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Cooperative Absorption-Induced Charge Transfer in a Solid

by

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Cooperative electronic excitation involving electron transfer among guest molecules in a solid is considered. The mutual interaction between two guest molecules with large dipole moments in excited states can lead to cooperative processes (two-electron transfer) which are forbidden in the absence of such interaction. The cooperative transition moments are calculated for coupled pairs of XeCl molecules within an Ar matrix at sum and difference frequencies.

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Cooperative Absorption-Induced Charge Transfer in a Solid

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Abstract

Cooperative electronic excitation involving electron transfer among guest molecules in a solid is considered. The mutual interaction between two guest molecules with large dipole moments in excited states can lead to cooperative processes (two-electron transfer) which are forbidden in the absence of such interaction. The cooperative transition moments are calculated for coupled pairs of XeCl molecules within an Ar matrix at sum and difference frequencies.

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I. Introduction

Cooperative transitions, which can be defined here as the simultaneous change of electronic states of coupled pairs of atoms (ions) or molecules whose orbitals do not overlap directly with another, have been studied since the early 1960's. One can distinguish cooperative transitions according to three types:

(1) Single-photon cooperative absorption (OPCA) [1] wherein one photon is simultaneously absorbed by the concurrent change of electronic states of two separate atoms (molecules),

$$A + B + \hbar\omega_L \rightarrow A^* + B^* \qquad \omega_L \simeq \omega_A + \omega_B \ , \tag{1a}$$

$$A^* + B + \hbar\omega_L \rightarrow A + B^* \qquad \omega_L \simeq \omega_B - \omega_A \ . \tag{1b}$$

(2) Cooperative excitation (CE) [2] wherein two atoms (molecules) simultaneously transfer their electronic energy to another atom,

$$A^* + B^* + C \rightarrow A + B + C^* \qquad \omega_A + \omega_B \simeq \omega_C \ . \tag{2}$$

(3) Two-photon cooperative absorption (TPCA) [3] in which two photons are simultaneously absorbed by a pair of atoms (molecules),

$$A + B + 2\hbar\omega_L \rightarrow A^* + B^* \qquad 2\omega_L = \omega_A + \omega_B \ . \tag{3}$$

Cooperative transitions have been detected experimentally in crystals containing rare-earth ions [4-8], whose optical transitions involve their inner orbitals, thus excluding any influence of the interatomic overlap on the cooperative transitions. As was shown by Dexter [1] the cooperative transitions in the rare-earth ions are caused by the dipole-dipole interaction due to the inter-electron correlation, which is responsible also for the van der Waals (London) attraction (see, for example, Ref. 9).

Cooperative transitions are inherently widespread since they are brought about by an interaction as common as the van der Waals attraction. However, there is little known about cooperative phenomena in systems other than the crystals containing the rare earth ions. There is the case of the energy transfer between OH and NH molecules in rare-gas solids [10,11] and the case of cooperative absorption in solid O_2 [12], but the latter case is caused, most probably, by direct overlap of molecular orbitals. One may hope that cooperative transitions occur in various other systems. It is of obvious interest to study this phenomenon beyond the scope of the rare-earth ions.

There are reasons to hope that the cooperative transitions can be detected in molecules whose electronic excitation is accompanied by a strong change in a static dipole moment. Due to the electrostatic interaction, the electronic states of those molecules are coupled one with another, even when the molecules are not located in close proximity, which creates conditions for cooperative transitions. The electronic excitation affects the static dipole moment most of all in molecules or other polyatomic systems with electron transfer [13-17]. From the point of view of cooperative transitions, small molecules with electron transfer, like rare gas-halogen molecules [17], are the most promising candidates. In large systems [13,18], cooperative phototransitions, at least OPCA, are unlikely.

The present paper deals with OPCA of pairs of guest molecules in a solid. The electronic excitation of guest molecules involves electron transfer and the formation of ionic molecules with large dipole moments, causing mutual interaction among the guest molecules. As an example of an excitation with electron transfer, we shall consider rare-gas solids containing halogen atoms. These excitations were studied experimentally in the case of Xe and Ar-Xe solids doped by Cl_2 or HCl molecules and exposed to UV radiation [19,20]. The irradiation generates free Cl atoms, which together with surrounding Xe atoms can be excited by photon absorption to ionic activated complexes. In the Xe solid, the ionic activated complex involves usually several Xe atoms with partly delocalized positive charge [21,22]. Due to this delocalization, the adjacent activated complexes can overlap, which may lead to cooperative absorption [23]. In the Ar-Xe solid with low concentration of Xe atoms [19], any Cl atom has most often only one neighboring Xe atom and consequently forms the activated complex Xe^+Cl^-. We shall treat this diatomic activated complex as an excited ionic molecule, whereas the initial pair of neutral Cl and Xe atoms will be treated as a ground state molecule.

The interaction between two XeCl molecules can lead to OPCA by: (a) sum frequency where two XeCl guest molecules are excited simultaneously by one photon whose energy is equal to the sum of the excitation ($X \rightarrow B$) energies of each molecule and (b) difference frequency where the de-excitation of a guest XeCl ($C \rightarrow A$) and the excitation of another guest XeCl molecule ($X \rightarrow B$) occur simultaneously by one photon whose energy is the difference of their energies (see Fig. 1). (The state labels A and B used here are not to be confused with the molecule labels A and B.) Their absorption intensities are determined by the cooperative (two-electron) transition moment. Cooperative emission, unlike cooperative absorption, depends also on the lifetime of the excited state. The lifetime of the excited Xe^+Cl^- molecules is of the order of 10^{-7} s [19], which is much smaller than the lifetime of excited rare-earth ions ($\sim 10^{-4}$ s) [24], so that the cooperative emission of the XeCl molecules is not of interest.

In the next section we look at the cooperative transition moment. A discussion is presented in Section III.

II. Cooperative Transition Moment

Let us consider two diatomic molecules A and B in a solid with no significant dipole moment in the ground state but a large dipole moment in an excited ionic state. In each of these molecules, one of the atoms (rare-gas atom, for example) is the electron donor whereas another atom (halogen atom, for example) is the electron acceptor. The donor and acceptor atoms are denoted by a, b and $\bar{a}$, $\bar{b}$, respectively. We assume that the wave functions of the molecules do not overlap either with host atoms or with one another. The molecules will be considered in the one-electron approximation, taking into account in each molecule only the electron which is transferred between the atoms by the excitation to the ionic state. The interactions between electrons will be considered in the zero overlap of atomic orbitals (ZOAO) approximation. In this approximation, as will be shown later, the values of interest are expressed by Coloumbic interactions, which are not sensitive to the orbital symmetry. For the sake of simplicity, we shall assume the atomic orbitals (AO) χ to be of s-symmetry. We shall consider the parameters of electron transfer excitation, which are sensitive to the orbital symmetry [16,25], as empirical parameters.

Due to the coupling between the ground (neutral) and excited (ionic) states [23,26], the molecular orbitals should be represented as a mix of both AO but with the predominant contribution of the donor AO, χ_a and χ_b, in the neutral state and of the acceptor AO, $\chi_{\bar{a}}$ and $\chi_{\bar{b}}$, in the ionic state. In the ZOAO approximation, the molecular orbitals are as follows:

$$\alpha_g = (1 - \tfrac{1}{2}\gamma_A^2)\chi_a + \gamma_A\chi_{\bar{a}} \qquad (4a)$$

$$\alpha_e = -\gamma_A\chi_a + (1 - \tfrac{1}{2}\gamma_A^2)\chi_{\bar{a}} \quad , \quad \langle\alpha_g|\alpha_e\rangle = 0 \tag{4b}$$

$$\beta_g = (1 - \tfrac{1}{2}\gamma_B^2)\chi_b + \gamma_B\chi_{\bar{b}} \tag{4c}$$

$$\beta_e = -\gamma_B\chi_b + (1 - \tfrac{1}{2}\gamma_B^2)\chi_{\bar{b}} \quad , \quad \langle\beta_g|\beta_e\rangle = 0 \quad , \tag{4d}$$

where α and β are the molecular orbitals of A and B respectively, α_g and β_g are the ground state orbitals, α_e and β_e are the molecular orbitals in the excited state, and γ_A and γ_B are the AO amplitudes which are considered as small. In Eqs. (4a-d), the values of the order of γ^3 or smaller are neglected. The molecular orbitals provide the expressions for the transition (g → e) moment and the static dipole moment in the ionic excited state:

$$\vec{\mu}_{A,g\to e} = \int d\vec{r}_1 \, \alpha_g \, \vec{r}_1 \, \alpha_e = \gamma_A \, \vec{\mu}_{A,e} \tag{5}$$

$$\vec{\mu}_{A,e} = \int d\vec{r}_1 \, \alpha_e \, \vec{r}_1 \, \alpha_e = e(\vec{R}_{\bar{a}} - \vec{R}_a) \quad , \tag{6}$$

where $\vec{R}_{\bar{a}}$ and $\vec{R}_a$ are the radius-vectors of the atoms. The same expressions are valid for molecule B. The static dipole moment of the ground state is small [26].

The large excited-state dipole moment gives rise to an electrostatic interaction between two molecules (A and B) when at least one of these molecules is in an excited state. Due to this interaction, the probability of the excitation of the molecule B, for example, depends on whether another molecule, A is in its ground or excited state. Such correlation between the electronic states of separated molecules can lead to simultaneous (cooperative) transitions (1).

The cooperative transition moment which determines the simultaneous optical transitions in both molecules is equal to the two-electron integral [1]. For the sum-frequency absorption, it is given by

$$\vec{\mu}_{AB}(gg \rightarrow ee) = e\iint d\vec{r}_1 d\vec{r}_2 \, \psi_{ee}(\vec{r}_1+\vec{r}_2) \, \psi_{gg} \quad , \qquad (7)$$

where $\psi_{ee}(12)$ is the two-electron wave function describing the state with both excited molecules and $\psi_{gg}(12)$ is the ground state wave function. The cooperative transition moment for the difference-frequency absorption is expressed as

$$\vec{\mu}_{AB}(ge \rightarrow eg) = e\iint d\vec{r}_1 d\vec{r}_2 \, \psi_{eg}(\vec{r}_1+\vec{r}_2) \, \psi_{ge} \quad . \qquad (8)$$

The wave function ψ is not antisymmetrized due to the ZOAO approximation. If the molecular orbitals are unperturbed by each other, then the two-electron functions $\psi(12)$ are simple products of molecular orbitals α and β, so that the integrals (7) and (8) are zero. (They are nonzero only when the interatomic correlation is taken into account.) We shall neglect the mutual perturbation of AO which was considered in Ref. 1, keeping in mind only the electron transfer. In such an approximation, the correlated wave functions are expressed as the superpositions of different products of the molecular orbitals α and β

$$\psi_{ij}(12) = \sum_{k,\ell=g}^{e} \xi_{ij,k\ell} \, \alpha_k(1)\beta_\ell(2) \quad , \quad i,j = g,e \quad , \qquad (9)$$

where 1 and 2 stand for the electrons of molecules A and B, respectively. As the interaction between the molecules is weak, the coefficient ξ can be found in the framework of perturbation theory as

$$\xi_{ij,ij} = 1 \quad , \tag{10}$$

$$\xi_{ij,k\ell} = \langle \alpha_k \beta_\ell | \hat{H}_{AB} | \alpha_i \beta_j \rangle \; / \; (E_{AB}^{(ij)} - E_{AB}^{(k\ell)}) \quad , \quad k,\ell \neq i,j , \tag{11}$$

$$i,j,k,\ell = g,e \quad .$$

where $E_{AB}^{(gg)}$, $E_{AB}^{(ge)}$ and so on are the energies of the molecules A and B in the corresponding states, and $\hat{H}_{AB}$ is the interaction Hamiltonian,

$$\hat{H}_{AB} = \frac{e^2}{\epsilon^*} (1/R_{ab} - 1/r_{1b} - 1/r_{2a} + 1/r_{12}) \quad , \tag{12}$$

where R_{ab} is the separation between the donor atoms a and b, e^2/R_{ab} is the energy of the Coulombic repulsion between the cores of the donor atoms, $-e^2/r_{1b}$ and $-e^2/r_{2a}$ are the terms for the electron attraction to the cores of the donor atoms, and e^2/r_{12} is the term for the interelectron repulsion; the cores of the acceptor atoms are neutral and are assumed not to have any electric moments. The effective dielectric constant ϵ^* takes into account the shielding of the electrostatic interaction by the medium. It is 1 for short distances and becomes equal to the bulk dielectric constant ϵ for distances exceeding the size of the Onsager cavity [27].

Due to the ZOAO approximation, the s-symmetry of AO and the neglect of the AO polarization, the integrals of the intermolecular interactions can be replaced by the interactions between point charges. For example,

$$\langle b | \chi_a \chi_a \rangle = e^2/R_{ab} \quad , \quad \langle a | \chi_{\bar{b}} \chi_{\bar{b}} \rangle = e^2/R_{a\bar{b}} \quad , \quad \langle \chi_a \chi_a | \chi_{\bar{b}} \chi_{\bar{b}} \rangle = e^2/R_{a\bar{b}} \quad . \tag{13}$$

Consequently, the first-order correction energies of each state are

$$U_{AB}^{(gg)} = \langle \alpha_g \beta_g | H_{AB} | \alpha_g \beta_g \rangle = 0 \tag{14a}$$

$$U_{AB}^{(ge)} = \langle \alpha_g \beta_e | H_{AB} | \alpha_g \beta_e \rangle = \gamma_A^2 V \tag{14b}$$

$$U_{AB}^{(eg)} = \langle \alpha_e \beta_g | H_{AB} | \alpha_e \beta_g \rangle = \gamma_B^2 V \tag{14c}$$

$$U_{AB}^{(ee)} = \langle \alpha_e \beta_e | H_{AB} | \alpha_e \beta_e \rangle = (1 - \gamma_A^2 - \gamma_B^2) V \quad , \tag{14d}$$

where

$$V = \frac{e^2}{\epsilon^*} (1/R_{ab} - 1/R_{a\bar{b}} - 1/R_{\bar{a}b} + 1/R_{\bar{a}\bar{b}}) \quad . \tag{15}$$

We should point out that the quantities in Eqs. (15) and (12) have different meanings. For example, r_{12} in (12) is the inter-electron distance, whereas $R_{\bar{a}\bar{b}}$ in (15) is the distance between acceptor atoms.

Substituting the molecular orbitals (4a-d) into expression (11) and taking into account the Eqs. (13), we obtain the correlated two-electron wave functions (9) as

$$\psi_{gg}(12) = \alpha_g(1)\beta_g(2) - \frac{\gamma_A \gamma_B V}{(E_A + E_B)} \alpha_e(1)\beta_e(2) \tag{16a}$$

$$\psi_{ge}(12) = \alpha_g(1)\beta_e(2) - \frac{\gamma_A \gamma_B V}{(E_A - E_B)} \alpha_e(1)\beta_g(2) - \frac{\gamma_A V}{E_A} \alpha_e(1)\beta_e(2) \tag{16b}$$

$$\psi_{eg}(12) = \alpha_e(1)\beta_g(2) - \frac{\gamma_A\gamma_B V}{(E_B-E_A)}\alpha_g(1)\beta_e(2) - \frac{\gamma_B V}{E_B}\alpha_e(1)\beta_e(2) \qquad (16c)$$

$$\psi_{ee}(12) = \frac{\gamma_A\gamma_B V}{(E_A+E_B)}\alpha_g(1)\beta_g(2) + \frac{\gamma_A V}{E_A}\alpha_g(1)\beta_e(2)$$

$$+ \frac{\gamma_B V}{E_B}\alpha_e(1)\beta_g(2) + \alpha_e(1)\beta_e(2) \quad , \qquad (16d)$$

where E_A and E_B are the excitation energies. After substitution of these wave functions into the integrals (7) and (8) for the cooperative transition moment within the "rotating-wave" approximation, we obtain

$$\vec{\mu}_{AB}(gg \to ee) = \gamma_A\gamma_B V\left[\frac{\vec{\mu}_{B,e}}{E_A} + \frac{\vec{\mu}_{A,e}}{E_B} - \frac{\vec{\mu}_{A,e}+\vec{\mu}_{B,e}}{(E_A+E_B)}\right] \quad , \qquad (17a)$$

$$\vec{\mu}_{AB}(ge \to eg) = \gamma_A\gamma_B V\left[\frac{\gamma_B^2 V}{E_B(E_A-E_B)}\vec{\mu}_{B,e} + \frac{V}{E_AE_B}(\vec{\mu}_{A,e} + \vec{\mu}_{B,e}) - \frac{\vec{\mu}_{A,e}}{E_B}\right] \quad , \qquad (17b)$$

where $\vec{\mu}_{A,e}$ and $\vec{\mu}_{B,e}$ are the static dipole moments of the excited states. According to this expression, the cooperative transition moment is proportional to the product $\gamma_A\gamma_B$ of the AO amplitudes in the molecular orbitals (4a-d) and to the electrostatic interaction between two excited molecules. In the dipole approximation, this interaction energy is

$$V = \frac{1}{\epsilon * R_{AB}^3}\left\{(\vec{\mu}_{A,e}\cdot\vec{\mu}_{B,e}) - \frac{3}{R_{AB}^2}(\vec{\mu}_{A,e}\cdot\vec{R}_{AB})(\vec{\mu}_{B,e}\cdot\vec{R}_{AB})\right\} \quad . \qquad (\quad)$$

According to Eqs. (17) and (18), the cooperative transition moment decreases with the intermolecular distance as R_{AB}^{-3}, which is the same as for the atom-atom cooperative transiton moment [1].

For the case of the difference-frequency transition (1b) with the transition moment (17b), the excitation energy E_B is larger than the emission energy E_A, since the XeCl molecule is excited to the B state whereas de-excitation takes place from the lower state C. For the case of the sum-frequency transition (1a) with the transition moment (17a), the interacting molecules can be considered as identical ($E_A = E_B$). For identical molecules the transition moment of the sum-frequency absorption in Eq. (17a) becomes

$$\vec{\mu}_{AB}(gg \to ee) = - \frac{VW}{2\epsilon^{*}E_{A}} (\vec{\mu}_{A,e} + \vec{\mu}_{B,e}) \quad , \tag{19}$$

where $W = \gamma^2$ is the population of the acceptor atom $\bar{a}$ in the neutral state or of the donor atom a in the excited state [see Eqs. (4a-d)]. If two ionic dipoles have parallel orientation ($\vec{\mu}_{A,e} = \vec{\mu}_{B,e} = \vec{\mu}_e$) and are perpendicular to the intermolecular distance ($\vec{\mu}_e \perp \vec{R}_{AB}$), one obtains

$$\mu_{AB}(gg \to ee) = \frac{W\mu_e^3}{\epsilon^{*}R_{AB}^3 E_A} \quad . \tag{20}$$

According to the last expression, the cooperative transition moment is proportional to the cube of the static dipole μ_e of the excited ionic state and inversely proportional to the cube of the intermolecular distance R_{AB}. Since the dipole-dipole interaction V is much smaller than the excitation energy, the sum-frequency condition (1a), $\omega_L = \omega_A + \omega_B$, is approximately fulfilled.

III. Discussion

Two neutral non-overlapping molecules interact with one with another via an electrostatic field due to dynamics or static dipole moments. For fixed electronic states, this leads to the well-known van der Waals interaction. If the molecules have two electronic states, then the electronic transitions in these molecules become coupled. This coupling can be realized as cooperative transitions which involve both molecules. Such transitions in non-polar molecules (atoms) with dynamic (dispersive) interaction were considered by Dexter [1]. Our theoretical arguments above show that cooperative transitions can also result from the coupling caused by the interaction of static dipole moments if these moments are not the same in the ground and excited states. As an example of molecules whose electronic transition is followed by an important change in the static dipole moment, we have considered the rare gas-halogen molecule XeCl in an Ar solid. In the ground state, a pair of interacting Xe and Cl atoms can be considered as a weakly-bound molecule where excitation to an ionic state Xe^+Cl^- gives rise to a large static dipole moment.

The intermolecular coupling described above is physically obvious. However, it has to be strong enough to result in some cooperative transition, for example, cooperative excitation of two molecules. Whether the cooperative excitation of two XeCl molecules can be really detected depends on the cooperative transition moment μ_{AB} of two interacting molecules, A and B. According to Eq. (20), μ_{AB} is determined by molecular parameters such as the $XeCl \rightarrow Xe^+Cl^-$ excitation energy E_a, Xe^+Cl^- static moment μ_e, and the $Xe \rightarrow Cl$ charge transfer W in the neutral XeCl molecule, as well as by the intermolecular distance R_{AB} and the medium dielectric constant ϵ^*.

In a typical Ar matrix with a Xe-Cl separation of 3.2 Å, the molecular constants are: $E_a = 3$ eV, $\mu_e = 15$ D and $W = 0.03$ [13]. We take the dielectric constant as $\epsilon^* = 1.6$. These parameters give $\mu_{AB} = 0.09$, 0.03 and 0.02 D for two XeCl molecules trapped as nearest neighbors ($R_{AB} = 5.3$ Å), second nearest neighbors (7.5 Å) and third nearest neighbors (8.4 Å), respectively.

The obtained transition moments of the sum-frequency cooperative absorption (1a) are not neglibly small, so that the cooperative absorption is expected to be detectable. According to estimations, the transition moments of the difference-frequency absorption (1b) are four to five times smaller than those of the absorption (1a).

When the concentration of impurity Cl_2 molecules increases, two guest molecules become closer than a nearest-neighbor substitutional trapping cage distance and start to occupy an interstitital site. Then, the cooperative transition moments reach relatively large values, and another possible mechanism due to indirect (via common host atoms) overlap of the wavefunctions of adjacent guest molecules [23] will enhance the cooperative transition moments. These results suggest the possibility of experimental detection of OPCA in Ar-Xe solids doped by Cl_2 molecules.

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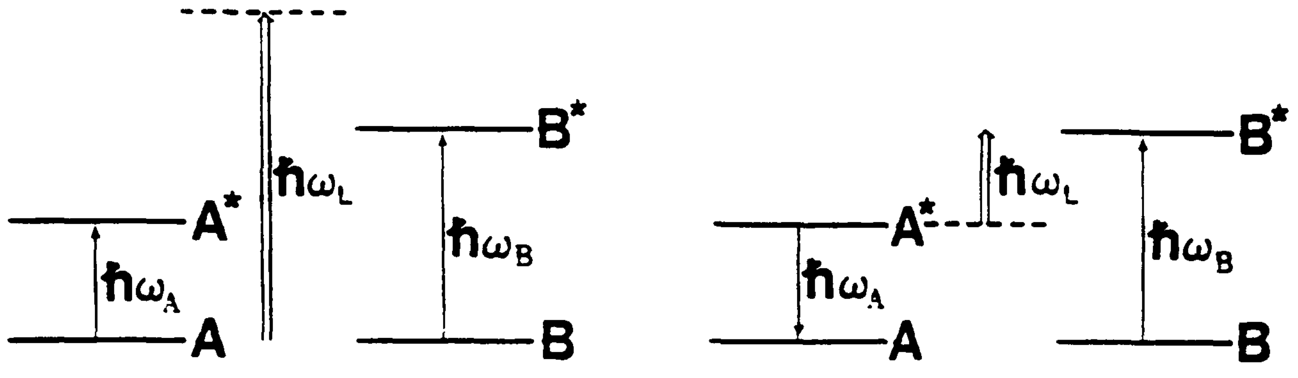
Figure Caption

1. Cooperative optical absorption by a pair of guest molecules A and B in a rare-gas solid matrix at (a) sum or (b) difference frequencies of the isolated constituents.

Fig. 1



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