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Excitation Transfer and Decay in Molecular Dimers Optically Excited

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The transfer of excitation in a dimer is treated as a resonance, using Feshbach's nuclear reaction formalism. The radiation field-matter interaction is treated simultaneously with the intermonomeric potential. This gives a unified point of view and allows one to see what the interference effects are. The Förster vibrational-relaxation mechanism and the Frenkel exciton are studied for the dimers, and explicit expressions for the decay probability are obtained.

I. INTRODUCTION

Excitation transfer in dimers can be understood as a nonradiative transition process. As such, it is extremely difficult to detect directly in an experiment. What is observed instead is the molecular luminescence. Thus, a thorough study of the radiative processes in dimers should show the features of excitation transfer. From a theoretical point of view, both potentials which cause radiative decay and excitation transfer should be treated on an equal basis. Essentially, it is the intermolecular interaction in the dimer which produces the excitation transfer, and the radiation field-matter interaction which causes the fluorescence decay. Up to now, the two mechanisms have always been separated, and the excitation transfer has been studied considering only the intermolecular interaction.

The excitation transfer in molecular dimers has been studied, introducing simplifying assumptions[1–3]: Each of the interacting molecules is a system of two levels; one is the ground state and the other is the considered excited state. Furthermore, when each of the monomers is individually electronically excited, there is only one vibrational mode Q of the molecule which is perturbed by the electronic excitation.

Depending on the importance of the interaction between the two molecules composing a dimer, there are several types of energy transfer between them. Consider first the case where the intermolecular distance is such that the energy associated with the interaction between the monomers is roughly of the same order as the separation between the monomeric vibrational levels. In this case, called the Frenkel excitation case,[4] if the two interacting molecules are identical, the electronic excitation is delocalized over both molecules,[5] and two different situations may arise. (a) The energy associated with the intermolecular interaction is smaller than the energy E_l necessary to deform the equilibrium nuclear configuration Q_0 of the ground electronic state of the monomer in order to obtain the nuclear equilibrium configuration $Q_0 + \lambda$ of the considered monomeric excited state: Here, even if the electronic excitation is delocalized over both interacting subunits, its localization is very sensitive to a deformation $\sim\lambda$ of the normal mode Q, which can produce trapping or expulsion of the electronic excitation depending on whether or not the deformation is towards the equilibrium nuclear configuration of the electronic excited state of the deformed monomer. (b) When the energy of the intermolecular interaction is larger than E_l, the excitation is still delocalized, even if a change of the order of λ is effected on the normal mode Q of one of the monomers.

This Frenkel case, described above, corresponds to values of the intermolecular interaction parameter which are limited to two cases: that of strong intermolecular interaction, where a different kind of excitation transfer occurs, called the Wannier exciton case[6]; and that of weak intermolecular interactions with the type of excitation transfer called a Förster exciton.[7]

The Wannier exciton case, which was first defined in crystals, can be visualized for dimers in the following way: As the interaction between the molecules becomes more and more important, i.e., when the intermolecular distance becomes of the order of intramolecular distances, one can arrive at a situation where the molecular orbitals centered on different monomers overlap each other. In this event, the contribution to the dimeric wave functions coming from charge-transfer wave functions becomes sizeable.[8] These charge-transfer wave functions correspond to removing one electron from an occupied orbital on one molecule to a virtual orbital on the neighboring molecule.

In Förster's case of excitation transfer, the intermolecular interaction is so small with respect to the monomeric vibrational energy separations that a stationary description of the excited dimeric states is no longer realistic,[7] and, thus, a dynamical description is necessary: In this case, the excitation transfer is so slow that vibrational relaxation on each excited monomer might occur in the meantime.

We shall study here Frenkel's and Förster's exciton transfers in dimers. The first case, as we have just discussed, corresponds to a stationary description of the dimeric excited state, although a dynamical description can also be formulated.[5] However, the stationary approach seems to be the more realistic one for the Frenkel exciton case. Henry and Kasha[9] have discussed this in detail, presenting a stationary description of the radiationless transitions in molecules. This can be generalized to the dimeric case.

We consider an excited dimer as a compound system of the dimer and the impinging photon which has caused the excitation. As such, it is possible to follow decay through the open channels. The channels considered are radiative decay and excitation transfer. In other words, we look at the exciton as a resonance in this compound system, and we study the possible decay channels. Recently, a similar point of view has been applied to the radiationless transitions of polyatomic molecules.[10,11] We shall closely follow the approach suggested by Feshbach[12,13] to treat resonances in compound systems.

It should be pointed out here that the qualitative features of the way the resonances decay for the different types of exciton can be traced to the exact formulation. However, in order to attain quantitative results, a simplified model for the dimer is assumed, and the integrals appearing in the expressions are approximated, disregarding some minor terms as well.

II. FORMAL DERIVATION

The Hamiltonian for the dimer includes the molecular Hamiltonians of the monomers A and B plus the intermolecular interaction H_{AB}. Thus, the total Hamiltonian for the field-dimer system will be

$$H = H_A + H_B + H_{AB} + H_{\mathrm{f}} + H_{\mathrm{fm}} \quad , \tag{1}$$

where H_{f} and H_{fm} are the radiation-field Hamiltonian and the field-matter interaction terms, respectively. We separate (1) into two parts:

$$H_0 = H^A_{\mathrm{BO}} + H^{\mathrm{B}}_{\mathrm{BO}} + H_{\mathrm{f}} \quad , \tag{2a}$$

$$V = T_N + H_{AB} + H_{\mathrm{fm}} \quad , \tag{2b}$$

where H_0 includes the Born-Oppenheimer terms of the monomers (the electronic kinetic-energy operators and the potential interactions within all the particles composing each molecule) and the free-field Hamiltonian, and where V contains the nuclear kinetic operators of A and B, the intermolecular interaction energy operator H_{AB}, and the field-matter interaction term H_{fm}.

We next pick up the open decay channels using a projection operator P and separate the Schrödinger equation into two coupled equations:

$$(E-PHP)P\psi = PHQ(Q\psi) \quad , \tag{3a}$$

$$(E-QHQ)Q\psi = QHP(P\psi) \quad , \tag{3b}$$

where Q is a projection operator orthogonal to P, which will eventually select the proper resonance. The following equation is immediately obtained for $P\psi$:

$$[E-PHP-PHQ(E-QHQ)^{-1}QHP]P\psi = 0 \quad . \tag{4}$$

Because P contains the open channels, we can define the incoming and outgoing waves for PHP as as the solutions of the homogeneous equation:

$$(E-PHP)\chi^{\pm} = 0 \quad . \tag{5}$$

Thus, we can write an expression for the transition amplitude

$$\tau_{fi} = \tau^{P}_{fi} + \langle \chi_f^- | PHQ(E-QHQ)^{-1}QHP | P\psi_i \rangle \tag{6}$$

by looking at Eq. (4) as a double potential equation for $P\psi$ and using Gell-Mann and Goldberger's formula.[14] The first term is the direct or prompt-process term, which we disregard, while the second is the resonant or time-delayed-process term, which, by using Eq. (3b), we can write as

$$\tau^{\text{Res}}_{fi} = \langle \chi_f^- | PHQ | Q\psi_i \rangle \quad . \tag{7}$$

In order to eliminate the unknown functions $P\psi$ and $Q\psi$, we start from a formal solution of the inhomogeneous equation (3a):

$$P\psi_i^+ = \chi_i^+ + (E^+ - PHP)^{-1}PHQ\psi_i^+ \quad , \tag{8}$$

and with the help of (3b) we get

$$Q\psi_i = (E-QHQ)^{-1}QHP[P\chi_i^+ + P(E^+ - PHP)^{-1}PHQ\psi_i] \quad . \tag{9}$$

Moreover, upon defining

$$QW(E)Q \equiv QHP(E^+ - PHP)^{-1}PHQ \; , \tag{10}$$

we get

$$Q\psi_i = (E-QHQ-QWQ)^{-1}QHP\chi_i^+ \quad . \tag{11}$$

The E^+ stands for $\lim_{\eta\to 0^+}(E+i\eta)$ and is needed in inverting Eq. (3a), because P contains the open channels. Finally, substituting (11) into (7), we obtain

$$\tau^{\text{Res}}_{fi} = \langle \chi_f^- | PHQ(E-QHQ-QWQ)^{-1}QHP | \chi_i^+ \rangle \; , \tag{12}$$

while the wave function $P\psi$ is obtained from (8) and (11):

$$P\psi_i = \chi_i + P(E-PHP)^{-1}PHQ(E-QHQ-QWQ)^{-1}QHP\chi_i \quad . \tag{13}$$

We clearly see in (12) that a resonance will appear at the singular points of the matrix element as a function of E. Thus, we are interested in the matrix elements of W. For a single resonant state s, we can write $Q = |s\rangle\langle s|$, and from (10) we have

$$\langle s | W | s \rangle = \langle s | VP(E^+ - PHP)^{-1}PV | s \rangle \quad ,$$

if P commutes with H_0. Depending on the nature of the decay channels, several possibilities arise. We analyze two cases.

(a) The projector P consists of a sum of n projectors, each projecting into a continuum of states defined by a constant density of states ρ_t. In this event, we can separate the right-hand side of (14) into real and imaginary parts[10,11] by taking the limit $\eta \to 0^+$:

$$\langle s | W | s \rangle = \Delta_s - i(\tfrac{1}{2}\Gamma s) \quad , \tag{15}$$

where

$$\Delta_s = \mathcal{P}\langle s | VP(E-PHP)^{-1}PV | s \rangle \quad , \tag{16a}$$

$$\Gamma_s = 2\pi \textstyle\sum_t |\langle s | VP | \chi_t \rangle|^2 \rho_t \quad ; \tag{16b}$$

thus, W is just a complex constant, and the main singularity in the transition matrix (12) is a simple complex pole. This means that $|s\rangle$ is a metastable state which will undergo an exponential decay of total width Γ_s. A slight deviation from the exponential law comes from the branch cut owing to the continuum spectrum. As its contribution is negligible,[15] we shall not worry about it. Radiative decay falls into this category. A more interesting example is radiationless transitions in the statistical limit[10,11,16,17] where the radiative decay defines one channel, and the quasicontinuum of vibrational states, degenerate with the excited state s, opens a nonradiative channel. We shall actually see in Sec. III that Förster's form of excitation transfer is also included in this case.

(b) P consists of two projectors, one given by a continuum of states of density ρ, the other defined by an isolated state μ, quasidegenerate with the excited state s. In this case, W in (14) will depend explicitly on the energy. Its imaginary part is

$$\text{Im}\langle s|W|s\rangle = -\pi |\langle s | VP | \chi \rangle|^2 \rho - \frac{\tfrac{1}{2}\Gamma_\mu |\langle s | VP | \mu \rangle|^2}{(E-E_\mu)^2 + \tfrac{1}{4}\Gamma_\mu^2} \quad , \tag{15$'$}$$

where Γ_μ is the relaxation width of the isolated state. When we substitute this expression for W into (12), we note that two complex poles occur, which cause the appearance of interference terms in the decay.[18] We shall see in Sec. IV that this is the case for the Frenkel exciton, and that the interference terms are oscillatory.

We now see the advantages of this formulation. No model has been assumed up to this point, and we can treat both decay channels at the same time. It is clearly seen that the main features of our treatment are model independent, although in order to obtain quantitative results, it is convenient to make some approximations.

III. FÖRSTER EXCITATION TRANSFER

We shall assume that a single level is excited, from which the decay will take place. In Förster's case, the coupling between the monomers is so weak that we can safely assume that one of the monomers A is excited. The two open decay channels will thus radiative decay into the dimer ground state or radiationless transfer to the other monomer B:

$$P=\sum_{\nu}|0\nu\rangle\langle 0\nu|+|1\mu\rangle\langle 1\mu| \ . \tag{17}$$

The functions $|0\nu\rangle$ are eigenstates of H_0, and they stand for the Born-Oppenheimer ground state times the one-photon states (of frequency k and polarization $\vec{e}$ implicitly assumed). The index ν labels the vibronic functions. This channel corresponds to one-photon process, i.e., radiative decay. The function $|1\mu\rangle$ is a singly excited B function times a ground-state A function, with vibronic quantum number μ, times a zero-photon state.

The characteristic feature of Förster's excitation transfer is that the coupling between the monomers is so weak that vibrational relaxation might take place before excitation transfer. However, this coupling is large enough to produce an excitation transfer by resonance interaction and not by simple reemission of the absorbed photon.[7] The fact that vibrational relaxation takes place before excitation can be expressed in a different way, by saying that the vibronic levels have a finite lifetime or have a large bandwidth. In this case, different vibronic levels will overlap, and we can consider the transfer as a transition to a quasicontinuum of density $(\Delta\epsilon)^{-1}$, where $\Delta\epsilon$ is the vibronic bandwidth (we use natural units in which $\hbar=1$).

Assuming the state $|s\rangle$ to be a simple Born-Oppenheimer product times a no-photon state, we get a total width given by Eq. (16b) after substituting the definitions of V, [Eq. (2b)] and P [Eq. (17)]:

$$\Gamma_s=\Gamma_{\rm rad}+\Gamma_{\rm tr} \ . \tag{18}$$

$\Gamma_{\rm rad}$ is the usual radiative width[19] given by

$$\Gamma_{\rm rad}=2\pi\rho_r\sum_{\nu}|\langle s|H_{fm}|0\nu\rangle|^2 \ , \tag{19}$$

where we have allowed radiative decay into several vibrational levels of the ground state 0. The other term $\Gamma_{\rm tr}$ in (18), is the excitation transfer rate

$$\Gamma_{\rm tr}=(2\pi/\Delta\epsilon)|\langle A^*B\lambda|H_{AB}+T_N|AB^*\mu\rangle|^2 \ . \tag{20}$$

In this weak-coupling case, we can consider that the excited vibronic functions are centered, respectively, on each of the monomers (see Ref. 5 for further details), so that

$$|A^*B\lambda\rangle=\tilde{\psi}(q_A,Q_A)\psi(q_B,Q_B)\tilde{\chi}_\sigma(Q_A)\chi_\omega(Q_B) \ , \tag{21a}$$

$$|AB^*\mu\rangle=\psi(q_A,Q_A)\tilde{\psi}(q_B,Q_B)\chi_\omega(Q_A)\tilde{\chi}_\sigma(Q_B) \ , \tag{21b}$$

where the ψ's represent electronic wave functions depending on both the electronic coordinate q and the nuclear coordinate Q, and where the χ's represent vibrational functions depending only on nuclear coordinates.

If we consider only the internal modes of vibration within each molecule, the operator T_N of the dimer will be the sum of the nuclear kinetic-energy operators T_N^A and T_N^B of the molecules A and B. In this case, T_N will not contribute to the matrix element appearing in (20) because $\psi(q,Q)$ and $\tilde{\psi}(q,Q)$ are orthogonal to each other for either monomer A or B. Then, if we first integrate the matrix element appearing in (20) over the electronic coordinates, we get for the excitation transfer rate the following expression:

$$\Gamma_{\rm tr}=\frac{2\pi}{\Delta\epsilon}\left|[\tilde{\chi}_\sigma(Q_A)\chi_\omega(Q_B)|U(Q)|\chi_\omega(Q_A(\tilde{\chi}_\sigma(Q_B)]_Q\right|^2 , \tag{22}$$

where

$$U(Q)=[\tilde{\psi}(q_A,Q_A)\psi(q_B,Q_B)|H_{AB}|\psi(q_A,Q_A)\tilde{\psi}(q_B,Q_B)] \ . \tag{23}$$

In both expressions the symbol $[\ ]_R$ stands for integration over the R coordinate; q and Q represent the electronic and nuclear coordinates, respectively. The intermolecular interaction operator H_{AB} depends on both q and Q coordinates. Furthermore, the dependence of H_{AB} on Q coordinates can be divided in two parts, namely, the intramolecular nuclear coordinates and the intermolecular ones. Thus, if the monomers are considered to be separated by a fixed large distance with respect to the intramolecular distances within each monomer, H_{AB} may be thought of as depending strongly on the electronic coordinates but weakly on the nuclear ones. In this case, the expression (22) can be written in the following form:

$$\Gamma_{\rm tr}\simeq(2\pi/\Delta\epsilon)U^2(Q_0)S_{\sigma\omega}^4\equiv(2\pi/\Delta\epsilon)u_{\sigma\omega}^2 \ , \tag{24}$$

where

$$S_{\sigma\omega}=[\tilde{\chi}_\sigma(Q_A)|\chi_\omega(Q_A)]_{Q_A}=[\chi_\omega(Q_B)|\tilde{\chi}_\sigma(Q_B)]_{Q_B} \tag{25}$$

are the Franck-Condon factors and Q_0 represents the set of nuclear coordinates describing the nuclei positions when they are at their equilibrium configuration for a given intermolecular distance.

Without going into statistical considerations, we follow Förster arguments[5,7] and introduce the Boltzmann factor g, so that we have

$$\Gamma_{\mathrm{tr}} \simeq (2\pi/\Delta\epsilon)\textstyle\sum_\sigma \sum_\omega g^*_\omega g_\sigma u^2_{\sigma\omega} \quad . \tag{26}$$

We see that in the Förster case we have an additive law for the widths of the radiative decay and the excitation transfer following an exponential law. It is thus an irreversible process. Even if we obtain the same transfer rate as Förster[5,7] for the excitation transfer, we note that the linear variation with the time which he gets, typical of a perturbation expansion,[20] is just a first approximation to the exponential law.

If we now analyze more closely the imaginary part of W, [Eq. (15′)] we find for the nonradiative part

$$\mathrm{Im}\langle s\,|\,W\,|\,s\rangle_{\mathrm{nr}} = \tfrac{1}{2}\Gamma' u^2/[(E-\epsilon')^2 + (\tfrac{1}{2}\Gamma')^2] \quad , \tag{27}$$

where Γ' is the natural width of a single vibronic level ($\Delta\epsilon$). According to what was stated above, in the Förster case we have a broad electronic level, so that $u^2 \ll (\frac{1}{2}\Gamma')^2$, i.e., $2|u| \ll \Delta\epsilon$.

IV. FRENKEL EXCITON CASE

There are two essential differences between the Förster case and the Frenkel exciton transfer. First, the final level of the nonradiative decay channel is a sharp one, because the excitonic transfer is expected to be faster than the vibrational relaxation; second, we can no longer consider the initial electronic excitation as going to a single monomer. This means that we have to account for the degeneracy of the states A^*B and AB^* in the resonance state s, as well as in the open channels projection operator.

In order to construct the resonance state s, we use a form of the usual Born-Oppenheimer approach applied to the dimers.[21] It has been shown that this approach retains its validity, at least in the strong- and intermediate-coupling cases. And it may also be valid in the weak-coupling case for an increasing number of vibronic levels, since the exciton binding energy becomes several times larger than the vibrational energy separation on each monomer.[21] The method consists in solving first the electronic problem, i.e., with a Hamiltonian obtained from (1), disregarding the free-field Hamiltonian H_f, the field-matter interaction term H_{fm}, and the kinetic energy of both monomers A and B. In this case, the states A^*B and AB^* are degenerate, so the electronic wave function is chosen to be of the form[21]

$$\phi^{\pm}(q, Q) = C_1^{\pm}(Q_A, Q_B)\tilde{\psi}(q_A, Q_A)\psi(q_B, Q_B)$$

$$+ C_2^{\pm}(Q_A, Q_B)\psi(q_A, Q_A)\tilde{\psi}(q_B, Q_B). \tag{28}$$

With H_{AB} as perturbation, we obtain explicit expressions for the coefficients $C_1^{\pm}$ and $C_2^{\pm}$, and the electronic energies $E^{\pm}$, when the following assumptions are introduced[3,21]: The ground- and excited-state potential energies are harmonic with the same force constant k, and the equilibrium positions Q^0 and $Q^0 + \lambda$, respectively. The intermolecular interaction is considered to depend only on the intermolecular distance R. With these assumptions the dimeric electronic energies become[21]

$$E^{\pm}(Q^+, Q^-) = V_0^* + W(R) + \tfrac{1}{2}k(Q^{+2} + Q^{-2}) - (k\lambda 2^{-1/2})Q^+$$

$$+ \tfrac{1}{2}k\lambda^2 \pm 2^{-1/2}[k^2\lambda^2 Q^{-2} + 2v^2(R)]^{1/2} \quad , \tag{29}$$

where

$$Q^+ = 2^{-1/2}(Q_A + Q_B), \qquad Q^- = 2^{-1/2}(Q_A - Q_B) \tag{30}$$

and V_0^* is the vertical excitation energy on each monomer.

The mixing coefficients of the electronic wave functions (28) are given by[21]

$$C_1^{\pm}(Q^-) = v[k^2\lambda^2(Q^-)^2 \pm k\lambda Q^- \,|\, k^2\lambda^2 Q^{-2} + 2v^2(R)\,|^{1/2}$$

$$+ 2v^2(R)]^{1/2} \,, \tag{31}$$

$$C_2^{\pm}(Q^-) = \pm\, C_1^{\pm}(-\,Q^-) \quad . \tag{32}$$

The total wave functions are obtained by multiplying the electronic wave functions (28) by the vibrational functions separable in the in-phase and out-phase combinations of Q_A and Q_B [22,23]:

$$\Xi_{\mu\nu}(Q^+, Q^-) = \xi_\mu(Q^+)\chi_\nu^{\pm}(Q^-) \quad . \tag{33}$$

In (33), $\chi_\nu^{\pm}(Q^-)$ are vibrational wave functions associated with two potential energies which depend on the intermolecular coupling $v(R)$, while $\xi_\mu(Q^+)$ is simply a displaced harmonic-oscillator wave function, which does not depend on $v(R)$ and obeys the same equation in the two dimeric electronic state.[22] The Born-Oppenheimer wave functions of the excited dimer can therefore be written as

$$\psi^{\pm}_{\mu\nu}(q, Q^+, Q^-) = \phi^{\pm}(q, Q^+, Q^-)\,\Xi^{\pm}_{\mu\nu}(Q^+, Q^-) \quad . \tag{34}$$

It should be pointed out that, as far as the Born-Oppenheimer approach is concerned, the preceding wave function adapts itself to different values of the intermolecular coupling. The electronic wave function is adapted to each value of $v(R)$ through the coefficients $C_1^{\pm}$ and $C_2^{\pm}$, and the vibrational functions (33) are adapted through the dependence on $v(R)$ on the electronic potentials.

We consider that in the Frenkel exciton case the resonant state s is one of the normalized functions (34), namely

$$|s) = [C_1^+(Q^-)\tilde{\psi}(q_A, Q_A)\psi(q_B, Q_B) + C_2^+(Q^-)\psi(q_A, Q_A)\tilde{\psi}(q_B, Q_B)]\xi_{\mu'}(Q^+)\chi^+_{\nu'}(Q^-), \quad (35)$$

and the state $|1\mu\rangle$ is given by the orthogonal one:

$$|1\mu) = [C_1^-(Q^-)\tilde{\psi}(q_A, Q_A)\psi(q_B, Q_B) + C_2^-(Q^-)\psi(q_A, Q_A)\tilde{\psi}(q_B, Q_B)]\xi_{\mu}(Q^+)\chi^-_{\nu}(Q^-), \quad (36)$$

where the parentheses indicate that we are dealing only with the molecular part of the state.

The Born-Oppenheimer state (35), which is a nonstationary state of the Hamiltonian (1), may be prepared by a broad-band optical excitation. This resonant state $|s\rangle$ of the upper potential (Fig. 1) is near the state $|1\mu)$ belonging to the lower excited electronic potential, which appears as a double-well potential in Fig. 1, where we illustrate a weak-coupling case.[24] For the intermediate- and strong-coupling cases, the main difference with respect to the preceding case is that the state $|1\mu)$ should belong to a single-well potential and should correspond to a higher vibrationally excited state in order to be near one of the upper potential levels.[24] In the three cases of weak, intermediate, and strong coupling, the state $|1\mu)$ may correspond to a highly vibrationally excited level, and will be practically forbidden for transitions from the ground vibronic state because of their small Franck-Condon factors.[22] Thus, the preparation of the dimer in the resonant state $|s\rangle$ is favored by the Franck-Condon factor, because $|s\rangle$ can be one of the lower-lying vibronic levels of the upper potential, and this preparation can be obtained by an instantaneous flash of incoherent light impinging on the dimers. Assuming that only the Born-Oppenheimer state $|s)$ carries dipole strength, in this broad-band case, we can regard the state $|s\rangle$ as fully excited,[16] and we can denote it as $|s)\,|\mathrm{vac})$ after excitation. The radiative decay will thus proceed from $|s\rangle$ to the one-photon electronic ground state $|0\nu;\vec{k}\vec{e}\rangle$, where we write explicitly the wave vector $\vec{k}$ and the polarization $\vec{e}$ of the emitted photon.

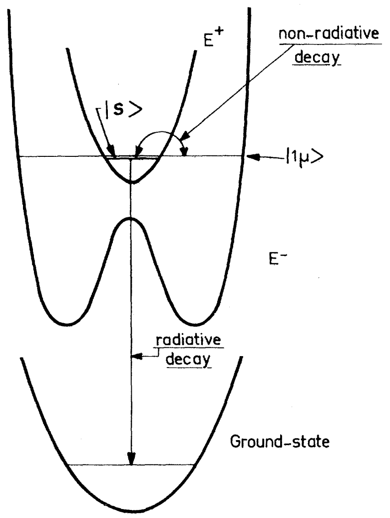

FIG. 1. The upper E^+ and the lower E^- electronic dimeric potentials in the weak-coupling case. The excitation oscillates between $|s\rangle$ and $|1u\rangle$ which belong to E^+ and E^-, respectively.

The interaction term between (35) and (36) is

$$u = (s|T_N|1\mu)\,, \quad (37)$$

because (35) and (36) are Born-Oppenheimer wave functions and (37) produces the vibronic mixing between the two.[21] Note that now the interaction between the resonant states $|s\rangle$ and $|1\mu\rangle$ does not arise, as in the Förster exciton case, from the intermolecular interaction. It appears from the deviation of the true stationary-state wave functions from those of the usual Born-Oppenheimer approximation. Here, as we shall see later, we take into account the vibronic correction, which gives the exact dimeric total wave functions, as a perturbation leading to a time-dependent formalism. In this sense, there is a parallelism between this approach for dimers and Lin's treatment for the radiationless transitions in molecules.[25]

We shall next obtain an explicit expression for the radiative decay rate of the resonance state $|s\rangle$. Thus, we shall concentrate on the *partial* process of transition from $|s\rangle$ to the one-photon ground state. The transition amplitude is given by[15,18,19]

$$F_{s0} = \langle s|Qe^{-iHt}P|0\nu\rangle = (2\pi i)^{-1}\int_{\mathcal{C}}\langle s|Q(E-H)^{-1}P|0\nu\rangle e^{-iEt}\,dE, \quad (38)$$

the imaginary Laplace transform of the resolvent, where $\mathcal{C}$ is a contour extending from $ic+\infty$ to $ic-\infty$, with c a positive constant large enough so that no singularities of the resolvent lie above $\mathcal{C}$.

From the Lippmann-Schwinger equation (13), we can extract an explicit expression for $P(E-H)^{-1}Q$:

$$P(E-H)^{-1}Q = P(E-PHP)^{-1}PHQ(E-QHQ-QWQ)^{-1}Q\;, \quad (39)$$

where E is now regarded as a complex variable. Using Eq. (39), we can write

$$\langle 0\nu|P(E-H)^{-1}Q|s\rangle = (E-E_0-k)^{-1}\langle 0\nu|H_{\mathrm{fm}}|s\rangle \times [E-E_s+\tfrac{1}{2}i\Gamma_r - u^2/(E-E_\mu+\tfrac{1}{2}i\Gamma_r)]^{-1}\,, \quad (40)$$

where E_0 is the molecular ground energy, and we have incorporated the radiative level shift into E_s. Γ_s is the radiative lifetime (19). The matrix element of H_{fm} will be simply the electric dipole matrix element between $|\mathrm{vac}\rangle$ and $|\vec{k}, \vec{e}\rangle$, and is almost constant.[10b]

In order to evaluate the integral in (38), we note that this matrix element has two complex poles at the energies

$$A_\pm = \tfrac{1}{2}(\epsilon - \tfrac{1}{2}i\Gamma \pm \{[E_s - E_\mu - \tfrac{1}{2}i(\Gamma_r - \Gamma_\mu)]^2 + 4u^2\}^{1/2})$$

$$= a_\pm - \tfrac{1}{2}ib_\pm , \tag{41}$$

with

$$\epsilon = E_s + E_\mu , \tag{42}$$

$$\Gamma = \Gamma_r + \Gamma_\mu . \tag{43}$$

Laplace transforming Eq. (40), we get

$$F_{0s} = \frac{\langle 0\nu | H_{fm} | s\rangle}{A_+ - A_-}\left(\frac{A_+ - E_\mu + \frac{1}{2}i\Gamma_\mu}{E_0 + k - A_+} e^{-i(E_0+k)t}(1 - e^{-i(A_+ - E_0 - k)t})\right.$$

$$\left. - \frac{A_- - E_\mu + \frac{1}{2}i\Gamma_\mu}{E_0 + k - A_-} e^{-i(E_0+k)t}(1 - e^{-i(A_- - E_0 - k)t})\right). \tag{44}$$

The *radiative* decay probability is now given by[15]

$$d^2P(t) = d\rho_r \, d\vec{k} \, |F_{0s}|^2 , \tag{45}$$

and integrating over the frequencies $d\vec{k}$ and the propagation directions $d\Omega_k$, we get

$$P(t) = \frac{\Gamma_r}{(a_+ - a_-)^2 + \frac{1}{4}(b_+ - b_-)^2}\left[\frac{(a_+ - E_\mu)^2 + \frac{1}{4}(b_+ - \Gamma_\mu)^2}{b_+}(1 - e^{-b_+ t}) + \frac{(a_- - E_\mu)^2 - \frac{1}{4}(b_- - \Gamma_\mu)^2}{b_-}(1 - e^{-b_- t})\right.$$

$$\left. + 2\mathrm{Re}\left(-i(A_+ - E_\mu + \tfrac{1}{2}i\Gamma_\mu)\frac{(A_-^* - E_\mu - \frac{1}{2}i\Gamma_\mu)}{(A_+ - A_-^*)}(1 - e^{i(A_-^* - A_+)t})\right)\right], \tag{46}$$

which contains two direct terms and an interference term. As the levels E_s and E_μ are almost degenerate (Fig. 1), for a sharp resonance we can expand the square root in Eq. (14) as

$$A_\pm = \tfrac{1}{2}\epsilon \pm u - \tfrac{1}{4}i\Gamma . \tag{47}$$

Expression (46) simplifies to (Fig. 2)

$$P(t) = \Gamma^{-1}\Gamma_r(1 - e^{-\Gamma t/2}) - [\Gamma_r/2(4u^2 + \tfrac{1}{4}\Gamma^2)]$$

$$\times [\tfrac{1}{2}\Gamma(1 - e^{-\Gamma t/2}\cos 2ut) + 2ue^{-\Gamma t/2}\sin 2ut] . \tag{48}$$

This expression for the radiative decay shows two competitive processes: One is the normal exponential decay, while the other one is the oscillatory excitation transfer between the states $|s\rangle$ and $|1\mu\rangle$. Inspection of Eq. (48) yields the frequency with which the excitation oscillates:

$$\nu = u/\pi . \tag{49}$$

Finally, we shall examine some properties of the coupling term u. To this end, we obtain an explicit expression for this term. First, we consider that the adiabaticity of the electronic wave function (28) resides only on the coefficients $C_1^\pm$ and $C_2^\pm$,[22] i.e.,

$$[T_N, \tilde{\psi}(q_A, Q_A)\psi(q_B, Q_B)] = [T_N, \psi(q_A, Q_A)\tilde{\psi}(q_B, Q_B)] = 0, \tag{50}$$

which is equivalent to the assumption that the Born-Oppenheimer separability applies to the states of each monomer involved in the resonance transfer.[1-3,21]

If we calculate the expression (37) for u, taking into account the equations (35), (36), and (50), and integrating only over the electronic coordinates, we find

$$u = \int C_1^+(Q^-)\xi_{\mu'}(Q^+)\chi_{\nu'}^+(Q^-)T_N C_1^-(Q^-)\xi_\mu(Q^+)\chi_\nu^-(Q^-)dQ^+ dQ^-$$

$$+ \int C_2^+(Q^-)\xi_{\mu'}(Q^+)\chi_{\nu'}^+(Q^-)\, T_N C_2^-(Q^-)$$

$$\times \xi_\mu(Q^+)\chi_\nu^-(Q^-)dQ^+ dQ^- , \tag{51}$$

where the kinetic-energy operator T_N can be written in terms of the in- and out-of-phase coordinates,[22] as follows:

$$T_N = -\frac{1}{2M}\frac{\partial^2}{\partial Q^{+2}} - \frac{1}{2M}\frac{\partial^2}{\partial Q^{-2}} \equiv T_N^+ + T_N^- . \tag{52}$$

Because the electronic potentials depending on the Q^- coordinate[22] are invariant under reflection $Q^- \to -Q^-$, the vibrational functions $\chi_\nu^\pm(Q^-)$ are even or odd depending on the value of the quantum number ν. Thus, taking into account Eq. (32) and (52), relation (51) becomes

$$u = [1 + (-1)^{\nu+\nu'+1}][\int \xi_{\mu'}(Q^+)T_N^+\xi_\mu(Q^+)dQ^+$$

$$\times \int C_1^+(Q^-)\chi_{\nu'}^+(Q^-)\chi_\nu^-(Q^-)C_1^-(Q^-)dQ^-$$

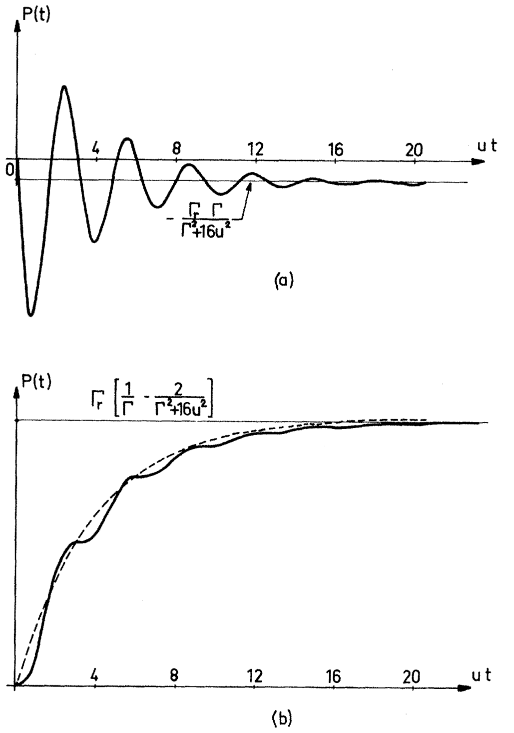

FIG. 2. (a) Contribution from the interference term to Eq. (48). It is a damped oscillation of frequency $\pi^{-1}u$. (b) The radiation transition probability, Eq. (48). The effect of the excitonic oscillation reflects as inflection points at times ν^{-2}, $2\nu^{-2}$, ... Dashed line denotes the normal exponential with asymptote Γ_r/Γ. All graphs are plotted for a value $\Gamma=\frac{1}{2}u$.

$$+\delta_{\mu\mu'}\int C_1^+(Q^-)\chi_{\nu'}^+(Q^-)T_N^-\chi_\nu^-(Q^-)C_1^-(Q^-)dQ^-] \;. \quad (53)$$

Inspection of this equation reveals the following properties of u: (a) It vanishes when the interacting states $|s\rangle$ and $|1\mu\rangle$ have vibrational functions $\chi_{\nu'}^+(Q^-)$ and $\chi_\nu^-(Q^-)$, respectively, which are both even or odd. This is in agreement with the correlation energy diagram discussed in Ref. 21. (b) When $\nu+\nu'$ is odd, both vibrational modes Q^+ and Q^- contribute to the frequency with which the transfer of excitation between $|s\rangle$ and $|1\mu\rangle$ occurs. (c) The second term in (53), in which a matrix element of the out-of-phase vibration nuclear kinetic operator appears, becomes important in the weak-coupling case. In this event, the dimeric electronic wave functions (28) depend strongly on the nuclear coordinates near $Q^-=0$; the coefficients $C_1^+(Q^-)$ and $C_2^+(Q^-)$, when the intermolecular coupling tends to 0, become step functions centered at $Q^-=0$.[21,22] The corresponding derivatives might assume important values near[26] $Q^-=0$, thus producing large values of μ. This implies a high-frequency oscillation between the two quasidegenerate states $|s\rangle$ and $|1\mu\rangle$ of the same quantum number related to the in-phase vibrations of the dimer.

V. CONCLUSIONS

Studying the whole scattering process of a photon impinging on a dimer, we have been able to interpret, in the Förster exciton case, the excitonic transfer as a decay process of a compound state. Moreover, we found an exponential decay law where the radiative and nonradiative widths are additive.

In the Frenkel exciton case, we constructed adiabatic Born-Oppenheimer wave functions which take into account the intermolecular interaction. The exciton transfer is thus hidden by a quasistationary description of the excited dimer. Here, the interaction between two quasidegenerate Born-Oppenheimer states, produced by the vibronic corrections, induces a damped oscillatory transfer between them. This is in competition with the radiative decay to the ground state, the two process being coupled to each other. The frequency with which the excitation oscillates between the two excited Born-Oppenheimer states depends drastically upon the parity of these functions. Furthermore, in weak-coupling cases, this frequency is larger for interacting states with equal μ (which is the vibrational quantum number associated with the in-phase dimeric vibrations) than for states with different μ.

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Mean Life of the Metastable 2^3P_1 State of the Two-Electron Oxygen Ion

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The mean life of the metastable $2\,^3P_1$ state of the O^{6+} ion has been determined by measuring the decay length of the $1\,^1S_0$-$2\,^3P_1$ (λ21.8) radiation emerging from a 20-MeV beam of highly stripped oxygen ions. The result is $\tau^{-1} = (6.6 \pm 0.5) \times 10^8$ sec^{-1} which compares favorably with our earlier measurement of $(6 \pm 1) \times 10^8$ sec^{-1}. Mixing of singlet levels above $n = 2$, a feature of some recent calculations of this lifetime, is needed to bring about overlap of theoretical and experimental results. Additional information concerning excitation of one- and two-electron ions in such beams is presented.

I. INTRODUCTION

Spin-orbit interactions in atoms have long been known to couple levels of different electronic spin. In light atoms, such as helium, the consequent violation of *LS* coupling is small; but in two-electron systems of higher Z, the violation is much enhanced. It is the increased strength of the spin-orbit interactions which obscures the clear separation of singlet and triplet systems. The spin-orbit interactions are stronger because the electrons are pulled in to substantially smaller radii and have higher velocities. For excited levels of sufficiently high Z, there then occur a variety of situations in which a radiative decay channel involving a spin flip is more probable than any which conserve spin. Such so-called intercombination transitions are common for heavy atoms, the best known, perhaps, being the one which yields the λ2537 resonance line of Hg.

A case in point is the $1\,^1S_0$-$2\,^3P_1$ transition in heliumlike ions, which begins to dominate the competing $2\,^3S_1$-$2\,^3P_1$ transition for $Z \geq 7$. The spin-orbit interactions admix the $2\,^1P_1$ state with the $2\,^3P_1$ state (and to a lesser extent admix higher singlet P states); the over-all transition probability can then be calculated approximately from the allowed singlet P-state transition probabilities, weighted by the corresponding percentage admixtures in the wave function. The $2\,^3P_{0,2}$ states decay within the triplet system since transitions to the ground state are forbidden by the selection rules on J.

Within the error limits of our earlier experiments,[1] and taking the smaller, allowed $2\,^3S_1$-$2\,^3P_1$ transition probabilities as known to good accuracy,[2] agreement was obtained with the calculations of Elton[3] and the more recent ones of Dalgarno, Drake, and Victor[4] and of Drake and Dalgarno[4] for the $1\,^1S_0$-$2\,^3P_1$ transition probability in both the N^{5+} and