a state $|r\rangle$ such that $E_{\alpha r} \approx \hbar\omega$ or $E_{r0} \approx \hbar\omega$. In principle similar remarks apply to $S^{\beta0}$, except that if $E_{\alpha0} > E_{\beta0}$ as in Fig. 2, then the condition $E_{\beta s} \approx \hbar\omega$ cannot be satisfied for any $|s\rangle$, if the initial state of B is the ground state. Hence there are just three possible resonances, as indicated by the dotted lines in Fig. 2. (Clearly if $E_{\beta0} > E_{\alpha0}$ there are two resonance conditions which may apply for molecule B, and one for A.)
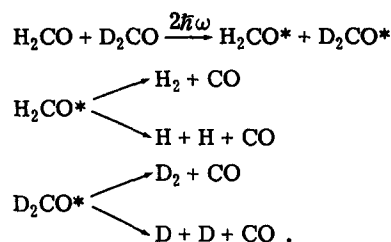
The two conditions where A has a state $|r\rangle$ or B has a state $|s\rangle$ with energy $\sim E_0 + \hbar\omega$ lead to resonance enhancement provided the corresponding transition moments μ^{r0}, μ^{s0} are nonzero. However, in such circumstances real transitions to these states are allowed

by single-photon absorption, and it is likely that these effects will swamp observation of the cooperative process which we are considering. Also, if $2\hbar\omega$ exceeds the ionization energy of either A or B, competition from the corresponding single-center two-photon ionization process will again be likely to render the cooperative process unobservable.

The third resonance condition where $E_{\alpha r} \approx \hbar\omega$ is of much more interest; this corresponds to having an energy level of molecule A at approximately $E_\alpha - \hbar\omega$. In this case there is no question of single-photon absorption from the laser beam at a frequency ω, but there is nonetheless a genuine resonance amplification of the tensor $S^{\alpha 0}$. Observation of the cooperative absorption process is therefore facilitated if the energy levels of A and B allow for this possibility.

Finally, we wish to make a few brief comments concerning methods of observation. As with conventional two-photon absorption, direct monitoring of the reduction in laser intensity as a result of the absorption process may not be the most practicable method for studying the effect. The fluorescent decay of either A or B from their excited states is likely to be more easily measured; note that fluorescence from only one species is sufficient to demonstrate the occurrence of the process.

Alternative methods could be devised according to the photochemistry of the sample, and as an example we consider the case of a mixture of H_2CO and D_2CO. These molecules have absorption lines associated with the $2_0^1 4_0^3$ transition at 30 340.15 and 30 147.62 cm^{-1}, respectively.[16] Irradiation with laser light at the *mean* of these two frequencies should thus lead to a cooperative two-photon process in which both species are simultaneously excited. The narrow bandwidth of any standard laser source should ensure that neither species is independently excited by a conventional single-photon absorption process. Evidence for cooperative two-photon absorption is then provided by detection of the decomposition product CO resulting from the reactions:

$$H_2CO + D_2CO \xrightarrow{2\hbar\omega} H_2CO^* + D_2CO^*$$

$$H_2CO^* \begin{cases} \longrightarrow H_2 + CO \\ \longrightarrow H + H + CO \end{cases}$$

$$D_2CO^* \begin{cases} \longrightarrow D_2 + CO \\ \longrightarrow D + D + CO \;. \end{cases}$$

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