Cooperative single-photon absorption at interfaces.
Static electric dipole effects

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Abstract

The pairwise absorption of light by chemically distinct molecules in close proximity can result in their cooperative single-photon excitation. It is shown how new characteristics emerge where the two molecular species concerned lie on opposite sides of a phase boundary or interface, as for example with two immiscible liquids, one polar and the other non-polar. Under such circumstances it is shown that if the polar phase has a component with a strong intramolecular charge transfer transition, it can thereby display significant absorption outside its normal absorption band. Such behaviour, which uniquely characterises the interface, occurs at a rate that is quadratically dependent upon the difference between the permanent dipole moments of the corresponding molecular ground and excited states of the polar species.

1. Introduction

In a great variety of media, it is well established that energy is transferred between excited-state and ground-state molecules by a resonance exchange mechanism. The nature of the energy transfer is strongly influenced by molecular separation, with non-radiative Förster energy transfer dominating for molecules in close proximity. Such a process may be regarded as the near-zone limit of a unified theory which also accommodates a longer-range radiative transfer process [1–10]. Whilst energy transfer per se plays a familiar role in various photophysical and photobiological systems, it is also implicated in a number of bimolecular or cooperative absorption and other processes, formally mediated by the same coupling mechanism [11–13]. In this Letter attention is focused on the case of single-photon bimolecular absorption, as illustrated classically in Fig. 1. Although our concern here is with UV/visible excitation, the process shares the sum-frequency character of fea-
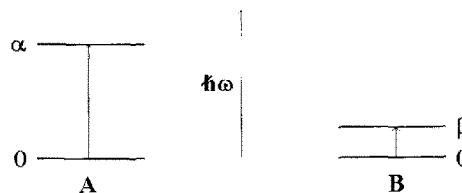

Fig. 1. Cooperative excitation process in which two molecules, A and B, are promoted to excited states, α and β respectively, through single-photon absorption at the sum excitation frequency.

tures observed in the infrared spectra of gases by Ketelaar [14]. The explicit quantum electrodynamical formulation has recently been the subject of studies by Hudis et al. [15] and Kweon and Lawandy [16], with an exactly time-reversed process being considered by John and Wang [17].

In the context of our current considerations of fluid molecular systems, we here consider the case where the two molecular species concerned lie on opposite sides of a phase boundary or interface, as for example might be found between two immiscible liquids. Spe-

cifically we shall deal with the cooperative excitation of two molecules, A and B, one of which can exhibit a significant degree of intramolecular charge redistribution on optical excitation. This species (A) can be thought of as polar. The process under consideration may thus be expressed as

$$A + B + \hbar\omega \rightarrow A^* + B^* ,$$
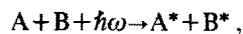
and for simplicity A and B may be regarded as initially in their electronic and vibrational ground states. Upon absorption each undergoes a transition in which molecule A is promoted to an upper electronic state and molecule B to a low-lying (either vibrational or electronic) excited state. The overall process must be energy-conserving, i.e. $E_{\alpha0} + E_{\beta0} = \hbar\omega$, where $E_{\alpha0}$ and $E_{\beta0}$ respectively denote the differences in energy between the final and initial molecular states of A and B.

In formulating the results for the rate of cooperative absorption it is found that there is a dominant driving term within the second-order molecular response tensor of the polar molecule A. In its formal structure this tensor is identically equal to the transition polarisability of electronic Raman scattering, and the driving term may be considered as a near-resonant contribution. This requires that the detuning $\Delta\omega$ between the incoming photon and the excitation frequency for the first electronically allowed transition of A is small, though still large enough to prevent single-photon absorption. In other words $\hbar\Delta\omega$ must be small compared with the photon energy $\hbar\omega$, but larger than the excited state bandwidth $\hbar\gamma$. The necessity of interaction with a molecule B in close proximity ensures that the cooperative excitation process occurs only at the interface and that it is characterised by absorption at a wavelength where neither single component displays intrinsic absorption. This is distinct from proximity-induced shifts in absorption frequency, associated with absorption by single molecules. The mismatch in energy between the incoming photon and the excited molecular state is taken up by the simultaneous excitation of the second molecule, i.e. the energy uptake $E_{\beta0}$ by molecule B is equal to $\hbar\Delta\omega$.

2. Theoretical formulation

We start with the overall Hamiltonian for the system which, within the framework of non-relativistic

molecular quantum electrodynamics, is [18–20]

$$H = H_{rad} + \sum_\xi H_{mol}(\xi) + \sum_\xi H_{int}(\xi) \tag{1}$$

of which the coupling between the molecules and the radiation field, described by the term

$$H_{int}^{(\xi)} = -\epsilon_0^{-1} \boldsymbol{\mu}(\xi) \cdot \boldsymbol{d}^\perp(\boldsymbol{R}_\xi) \tag{2}$$

may be regarded as a perturbation on basis states which are product eigenfunctions of H_{rad} and H_{mol}. The symbols $\boldsymbol{\mu}(\xi)$ and $\boldsymbol{d}^\perp(\boldsymbol{R}_\xi)$ denote the molecular electric dipole and the transverse electric displacement operators respectively, the latter explicitly expressible through a mode expansion as

$$\boldsymbol{d}^\perp(\boldsymbol{R}_\xi) = i \sum_{k,\lambda} \left(\frac{\epsilon_0 \hbar\omega_k}{2V} \right)^{1/2} [\boldsymbol{e}_k^{(\lambda)} a_k^{(\lambda)} \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_\xi)$$
$$- \bar{\boldsymbol{e}}_k^{(\lambda)} a_k^{+\,(\lambda)} \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_\xi)] , \tag{3}$$

where V is a quantisation volume, $\boldsymbol{k}$ denotes photon wave-vector and $\boldsymbol{e}_k^{(\lambda)}$ polarisation; the symbols $a_k^{(\lambda)}$ and $a_k^{+\,(\lambda)}$ respectively signify the corresponding annihilation and creation operators. Although the process under consideration is insensitive to polarisation, we allow $\boldsymbol{e}_k^{(\lambda)}$ to be complex to admit the possibility of circular or elliptical polarisations; $\bar{\boldsymbol{e}}_k^{(\lambda)}$ is then the complex conjugate vector.

The rate Γ of photoabsorption by each interface pair can be calculated using third-order perturbation theory and the Fermi Golden Rule,

$$\Gamma = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho_f , \tag{4}$$

where the transition matrix element from an initial state i to a final state f is

$$M_{fi} \cong \sum_{r,s} \frac{\langle f|H_{int}|r\rangle \langle r|H_{int}|s\rangle \langle s|H_{int}|i\rangle}{(E_i - E_r)(E_i - E_s)} , \tag{5}$$

and all states refer to the *system* comprising the molecule and the radiation. The parameter ρ_f in Eq. (4) relates to the final state of the system, and is expressible as a convolution of the densities of states for A* and B*, i.e. $\rho_f = \int \rho_\alpha(E)\rho_\beta(\hbar\omega - E)\, dE$. The detuning energy is regarded as exceeding the natural bandwidth of the electronic excited state; this removes the necessity for explicit inclusion of damping in the energy terms, though they can if required be incorporated by the usual methods.

In any such process the time-ordered diagrams that represent the contributions to M_{fi} number twelve in total. Each diagram represents a different time-ordering of the basic processes of the absorption of a real photon from the incident light, and the propagation of a virtual photon either from A to B or vice versa. In the following we shall for simplicity assume that the transitions $|0\rangle \to |\alpha\rangle$ and $|0\rangle \to |\beta\rangle$ undergone by molecules A and B are both electric dipole allowed. If B is centrosymmetric, as might befit a nonpolar species, it is then impossible for the real photon to be absorbed at this molecule since the second-order process necessarily entailed is forbidden. Thus the process is fully represented by a reduced set of six time-ordered diagrams as illustrated elsewhere [15–17]. Two examples are shown in Fig. 2.

The result for the matrix element after summation over the complete set of virtual photon states yields the following matrix element, expressed in terms of the repeated index summation convention:

$$M_{\text{fi}} = -i \left(\frac{n\hbar\omega_k}{2V\epsilon_0} \right)^{1/2} e_k \mu_i^{\beta 0} S_{jk}^{\alpha 0}(\omega)$$

$$\times V_{ij}(\omega_{\beta 0}, \boldsymbol{R}) \exp(i\boldsymbol{k}\cdot\boldsymbol{R}_{\text{A}}), \qquad (6)$$

where n is the number of laser photons in the quantisation volume, $\boldsymbol{\mu}^{\beta 0}$ is the transition dipole moment for molecule B and $S^{\alpha 0}(\omega)$ is a second rank molecular transition tensor for A. The tensor V_{ij} is the retarded resonance electric dipole coupling, represented as
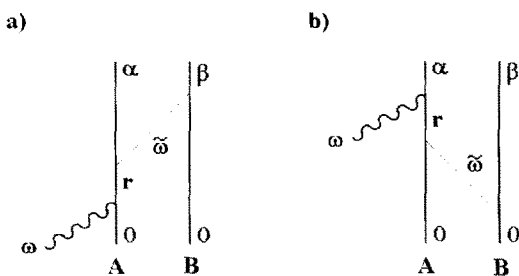
a)   b)

Fig. 2. Two typical time-ordered diagrams for cooperative single-photon absorption, time running upwards. The intermolecular coupling in each case represented by dashes is mediated by a virtual photon of frequency $\tilde{\omega}$.

$$V_{ij}(\omega_{\beta 0}, \boldsymbol{R}) = \frac{\exp(i\omega_{\beta 0}R/c)}{4\pi\epsilon_0 R^3}$$

$$\times [\, (1 - i\omega_{\beta 0}R/c)(\delta_{ij} - 3\hat{R}_i\hat{R}_j)$$

$$- (\omega_{\beta 0}R/c)^2(\delta_{ij} - \hat{R}_i\hat{R}_j)\,]\,, \qquad (7)$$

within which the molecular separation vector $\boldsymbol{R} \equiv \boldsymbol{R}_{\text{B}} - \boldsymbol{R}_{\text{A}}$ represents the displacement of B with respect to A. In passing we note that the formal derivation of the coupling tensor [4] leads to the above fully complex result; inclusion of the imaginary part obviates the problem of oscillatory range-dependence that will otherwise arise [15,16]. The single term in the square brackets of Eq. (7) not involving $\omega_{\beta 0}R/c$ provides the dominant contribution in the limit of $\omega_{\beta 0}R/c \ll 1$. In this case the quadratic dependence of the absorption rate on the matrix element leads to the familiar R^{-6} dependence.

3. Static dipole effects

Attention can now be turned to the structure of the molecular tensor $S^{\alpha 0}$ for molecule A. Novel features here emerge through the static dipoles of the ground and excited states associated with the charge transfer transition, i.e. the optically induced internal charge redistribution. In fact $S^{\alpha 0}$ has exactly the same form as an (electronic) Raman scattering tensor, being expressed by

$$S_{jk}^{\alpha 0}(\omega) = \sum_r \left(\frac{\mu_k^{\alpha r}\mu_j^{r0}}{E_{\alpha r} - \hbar\omega} - \frac{\mu_j^{\alpha r}\mu_k^{r0}}{E_{r0} - \hbar\omega} \right). \qquad (8)$$

The features of the result that are significant in the present context emerge once the above tensor is separated into a combination of near-resonant terms and non-resonant background terms.

The representation shown in Fig. 3 shows how, in summing over the states $|r\rangle$ in Eq. (8), the first term might dominate for a state close in energy to the final state. Assuming that the natural bandwidth γ of the excited electronic state of A is small compared to the detuning frequency $\Delta\omega$, (and $\Delta\omega \ll \omega$), then the molecular tensor can be expressed in terms of a charge transfer (CT) driving term (originating from the terms with $r=0$, α) and a background (BG) term ($r \neq 0$, α). A similar dependence on charge transfer
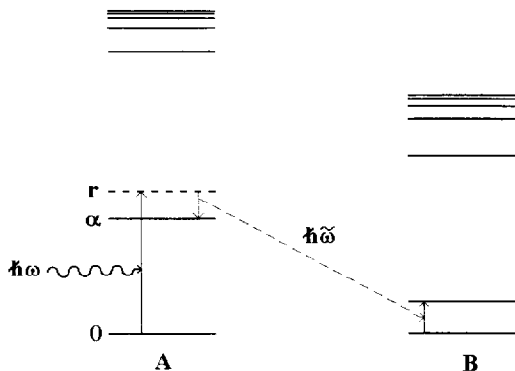
Fig. 3. Energetics of the dominant mechanism, associated with Fig. 2(a), showing absorption near resonance with molecule A. The transition $|0\rangle \rightarrow |\alpha\rangle$ is that which is associated with intra-molecular charge transfer.

dipoles is a well attested feature of two-photon absorption processes; see for example Meath and Power [21]. The separation of the molecular tensor can thus be expressed as

$$S_{jk}^{\alpha 0} = S_{jk}^{(CT)} + \sum_{r \neq 0,f} S_{jk}^{(BG)} \qquad (9)$$

where the driving term is explicitly

$$S_{jk}^{(CT)} = \mu_k^{\alpha 0}\left(\frac{\mu_{Aj}^{\alpha\alpha} - \mu_{Aj}^{00}}{\hbar\omega - E_{\alpha 0}}\right) - \mu_j^{\alpha 0}\left(\frac{\mu_{Ak}^{\alpha\alpha} - \mu_{Ak}^{00}}{\hbar\omega}\right) \qquad (10)$$

and each term manifests a linear dependence on a difference in the ground and excited state dipoles, as associated with charge transfer. Even here it can be seen that the first term strongly dominates the second: it is clear that the latter will add only a contribution similar in magnitude to any other component in the background sum, and could thus be incorporated in the second term of Eq. (9). Therefore the result can be concisely expressed as

$$S_{jk}^{(CT)} = \frac{d_j \mu_k^{\alpha 0}}{\hbar\omega - E_{\alpha 0}}, \qquad (11)$$

where d represents the vector difference in static dipole moments of the ground and final excited electronic states of molecule A. The denominator of (11), which represents the detuning, can be identified as the energy uptake of molecule B, in other words it is equal to $E_{\beta 0}$.

From Eqs. (4) and (6) the rate of absorption is now given by

$$\Gamma = \frac{n\pi\omega\rho_f}{V\epsilon_0} e_k \bar{e}_n \mu_i^{\beta 0} \bar{\mu}_l^{\beta 0} S_{jk}^{\alpha 0} \bar{S}_{mn}^{\alpha 0} V_{ij} \bar{V}_{lm} . \qquad (12)$$

Writing the result explicitly in terms of the intensity I of incident radiation through the relation $I = n\hbar c\omega / V$, using the short-range limit of the coupling tensor (7) and expressing the result in terms of the driving charge transfer tensor (11), we then have

$$\Gamma \approx \frac{I\rho_f}{16\pi c\epsilon_0^3 \hbar E_{\beta 0}^2 R^6}$$

$$\times | (\boldsymbol{\mu}^{\alpha 0}\cdot\boldsymbol{e})[(\boldsymbol{\mu}^{\beta 0}\cdot\boldsymbol{d}) - 3(\boldsymbol{\mu}^{\beta 0}\cdot\hat{\boldsymbol{R}})(\boldsymbol{d}\cdot\hat{\boldsymbol{R}})]|^2, \qquad (13)$$

which is quadratically dependent on the magnitude of d, the charge transfer dipole vector. As it stands Eq. (13) is applicable only to molecules with a fixed mutual orientation; where an interface between two immiscible liquids is concerned, a triple rotational average [11] has to be performed to represent complete orientational decoupling of each molecule with respect not only to the polarisation of the incoming radiation but also their mutual displacement vector R. The result then reduces to

$$\Gamma \approx \frac{|d|^2 |\mu^{\alpha 0}|^2 |\mu^{\beta 0}|^2 I\rho_f}{72\pi c\epsilon_0^3 \hbar E_{\beta 0}^2 R^6} . \qquad (14)$$

To gain some insight into the likely magnitude of the effect, it is instructive to broadly compare the above result for the rate of bimolecular absorption with the corresponding result for conventional single-photon absorption. For simplicity we consider that absorption associated with the $|0\rangle \rightarrow |\beta\rangle$ transition of molecule B, for which the rate equation takes the form $\Gamma = (\pi I / 3\epsilon_0\hbar c)|\mu^{\beta 0}|^2\rho_\beta$. We may also assume that similar intensities, I, are involved and that the bimolecular density of states ρ_f is similar in magnitude to ρ_β (the former will in fact exceed ρ_β unless the excited state $|\alpha\rangle$ is a discrete structureless level). Putting in some realistic figures $|d| = 5$ D, $|\mu^{\alpha 0}| = 1$ D, $E_{\beta 0}/hc = 1500$ cm^{-1} and $R = 0.5$ nm, we find a bimolecular rate smaller by two orders of magnitude than the normal single-centre absorption rate. In practice, even the use of cw lasers may offer intensity levels at which dipole-assisted bimolecular absorption should be observed.

4. Conclusion

The theory derived above deals with the process whereby a molecule with a well-characterised charge transfer transition can, in the vicinity of another species with suitable energy levels, exhibit absorption of radiation in a wavelength region where it is normally transparent. The quadratic dependence of the absorption rate on the charge transfer dipole moment invites experimental study of the process with any species demonstrating a large shift of its electron distribution in an accessible electronic excited state. It is estimated that relatively low intensities should then be sufficient for the observation of the effect.

In considering potential applications of the process, it should be borne in mind that the short-range dependence of the bimolecular absorption rate on distance runs as R^{-6}, so that essentially only molecules that are nearest neighbours across an interface will make any substantial contribution to the signal. This may be contrasted, for example, with the relatively weak surface sensitivity of second harmonic generation, where signals from within a bulk fluid phase can arise from molecules as much as one quarter of the laser wavelength below the surface. As such, the bimolecular photoabsorption process may prove useful as a new tool for the characterisation of interfaces.

Acknowledgement

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