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Synergistic photoabsorption: Range effectiveness of the cooperative and distributive mechanisms

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A recently discovered two-photon absorption process can produce novel features in spectra obtained with intense broadband radiation. Two mechanisms termed *cooperative* and *distributive* contribute to the effect, which involves synergistic photoabsorption by molecular pairs. In the former mechanism, each molecule of the pair absorbs a single photon; in the latter, two photons are absorbed by one of the molecules. In contrast to earlier suggestions, it is here shown that the distributive mechanism is far more significant over large intermolecular distances.

On passing pulses of mode-locked laser light through suitable media, a process of self-phase modulation results in the generation of a broad white-light continuum.[1] Such radiation has found numerous challenging applications in the physical, chemical, and biological sciences, mostly in connection with studies of the ultrafast kinetics of chemical transients.[2] Although the interpretation of results from such experiments is mostly based on the assumption of a Beer-Lambert absorption law, recent work has shown that the validity of this premise is in doubt.[3] In fact, at high intensities a synergistic photoabsorption mechanism allows for photon pairs with differing frequencies to provide the energy for the concerted excitation of molecules in close proximity.[4] This nonlinear process can result in a rate of absorption which departs significantly from normal Beer-Lambert behavior.

The synergistic process of interest, which involves two molecules (A) and two photons ($\hbar\omega$ and $\hbar\omega'$) from the continuum, may be expressed by the equation

$$2A+\hbar\omega+\hbar\omega'\rightarrow 2A^* , \tag{1}$$

and the interesting features arise where neither photon has a frequency to match an absorption band in the sample. In such a situation there are two mechanisms which can provide the means for the concerted excitation. One, known as the *cooperative mechanism,* involves absorption of single laser photons by each molecule, with the energy mismatch at either center propagated to its partner by means of virtual photon coupling, as illustrated in Fig. 1(a). In the other case, known as the *distributive mechanism,* either one of the molecules absorbs both laser photons and a virtual photon conveys the entire excitation energy to the partner, as illustrated in Fig. 1(b).

The ultrashort time scale of laser-continuum pulses produces many interesting implications for quantum-measurement theory,[5] and on the basis of time-energy uncertainty considerations, it has been suggested that the cooperative mechanism should be appreciably more significant than the distributive mechanism in mediating the synergistic effect.[3] However, a more detailed comparison of the rate equations shows that, in fact, subject to selection rule constraints,[3] the converse is generally true. This can be demonstrated as follows. The rates of cooperative absorption, Γ_{2c}, and distributive absorption, Γ_{2d}, are given by equations (3.3), (3.4), (3.8) and (3.9) of Ref. 3, i.e.,

$$\Gamma_{2c}=(2\hbar^2c^2\epsilon_0^2)^{-1}\pi \times\int_0^\infty K_2(\omega_0,\Omega)I(\omega_0+\Omega)I(\omega_0-\Omega)d\Omega , \tag{2}$$

$$\Gamma_{2d}=(2\hbar^2c^2\epsilon_0^2)^{-1}\pi \times\int_0^\infty K_2'(\omega_0,\Omega)I(\omega_0+\Omega)I(\omega_0-\Omega)d\Omega , \tag{3}$$

where, using the repeated index convention for tensor contractions, we have

$$K_2(\omega_0,\Omega)=|e_ie_jS_{ik}^{fi}(\omega_0+\Omega)S_{jl}^{fi}(\omega_0-\Omega)[V_{kl}(\Omega,\mathbf{R})+\bar{V}_{kl}(\Omega,\mathbf{R})\exp(i\Delta\mathbf{k}\cdot\mathbf{R})]|^2 \tag{4}$$

and

$$K_2'(\omega_0,\Omega)=\left|e_ie_j\chi_{(ij)k}^{fi}(\omega_0+\Omega,\omega_0-\Omega)\mu_l^{fi}V_{kl}(\omega_0,\mathbf{R})\left[1+\exp\left[i\sum\mathbf{k}\cdot\mathbf{R}\right]\right]\right|^2 . \tag{5}$$

Here $I(\omega)$ is the irradiance per unit circular frequency, S_{ij}^{fi} and X_{ijk}^{fi} are the electronic Raman and hyper-Raman tensors for the $|f\rangle\leftarrow|i\rangle$ transition, $\mathbf{R}$ is the vector $\mathbf{AB}$, and $\sum\mathbf{k}$, $\Delta\mathbf{k}$, and $\mathbf{e}$ are the sum of the propagation vectors, the difference in the propagation vectors, and the polarization vector of the absorbed photons, respectively. Finally, the tensor $V_{kl}(\Omega,\mathbf{R})$ is the complex resonance electric-dipole–electric-dipole coupling tensor given by[6,7]

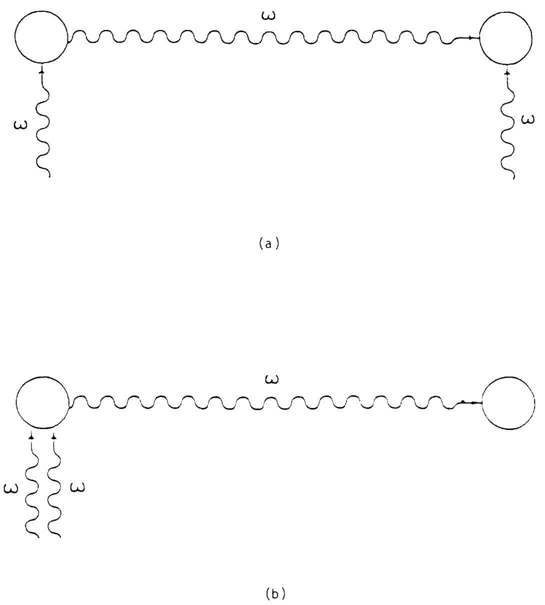

FIG. 1. Two mechanisms for synergistic absorption of photons ω,ω'; (a) shows the cooperative mechanism and (b) the distributive mechanism. In each case the energy mismatch is conveyed by a virtual photon $\tilde{\omega}$.

$$V_{k1}(\Omega,\mathbf{R}) = (4\pi\epsilon_0 R^3)^{-1}[(\delta_{kl}-3\hat{R}_k\hat{R}_l)(1-i\Omega R/c) - (\delta_{kl}-\hat{R}_k\hat{R}_l)(\Omega R/c)^2]e^{i\Omega R/c} \; . \quad (6)$$

Two key features of this expression are worth noting. First, aside from the oscillatory phase factor the R dependence is dominated by the leading R^{-3} term where $\Omega R/c \ll 1$, and by the final R^{-1} term where $\Omega R/c \gg 1$. Second, the factor $(\delta_{kl}-\hat{R}_k\hat{R}_l)$ in the final term is purely transverse with respect to the intermolecular vector $\mathbf{R}$, whereas the preceding terms with the factor $(\delta_{kl}-3\hat{R}_k\hat{R}_l)$ have partly transverse and partly longitudinal character.

In general, explicit evaluation of the tensor contractions in Eqs. (4) and (5) requires a knowledge of the relative orientations of the two molecules both with respect to each other and also with respect to the radiation field. Consequently the detailed dependence on molecular separation R is not in general expressible in a simple functional form. However, the situation changes when an isotropic system is considered. Here, the appropriate result is derived by performing a series of three rotational averages on Eqs. (4) and (5). These involve rotating the A-B system with respect to the radiation field vectors, and then both A and B with respect to the intermolecular vector $\mathbf{R}$. The results, which *per se* are of considerable length and are given in detail elsewhere,[8,9] nonetheless display a readily identifiable range dependence expressible in terms of an excitation transfer function $A(k,R)$. This is defined by the contraction of the resonance coupling tensor with its complex conjugate, i.e.,

$$A(k,R) \equiv V_{kl}(ck,\mathbf{R})\bar{V}_{kl}(ck,\mathbf{R}) \quad (7)$$

and leads to the explicit result,

$$A(k,R) = 2(4\pi\epsilon_0 R^3)^{-2}(3+k^2R^2+k^4R^4) \; . \quad (8)$$

This function has a range dependence which is of particular interest in two special cases.

At short distances $R \le R_{\max}$ over which the energy-exchange photon is of purely virtual character, both K_2 and K_2' show the familiar R^{-6} behavior associated with Förster-type energy transfer.[10] The extent of $R_{\max}$ is given by

$$R_{\max}^{\text{coop}} = \tfrac{1}{4}hc(\hbar\omega - E_{fi})^{-1} \quad (9)$$

for the cooperative case, and

$$R_{\max}^{\text{dist}} = \tfrac{1}{4}hc/E_{fi} \quad (10)$$

for the distributive case. One of the most crucial factors in comparing the cooperative and distributive mechanisms for synergistic absorption is the difference in the limits given by Eqs. (9) and (10). Outside these regions, where $R \gg R_{\max}$, the asymptotic form of the range dependence is simply expressed by K_2, $K_2' \sim R^{-2}$. This reflects the fact that over long distances, and hence comparatively long time scales, the energy conservation constraints at A and B become much more limiting; conse-

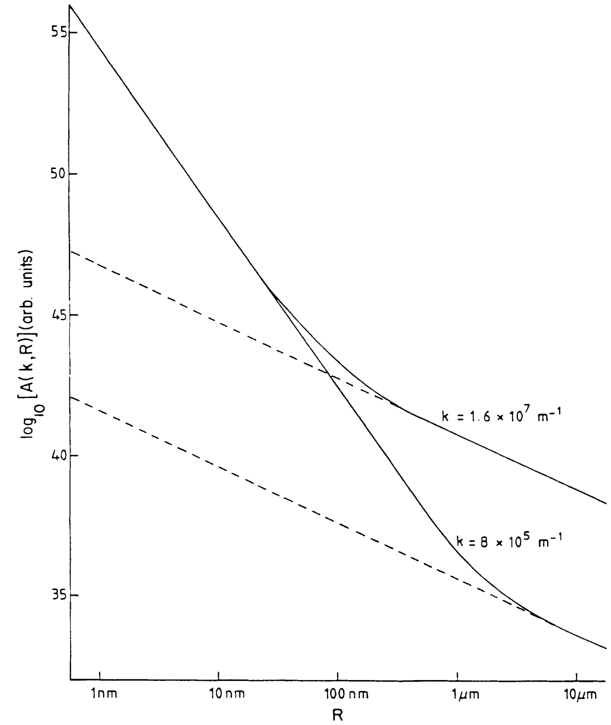

FIG. 2. Log-log plots of the excitation transfer function $A(k,R)$ against intermolecular distance R. Distributive absorption is represented by the upper curve, cooperative by the lower.

quently the energy-exchange photon assumes a real character, and the normal inverse-square dependence of classical radiative energy transfer ensues. These features reflect the properties of the resonance coupling tensor referred to earlier.

Figure 2 shows log-log plots of $A(k,R)$ on an arbitrary vertical scale for two values of k. The upper curve, plotted for $k=1.6\times10^7\ \mathrm{m}^{-1}$, corresponds to distributive conveyance of an electronic energy E_{fi} associated with a wavelength of about 400 nm. The lower curve with $k=8\times10^5\ \mathrm{m}^{-1}$ corresponds to the cooperative mechanism where only an electronic energy *difference* (nominally $E_{fi}/20$) is conveyed; here the difference equates to a vibrational energy with a wave number of around 1250 cm^{-1}. At short distances the two graphs are indistinguishable and display the near-zone R^{-6} dependence. However, the extent of the near zone for the former case is much shorter, with the limiting far-zone R^{-2} behavior already established at $R=1\ \mu\mathrm{m}$; for the latter case far-zone behavior obtains at $R=10\ \mu\mathrm{m}$. The result of this difference is that the long-range rates (which vary with k^4) differ by a factor of $(20)^4=160\,000$ in favor of the distributive mechanism.

In conclusion, although it has been shown that the volume of space within which the distributive mechanism can apply *by virtual photon coupling* is far smaller than the corresponding volume for the cooperative mechanism, the real significance of this result is that the onset of long-range behavior occurs sooner in the distributive case. Consequently, the limiting behavior associated with energy transfer by a *real* photon, with its attendant *increase* in effective rate, occurs at shorter distances for the distributive mechanism. Thus, where selection rules allow both mechanisms to operate, the distributive mechanism is far more significant than the cooperative mechanism over long intermolecular distances.

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