to the presence of a relatively weakly bonded, imperfectly ordered state. Apparently this latter state is necessary for viscous flow to occur since its free-volume contribution is the one playing the significant role in determining the viscosity of $B_2O_3$.

The success of a two-state equation in predicting the volume and viscosity of $B_2O_3$ over such a large temperature and viscosity range is a result not generally true for other liquids. In most liquids this data must be fitted by a free volume of the form $V_f \propto (T-T_0)$. This form of $V_f$ can not result from a two-state situation.

It is curious that the two liquids $H_2O$ and $B_2O_3$ (both highly bonded, open structural, two-dimensional network liquids; both exhibiting peculiar volume–temperature behavior) are those liquids in which a two-state approximation has met with the greatest success. It would appear that the alternative presence of two distinct states or a multiplicity of states is an important factor in determining the properties of liquids.

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# Cooperative Exciton States in Molecular Crystals

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In this paper we calculate the transition probability for excitation of double-exciton states in absorption and emission processes in molecular crystals. The formalism is based on the tight-binding approximation, treating the intermolecular electrostatic and exchange interactions and the interaction with the radiation field by perturbation theory. It is found that:

(1) A major contribution to the transition probability for cooperative excitation to electronic states arises from intermolecular Coulomb interactions, while the contribution of intermolecular electron-exchange interactions is relatively small.

(2) Contributions to the transition probability from high-order-transition multipole interactions are of considerable importance.

(3) Approximate selection rules for cooperative electronic excitation imply that for one component the initial and final states are of the same parity, while for the second component the transition is symmetry allowed.

(4) Theoretical evidence is obtained for the appearance of double-excitation bands in the infrared spectra of solids in the overtone region.

(5) A major contribution to the intensity of the double-vibrational-exciton states arises from an intermolecular Fermi resonance effect.

(6) The direct detection of the radiative annihilation of a double-exciton state is not likely to be experimentally feasible.

## I. INTRODUCTION

TWO-electron excitations in atomic systems have been known for many years.[1] For the case of the isolated atom, these transitions arise from correlation effects which cannot be described within the Hartree–Fock scheme.[2] Now, there exist analogous transitions in molecular crystals. In the crystal, two excitons may be produced by a single photon[3–5] because of the influence of intermolecular interactions, as would be expected from the classical analog, which is a system containing two weakly coupled oscillators exhibiting combination frequencies. Consider the conventional theory of the electronic states of molecular crystals. In the usual formalism, it is assumed that the ground state of the molecule is not seriously perturbed by the weak intermolecular forces characteristic of the crystal. Moreover, if the spatial extent of the electron density is about the same in the ground state and in a set of excited states, a further considerable simplification of the analysis is possible. For, if the intermolecular

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[1] U. Fano, Phys. Rev. **124**, 1866 (1961).

[2] Some contributions to the transition probability arise from the weak orthogonality conditions imposed on the Hartree–Fock wavefunction. For example, in the two-electron excitation of the helium atom $1s^2 \rightarrow 2s2p$ the overlap integral $\langle 1s \mid 2s \rangle$ does not vanish. However, the correlation effects are dominant in determining the transition probability.

[3] L. N. Ovander, Soviet Phys.—Solid State **4**, 212 (1962) [Fiz. Tver. Tela **4**, 294 (1962)].

[4] T. Miyakawa, J. Phys. Soc. Japan **17**, 1898 (1962).

[5] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

overlap is small in all states of interest (i.e., overlap integrals between the molecular orbitals on adjacent molecules $\sim 10^{-2}$–$10^{-3}$), then the Heitler–London tight-binding-product wavefunction is the proper zero-order approximation to the crystal wavefunction. Since the intermolecular interactions are much smaller than the intramolecular interactions, the free-molecule wavefunctions suffice as basis functions for the product function approximating the crystal wavefunction. The analysis of the crystal states just given is due to Frenkel, and has been found to be very useful in the description of the lower excited electronic states of crystals of aromatic molecules, as well as for the description of vibrational exciton states.[6]

In this paper, we consider the cooperative excitation, in a molecular crystal, of two Frenkel excitons by a single photon. It has been shown by Dexter[5] that the double excitation of a pair of atoms can be interpreted as arising from first-order corrections to the zero-order wavefunction induced by the intermolecular interactions, and may thereby be considered to be an intermolecular correlation effect. From a somewhat different point of view, we may consider the interactions causing the transition from the ground state to the double-exciton state to consist of two components: the interaction with the radiation field and the intermolecular interaction. The intermolecular electrostatic and exchange interactions may be treated in the same way as is the interaction with the radiation field, i.e., the transition probability may be expanded in powers of $e^2$. This analysis strongly resembles the treatment of Bremsstrahlung radiation.[7]

In the present work, we consider the transition probability for double-exciton states in absorption and emission processes and establish the selection rules for creation of the double-exciton states from electronic and vibrational excitations in molecular crystals.

## II. BRIEF SURVEY OF THE AVAILABLE EXPERIMENTAL DATA

The unambiguous assignment of an observed transition to a simultaneous multiple-electron–multiple-molecule excitation is not simple, since there are usually a large number of possible excitations with energies close to twice the fundamental energy. Clear evidence for a two-atom cooperative optical absorption involving only one photon has been obtained by Varsanki and Dieke from studies of $PrCl_3$.[8] In addition, Milgram and Givens[9] have found an absorption at 25 eV in LiF which has been interpreted by Miyakawa[4] to arise from double excitation. It is interesting to note that the intensity of this transition is about the same as that of the allowed singlet transition at 12.9 eV in LiF. We show in this paper that the transition probability for excitation of a double-exciton state should not exceed $\sim 1\%$ of the transition probability to the single-exciton state. For this reason, the assignment of the 25-eV transition in LiF seems less certain than that of the transition observed in $PrCl_3$.

A survey of the reported spectra of crystals of organic molecules reveals no reported multiple excitations. However, Weigl[10] has studied the absorption spectrum of a pinacyanole dye in a crystalline film and found a strong transition at 15 000 cm$^{-1}$ ($f\sim 1$), which corresponds to a strong transition in the solution spectrum, and a weak transition at 28 000 cm$^{-1}$, for which there is no counterpart in the solution spectrum. This latter transition, if not arising from an impurity, might be due to a double excitation. It is clear that further experimental study of films of cationic dyes is of considerable interest.

Perhaps the most striking evidence for the existence of double excitations in molecular crystals is found in the work of Ron and Hornig.[11] These investigators studied the infrared spectrum of solid HCl. Because of the anharmonicity of molecular vibration, a state of the crystal with a single molecule excited to the second vibrational state has lower energy than a crystal state wherein two molecules are each excited to the first vibrational state. As a result, if the anharmonicity is large enough, the overtone transition is well separated from the double-excitation transition, and both transitions are amenable to observation. Indeed, the infrared spectrum of solid HCl reveals two relatively strong transitions in the region 5000–6000 cm$^{-1}$: a sharp line with half-width of 20 cm$^{-1}$ at 5313 cm$^{-1}$, and a broad line with half-width of 90 cm$^{-1}$ at 5465 cm$^{-1}$. The intensity ratio of the two transitions is of the order of $f_{5465}/f_{5313}\sim 1$. Ron and Hornig[11] have assigned the 5313-cm$^{-1}$ transition to an overtone level of a single molecule, and the 5465-cm$^{-1}$ transition to a double excitation. As clearly stated by these investigators, the occurrence of double excitations in the infrared spectra of molecular crystals should be a very general phenomenon and may account for much of the structure in the overtone region. Thus, the transitions at 6050 and 6550 cm$^{-1}$ in ice may be interpreted as arising from the overtone transition and a double

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[6] This is not the case for the excited electronic states of the rare-gas crystals, where large nonorthogonality corrections make the tight-binding scheme inapplicable. When the lowest excited states of these systems are described in terms of Frenkel excitons, charge-transfer states must also be included in the representation. [S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 2911 (1964)]. An alternative treatment of these excited states can be carried through in terms of the Wannier formalism [R. S. Knox *Theory of Excitons* (Academic Press Inc., New York, 1964)].

[7] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1961).

[8] F. Varsanki and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

[9] A. Milgram and M. P. Givens, Phys. Rev. **125**, 1506 (1962).

[10] J. Weigl, J. Chem. Phys. **24**, 364 (1956).

[11] A. Ron and D. F. Hornig, J. Chem. Phys. **39**, 1129 (1963).

excitation, respectively. Further evidence for cooperative excitations in the infrared spectra of gaseous mixtures has been reported by Ketelaar and Rettschnik.[12] Some evidence for mixed electronic–vibrational cooperative excitation was recently reported by Yatsiv *et al.*[13]

## III. TRANSITION PROBABILITY FOR DOUBLE EXCITATION

We consider first the second-order process leading to simultaneous excitation of a pair of atoms (or molecules) by a photon of energy $\hbar\omega$. Let the atoms be labeled a and b. The interaction responsible for the transition from the ground state $|0_a0_b\rangle$ to the excited state $|f_ag_b\rangle$ consists of two parts: interaction with the radiation field $H_{\mathrm{rad}}$, which leads to absorption of the photon, and the electrostatic intermolecular interaction $V_{\mathrm{ab}}$,

$$H=H_{\mathrm{rad}}+V_{\mathrm{ab}}. \tag{1}$$

The interaction with the radiation field is conveniently represented in the form[7]

$$H_{\mathrm{rad}}=-(e^2/mc^2)\sum_k[\mathbf{P}_k\cdot\mathbf{A}(\mathbf{r}_k)], \tag{2}$$

where $\mathbf{P}_k$ and $\mathbf{r}_k$ are the momentum and position of the $k$th electron and $\mathbf{A}$ is the vector potential of the electromagnetic field. Since we are not concerned with two-photon transitions or light-scattering processes, the term $H_{\mathrm{rad}}$ involving $A^2$ can be neglected,[7] as has already been done in Eq. (2). As usual, the intermolecular pair potential has the form

$$V_{\mathrm{ab}}\quad\sum_{\mathrm{I,J}}\frac{Z_{\mathrm{I}}Z_{\mathrm{J}}e^2}{R_{\mathrm{IJ}}}-\sum_{\mathrm{I},j}\frac{Z_{\mathrm{I}}e^2}{R_{\mathrm{I}j}}-\sum_{\mathrm{J},i}\frac{Z_{\mathrm{J}}e^2}{R_{\mathrm{J}i}}+\sum_{i,j}\frac{e^2}{r_{ij}}, \tag{3}$$

where I and J refer to the nuclei on the different Molecules a and b, $i$ refers to the electrons on Molecule a and $j$ to the electrons on Molecule b.

Of the terms in the interaction Hamiltonian, Eq. (1), the operator involving the radiation field has nonvanishing matrix elements for transitions to intermediate states involving the change of a single atomic (or molecular) electronic state, and for which momentum is conserved. On the other hand, the electrostatic interaction has nonvanishing matrix elements for transitions to states wherein the radiation field is unchanged, and induces a double excitation to an intermediate state. The possible intermediate states involved in the transition $|0_a0_b\rangle\rightarrow|f_ag_b\rangle$ arise as follows:

(a) A photon of energy $\hbar\omega$ is absorbed and the intermediate state $|0_ap_b\rangle$ (or $|p_a0_b\rangle$) excited. The final state is then reached via a transition induced by the perturbation $V_{\mathrm{ab}}$.

(b) The transition to an intermediate state $|p_ag_b\rangle$ (or $|f_ap_b\rangle$) is induced by the electrostatic interaction $V_{\mathrm{ab}}$, which is then followed by absorption of a photon to yield the desired final state.

The two pathways described are schematically outlined in Fig. 1. It is now seen that the transition probability for double excitation is, from second-order perturbation theory,

$$\begin{aligned}K=&\sum_{p;|0p\rangle\neq|00\rangle}[\langle 00\,|\,H_{\mathrm{rad}}\,|\,p0\text{ or }0p\rangle\langle p0\text{ or }0p\,|\,V_{\mathrm{ab}}\,|fg\rangle/(\mathcal{E}_0{}^{\mathrm{a}}+\hbar\omega-\mathcal{E}_p{}^{\mathrm{a}})]\\&+\sum_{p;|pg\rangle\neq|00\rangle}[\langle 00\,|\,V_{\mathrm{ab}}\,|fp\text{ or }pg\rangle\langle fp\text{ or }pg\,|\,H_{\mathrm{rad}}\,|fg\rangle/(2\mathcal{E}_0{}^{\mathrm{a,b}}-\mathcal{E}_p{}^{\mathrm{a}}-\mathcal{E}_g{}^{\mathrm{b}})],\end{aligned} \tag{4}$$

where the summations are extended over all possible intermediate states. Since energy is conserved in the transition,

$$\hbar\omega=\mathcal{E}_f{}^{\mathrm{a}}+\mathcal{E}_g{}^{\mathrm{b}}-\mathcal{E}_0{}^{\mathrm{a}}-\mathcal{E}_0{}^{\mathrm{b}}, \tag{5}$$

where $\mathcal{E}_i{}^{\mathrm{a}}$ represents the energy of the $a$th atom or molecule, in its $i$th electronic state. Now, $H_{\mathrm{rad}}$ is a sum of one-electron operators. Thus, using the conservation condition (5), Eq. (4) may be rewritten in the form

$$\begin{aligned}K=&\sum_{|p_a\rangle\neq|0_a\rangle}[\langle 0_a\,|\,H_{\mathrm{rad}}\,|\,p_a\rangle\langle p_a0_b\,|\,V_{\mathrm{ab}}\,|f_ag_b\rangle/(\mathcal{E}_f{}^{\mathrm{a}}+\mathcal{E}_g{}^{\mathrm{b}}-\mathcal{E}_0{}^{\mathrm{a}}-\mathcal{E}_p{}^{\mathrm{a}})]\\&+\sum_{|p_b\rangle\neq|0_b\rangle}[\langle 0_b\,|\,H_{\mathrm{rad}}\,|\,p_b\rangle\langle 0_ap_b\,|\,V_{\mathrm{ab}}\,|f_ag_b\rangle/(\mathcal{E}_f{}^{\mathrm{a}}+\mathcal{E}_g{}^{\mathrm{b}}-\mathcal{E}_0{}^{\mathrm{b}}-\mathcal{E}_p{}^{\mathrm{b}})]\\&+\sum_{|p_ag_b\rangle\neq|0_a0_b\rangle}[\langle 0_a0_b\,|\,V_{\mathrm{ab}}\,|\,p_ag_b\rangle\langle p_a\,|\,H_{\mathrm{rad}}\,|f_a\rangle/(\mathcal{E}_0{}^{\mathrm{a}}+\mathcal{E}_0{}^{\mathrm{b}}-\mathcal{E}_p{}^{\mathrm{a}}-\mathcal{E}_g{}^{\mathrm{b}})]\\&+\sum_{|f_ap_b\rangle\neq|0_a0_b\rangle}[\langle 0_a0_b\,|\,V_{\mathrm{ab}}\,|f_ap_b\rangle\langle p_b\,|\,H_{\mathrm{rad}}\,|\,g_b\rangle/(\mathcal{E}_0{}^{\mathrm{a}}+\mathcal{E}_0{}^{\mathrm{b}}-\mathcal{E}_p{}^{\mathrm{b}}-\mathcal{E}_f{}^{\mathrm{a}})].\end{aligned} \tag{6}$$

The reader should note that the transition matrix elements displayed in Eq. (6) depend upon one-electron transition probabilities between the ground state and the intermediate states, $\langle 0\,|\,H_{\mathrm{rad}}\,|\,p\rangle$, and between the intermediate states and the final state, $\langle p\,|\,H_{\mathrm{rad}}\,|f\rangle$ and $\langle p\,|\,H_{\mathrm{rad}}\,|\,g\rangle$. Equation (6) is similar in form to an expression derived by Dexter, but the restrictions imposed on the third and fourth sums in Eq. (6) (i.e., $2\mathcal{E}_0\neq\mathcal{E}_p{}^{\mathrm{a}}+\mathcal{E}_g{}^{\mathrm{b}}$) are less stringent than those used by Dexter.[5]

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[12] J. A. A. Ketelaar and R. P. H. Rettschnik, Z. Physik **173**, 101 (1963).

[13] S. Yatsiv, L. Adato, and A. Goren, Phys. Rev. Letters **11**, 108 (1963).

As usual, the perturbation expansion (4) diverges when $\hbar\omega = \mathcal{E}_p{}^a - \mathcal{E}_0{}^a$, i.e., when the energy of the absorbed photon exactly matches the energy difference between the ground state and an excited state of one of the component molecules. When the system possesses such a channel for direct excitation, nondegenerate perturbation theory cannot be used. In this case, the system is characterized as having two degenerate or nearly degenerate levels arising, respectively, from a single excitation of one of the components and from the simultaneous double excitation of both components. If the electrostatic interaction is sufficiently large, these levels will be split and might be observed separately. We seek, in this case, a representation which is diagonal in the intermolecular electrostatic interaction. The new wavefunctions are

$$\psi_+ = \alpha \mid 0_a p_b\rangle + \beta \mid f_a g_b\rangle,$$

$$\psi_- = \beta \mid 0_a p_b\rangle - \alpha \mid f_a g_b\rangle, \tag{7}$$

with the corresponding energies

$$E_\pm = \tfrac{1}{2}[\mathcal{E}_0{}^a + \mathcal{E}_p{}^b + \mathcal{E}_f{}^a + \mathcal{E}_g{}^b - 2\mathcal{E}_0{}^a - 2\mathcal{E}_0{}^b] \pm \tfrac{1}{2}y \tag{8}$$

$$y = (4 \mid W \mid^2 + \delta^2)^{\frac{1}{2}}, \tag{9}$$

where $y$, the energy difference between the split levels, is defined in terms of the energy separation between the singly and doubly excited states, while

$$\delta = \mathcal{E}_0{}^a + \mathcal{E}_p{}^b - \mathcal{E}_f{}^a - \mathcal{E}_g{}^b \tag{10}$$

and the matrix element coupling the states is

$$W = \langle 0_a p_b \mid V_{ab} \mid f_a g_b\rangle. \tag{11}$$

The expansion coefficients $\alpha$ and $\beta$ are determined in terms of $y$ and $\delta$ to be

$$\alpha = [(y+\delta)/2y]^{\frac{1}{2}},$$

$$\beta = [(y-\delta)/2y]^{\frac{1}{2}}. \tag{12}$$

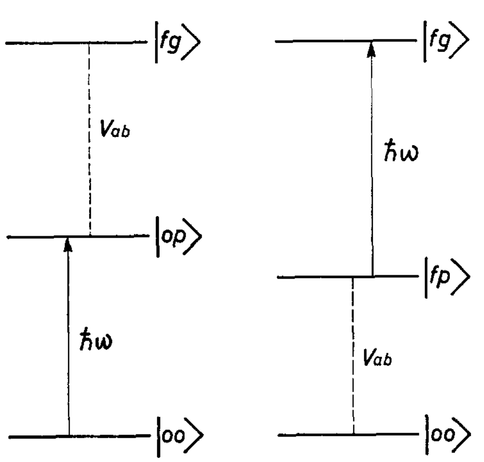

FIG. 1. Schematic representation of the processes leading to the cooperative excitation of a pair of atoms or molecules. Dotted and solid lines represent the intermolecular interactions and the interaction with the radiation field, respectively.

Having removed the degeneracy of the states, ordinary perturbation theory may again be used with the states $|\psi_+\rangle$ and $|\psi_-\rangle$, the transition probability being determined by the matrix elements displayed in Eq. (4), but where the final state is $|\psi_\pm\rangle$ and the summation *excludes* the intermediate state $|0p\rangle$.

It is interesting to note that for this case of near degeneracy intensity stealing from an allowed single excitation becomes very efficient, and for the limiting case of $\delta = 0$ the intensity is equally distributed between the single excitation and the cooperative excitation. However, when $\delta = 0$ it is not possible to distinguish between direct single-photon excitation to $|0p\rangle$ followed by energy redistribution, and the preceding. That is, when $\delta = 0$ the state $|0p\rangle$ is not only degenerate with $|fg\rangle$ but also is no longer distinct from it as long as $\langle 0p \mid V_{ab} \mid fg\rangle$ is nonvanishing.

To proceed with our analysis, the intermolecular interaction matrix elements must be evaluated. It has been customary to estimate these terms by introducing a multipole expansion for $V_{ab}$ and truncating the series after the dipole term.[14–16] Furthermore, intermolecular electron-exchange interactions and charge-transfer interactions are usually neglected. In recent studies[17] of the electronic excited states of molecular crystals of organic molecules, it has been demonstrated that these approximations are valid only for the description of very strong electronic transitions (characterized by an oscillator strength of the order of unity), while, in general, the computation of intermolecular interaction energies cannot be reduced to dipole–dipole terms alone, since short-range higher-order multipole interactions make an important contribution to the diagonal and the off-diagonal energy matrix elements.

The pertinent interaction matrix elements combining a singly excited intermediate state with the final state, i.e., $\langle 0p \mid V_{ab} \mid fg\rangle$, and the ground state with a doubly excited intermediate state, i.e., $\langle 00 \mid V_{ab} \mid pg\rangle$, can be displayed in the general form

$$\langle \alpha_a \beta_b \mid V_{ab} \mid \gamma_a \delta_b\rangle = J_{ab}{}^{\alpha\beta\gamma\delta} + K_{ab}{}^{\alpha\beta\gamma\delta}. \tag{13}$$

In Eq. (13), the excitation-transfer matrix element is

$$J_{ab}{}^{\alpha\beta\gamma\delta} = \langle \varphi_a{}^\alpha \varphi_b{}^\beta \mid V_{ab} \mid \varphi_a{}^\gamma \varphi_b{}^\delta\rangle, \tag{14}$$

while the electron-exchange matrix element is

$$K_{ab}{}^{\alpha\beta\gamma\delta} = \langle (\mathcal{A}-1) \varphi_a{}^\alpha \varphi_b{}^\beta \mid V_{ab} \mid \varphi_a{}^\gamma \varphi_b{}^\delta\rangle, \tag{14a}$$

where $\varphi_c{}^\eta$ is the electronic wavefunction corresponding to the state $\eta$ of Molecule c, and $\mathcal{A}$ is the intermolecular

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[14] A. S. Davydov, *Theory of Molecular Excitons* (McGraw-Hill Book Co., Inc., New York, 1962).

[15] D. S. McClure, Solid State Phys. **8**, 1 (1959).

[16] D. P. Craig and S. H. Walmsly, *Physics and Chemistry of the Organic Solid State*, M. M. Labes, D. Fox, and A. Weissberger, Eds. (John Wiley & Sons, Inc., New York, 1963), Vol. 1, p. 585.

[17] R. Silbey, J. Jortner, and S. A. Rice, J. Chem. Phys. **42**, 1515 (1965).

antisymmetrization operator permuting electrons between molecules.

Focusing our attention on the case of spin-allowed transitions, some simplifications of the formalism are possible. It has been previously demonstrated that for the singlet excited states of typical molecular crystals (e.g., anthracene), the intermolecular electron-exchange interactions are of the order of 10–50 cm$^{-1}$, and are small relative to the contribution arising from the excitation exchange.[17,18]

For the purpose of making order-of-magnitude estimates, the electrostatic interaction is displayed in terms of a multipole expansion:

$$V_{\mathrm{ab}}=e^2R^{-3}\sum_{i,j}[\alpha_{ij}Q_1{}^iQ_1{}^j+e^2R^{-4}(\beta_{ij}Q_1{}^iQ_2{}^j+\beta'_{ij}Q_2{}^iQ_1{}^j)$$
$$+e^2R^{-5}\gamma_{ij}Q_2{}^iQ_2{}^j+e^2R^{-5}(\delta_{ij}Q_1{}^iQ_3{}^j+\delta'_{ij}Q_3{}^iQ_1{}^j)+\cdots], \tag{15}$$

where $R$ is the intermolecular separation, and $Q_k{}^i$ is the $k$th multipole-moment operator of the $i$th electron (the electrons being labeled so that Electrons $i$ and $j$ correspond to Molecules a and b, respectively). The geometrical factors $\alpha_{ij}$, $\beta_{ij}$, $\cdots$, are determined by the relative orientation of the two molecules. For strongly allowed $0\to f$ and $p\to g$ (or $0\to p$ and $0\to g$) transitions, the dipole–dipole term in the matrix elements of $V_{\mathrm{ab}}$ in Eq. (14) is expected to be dominant, and can be expressed in the form

$$\langle 0p\mid V\mid fg\rangle=\gamma e^2R^{-3}\langle 0\mid \sum_i Q_1{}^i\mid f\rangle\langle p\mid \sum_j Q_1{}^j\mid g\rangle$$
$$\langle 00\mid V\mid fg\rangle=\gamma e^2R^{-3}\langle 0\mid \sum_i Q_1{}^i\mid f\rangle\langle 0\mid \sum_j Q_1{}^j\mid g\rangle, \tag{16}$$

where $\gamma$ is a geometrical factor of the order of unity.

It will be useful at this stage to consider some approximate selection rules for cooperative excitation. We face the usual difficulties encountered in the use of a perturbation expansion and can proceed with our analysis only if a small number of terms dominate the behavior of the series. In our case, the expression for the transition matrix element can be displayed in the approximate form

$$K=\mathcal{H}_{0\to p}(\langle 0p\mid V\mid fg\rangle/W_1)+\mathcal{H}_{q\to g}(\langle 00\mid V\mid fg\rangle/W_2), \tag{6a}$$

where the energy denominators are $W_1=\hbar\omega-(\mathcal{E}_p{}^{\mathrm{a}}-\mathcal{E}_0{}^{\mathrm{b}})$ and $W_2=\hbar\omega-(\mathcal{E}_q{}^{\mathrm{a}}-\mathcal{E}_0{}^{\mathrm{a}})$ and $\mathcal{H}_{i\to j}$ is the radiative-transition-probability matrix element between the states $i$ and $j$. From this qualitative result, we conclude that:

(1) The ratio $\rho$ between the transition probability for the cooperative excitation and a typical one-photon allowed transition is of the order of

$$\rho\approx\mid\langle 0p\mid V\mid fg\rangle/W_1\mid^2 \quad\text{or}\quad \rho\approx\mid\langle 00\mid V\mid fg\rangle/W_2\mid^2.$$

Since the energy denominator is characteristically of the order of 1 eV, in order to obtain a value of $\rho\sim 0.01$ the interaction-energy matrix element must be of the order of $10^{-1}$ eV. (2) Electron-exchange interactions, being of the order of magnitude of 50 cm$^{-1}$, do not lead to an appreciable contribution to the transition probability for cooperative excitation.

(3) Large contributions arise for the case of strongly allowed transitions $0\to f$ and $p\to g$ (or $0\to f$ and $0\to g$). We are able, then, to utilize, e.g., (16). In this case, the transition moment is of the order of magnitude of a molecular dimension $L$, and we find that

$$\rho\approx(e^2L^2/WR^3)^2. \tag{17}$$

Setting $L=1$ Å, $R\approx 5$ Å, $W=1$ eV, we obtain $\rho=0.04$

(4) Contributions by higher-transition-multipole interactions are expected to be of importance in the case of weakly allowed transitions. Thus, in the case of a quadrupole–dipole virtual transition, it is to be expected that the relative transition probability (17) will be reduced by a factor of the order of $(L/R)^2$, as has been discussed by Dexter.[5]

It should be noted that there is a close analogy between the approximate selection rules for the linear process of a cooperative excitation and the nonlinear processes involving two-photon transitions.[19–21] It is now well established that two-photon transitions can be treated within the framework of perturbation theory, expanding the transition probability in terms of $e^2$ up to second order. In this case, the nonlinear optical process involves the stages $\mid 0\rangle$, $\hbar\omega_1$, $\hbar\omega_2\to\mid p\rangle$, $\hbar\omega_1\to\mid f\rangle$, where $\mid p\rangle$ is an intermediate state. Hence, for the two-photon transitions to occur, it is required that the transitions $\mid 0\rangle\to\mid p\rangle$ and $\mid p\rangle\to\mid f\rangle$ be allowed, thereby leading to an even-parity (or symmetry-forbidden) transition. In the case of the cooperative excitation, the approximate selection rules require that for one component, the transition proceeds via an intermediate state, so that the initial and final states are of the same parity (or the same symmetry, for nondegenerate states), while the transition for the second component is symmetry allowed. Both the exact selection rules for the two-photon absorption and the approximate selection rules for the cooperative excitations can be relaxed by introducing the contribution of higher-transition-multipole interactions. It should be stressed that in the case of two-photon absorption, the contribution of transition multipoles higher than the dipole moment are negligible [of the order of $(L/\lambda)^2$, relative to dipole term, where $\lambda$ is the wave-

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[18] J. Jortner, S. A. Rice, S. I. Choi, and J. L. Katz, J. Chem. Phys. **42**, 309 (1965).

[19] M. Goeppert-Mayer, Ann. Phys. **9**, 273 (1931).

[20] D. A. Kleinman, Phys. Rev. **125**, 87 (1962).

[21] E. M. Evleth and W. I. Peticolas, J. Chem. Phys. **41**, 1400 (1964).

length of the exciting light], while, in the case of cooperative excitation, the contribution of the higher multipoles to the electrostatic interaction energy may be of considerable importance. Another important mechanism for the relaxation of the selection rules cited arises from vibronic coupling in molecular systems, i.e., the effect of nuclear motion on the mixing of electronic states.

## IV. COOPERATIVE EXCITON STATES

The theory presented in Sec. III is directly applicable to the case of a pair of interacting atoms or molecules. We proceed to examine now, in some detail, the nature of the cooperative excitation of Frenkel states in molecular solids. At the outset, we make the usual assumption that the intermolecular overlap is very small. As is well known, in the case of dipole-allowed transitions, long-range electrostatic interactions of the dipole–dipole type are of considerable importance over distances of the order of magnitude of the wavelength of light,[17] and these interactions determine the energy of the states concerned. Under conditions such that crystal momentum is conserved, the long-range dipole–dipole interactions are absolutely convergent. Consider now the modifications which must be made in the formalism so as to make it applicable to cooperative exciton states in the tight-binding approximation. The double-exciton state corresponding to the presence of two excited atoms (molecules) in the solid, can be displayed in the general form[22]:

$$\Psi_{\mathbf{K},\mathbf{K}'}{}^{fg}=\{1/[N(N-1)]^{\frac{1}{2}}\}\times\sum_{n,n'}\exp[i(\mathbf{K}\cdot\mathbf{R}_n+\mathbf{K}'\cdot\mathbf{R}_{n'})]\,|\,nn'\rangle\Delta_{nn'},\qquad(18)$$

where the localized double-excitation representation is

$$|\,nn'\rangle=\mathcal{A}\varphi_n{}^f\varphi_{n'}{}^g\prod_{j;\,j\neq n,n'}{}''\,\varphi_j{}^0\qquad(19)$$

and the exclusion factor $\Delta_{nn'}$ is given by

$$\Delta_{nn'}=1-\delta_{nn'}.\qquad(20)$$

The ground state of the crystal is represented in the Heitler–London scheme by the product wavefunction

$$\Psi_0=\mathcal{A}\prod_s\varphi_s{}^0\qquad(21)$$

and is characterized by zero crystal momentum. Momentum conservation in the excitation process now implies that for the double-exciton state (19) $\mathbf{K}=-\mathbf{K}'$. Two kinds of intermediate states must be considered:

(1) A single-exciton state

$$\Psi_{\mathrm{k}}{}^p=(1/N^{\frac{1}{2}})\sum_j\exp(i\mathbf{k}\cdot\mathbf{R}j\,|\,j\rangle),\qquad(22)$$

with

$$|\,j\rangle=\mathcal{A}\varphi_j{}^p\prod_{l\neq j}{}'\varphi_l{}^0.\qquad(23)$$

This intermediate state can be reached by photon absorption. Momentum conservation implies that $\mathbf{k}=\mathbf{q}$, where $\mathbf{q}$, the wave vector of the incident photon, is much smaller than the reciprocal lattice spacing.

(2) An intermediate double-photon state $\Psi_{\mathbf{K}_1,-\mathbf{K}_1}{}^{fp}$. The transition to this state is induced by the crystal potential $V$, which is conventionally represented as the sum of pair interactions,

$$V=\sum_{s<t}V_{st}.\qquad(24)$$

The transition-probability matrix element for the cooperative excitation to the double-exciton state is now just

$$K=\sum_p\sum_{\mathbf{K}}\frac{\langle\Psi_0\,|\,H_{\mathrm{rad}}\,|\,\Psi_{\mathrm{q}}{}^p\rangle\langle\Psi_{\mathrm{q}}{}^p\,|\,V\,|\,\Psi_{\mathbf{K},-\mathbf{K}}{}^{fg}\rangle}{E_0+\hbar\omega-E_p}+\sum_p\sum_{\mathbf{K}}\frac{\langle\Psi_0\,|\,V\,|\,\Psi_{\mathbf{K},-\mathbf{K}}{}^{fp}\rangle\langle\Psi_{\mathbf{K},-\mathbf{K}}{}^{fp}\,|\,H_{\mathrm{rad}}\,|\,\Psi_{\mathbf{K},-\mathbf{K}}{}^{fg}\rangle}{E_0-(E_p+E_f)},\qquad(25)$$

where $E_0$ is the ground-state energy of the crystal, $E_p$ is the energy corresponding to the single-exciton state $\Psi_{\mathrm{q}}{}^p$, while $(E_p+E_f)$ is the energy corresponding to the double-exciton state $\Psi_{\mathbf{K},-\mathbf{K}}{}^{fp}$.

The interaction matrix elements in Eq. (25) can be rewritten in the following form:

$$\langle\Psi_{\mathrm{q}}{}^p\,|\,V\,|\,\Psi_{\mathbf{K},-\mathbf{K}}{}^{fg}\rangle=[1/N(N)^{\frac{1}{2}}]\sum_j\sum_n\sum_{n'}\exp(-i\mathbf{K}\cdot\mathbf{R}_n+i\mathbf{K}\cdot\mathbf{R}_{n'}-i\mathbf{q}\cdot\mathbf{R}_j)\times\langle{}_n{}^f\varphi_{n'}{}^g\,|\,\sum_{r<t}V_{rt}\,|\,\varphi_s{}^0\varphi_j{}^p\rangle,\qquad(26)$$

$$\langle\Psi_0\,|\,V\,|\,\Psi_{\mathbf{K},-\mathbf{K}}{}^{fp}\rangle=N^{-1}\sum_n\sum_{n'}\exp(-i\mathbf{K}\cdot\mathbf{R}_n+i\mathbf{K}\cdot\mathbf{R}_{n'})\times\langle\varphi_n{}^f\varphi_{n'}{}^p\,|\,\sum_{r<t}V_{rt}\,|\,\varphi_s{}^0\varphi_{s'}{}^0\rangle.\qquad(27)$$

Neglecting three- and four-center interactions, we need only consider the terms where $n=s$ and $n'=j$ in Eq. (26), and $n=s$ and $n'=s'$ in Eq. (27). It is immediately apparent that the new feature introduced by considering cooperative excitation to a double-exciton state, rather than the cooperative localized excitation of a pair of atoms or molecules, is that now the interaction matrix element is determined by the pair interactions summed over the entire crystal lattice. For the case of single-exciton states, the long-range dipole–dipole interaction is of considerable importance in determining the transition probability for cooperative excitations in a pure molecular solid. We now represent the inter-

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[22] D. L. Dexter and W. R. Heller, Phys. Rev. **91**, 273 (1953).

action energies as the sum of a short-range contribution (high-order multipole interactions, and electron-exchange interactions) and of a long-range interaction [involving the dipole–dipole interaction modulated by the trigonometric factor $\exp(i\mathbf{K}\cdot\mathbf{R})$]. The contribution of the modulated dipole sums can be evaluated using a continuum approximation, whereas the evaluation of the short-range terms requires detailed knowledge of the atomic or molecular wavefunctions. When potential retardation effects are neglected, the total interaction matrix element can be represented in the form

$$\langle\Psi_0 \mid V \mid \Psi_{\mathrm{K},-\mathrm{K}}{}^{fp}\rangle$$

$$=\{\mu_{0\to f}\mu_{0\to p}(8\pi/3\Omega)P_2(\cos\theta)[j_0(\rho)+j_2(\rho)]\}+X, \quad (28)$$

where $P_2$ $(\cos\theta)$ is the second Legendre polynomial, $\theta$ being the angle between the propagation vector of the exciton $\mathbf{K}$ and the transition moment $\boldsymbol{\mu}_{\mu_0\to f}=\langle\varphi^0 \mid \mathbf{r} \mid \varphi^f\rangle$ of a single molecule. Since we consider only transverse excitons excited by electromagnetic radiation, $\boldsymbol{\mu}$ is orthogonal to $\mathbf{K}$ and $P_2=-\frac{1}{2}$. The spherical Bessel functions $j_0$ and $j_2$ have the argument $\rho=\mid \mathbf{K} \mid R_0$ where $R_0$ is the lattice spacing. Finally, $\Omega$ is the volume of the unit cell in the lattice, and $X$ represents the contribution to the matrix element of short-range interactions.

The general expression for the transition matrix elements can now be displayed in the approximate form

$$K=\sum_p\sum_{\mathrm{K}}\left(\frac{\mathcal{H}_{0\to p}}{\Delta E_1}\left\{\frac{\mu_{0\to f}\mu_{p\to g}}{R_0{}^3}[j_0(\rho)+j_2(\rho)]+X_1\right\}\right.$$

$$\left.+\frac{\mathcal{H}_{p\to g}}{\Delta E_2}\left\{\frac{\mu_{0\to f}\mu_{0\to g}}{R_0{}^3}[j_0(\rho)+j_2(\rho)]+X_2\right\}\right). \quad (29)$$

To make a crude numerical estimate, we consider only the region of the Brillouin zone where $\rho\ll 1$, so that $j_0(\rho)+j_2(\rho)=1$. The result obtained is then analogous to that for the case of two isolated atoms. It does not seem to us profitable at the present stage of development to extend the analysis to crystals containing more than one molecule per unit cell. It should be noted, however, that the experimental value of the Davydov splitting in such systems can be used to make an estimate of the electrostatic-interaction matrix elements which determine the transition probability for cooperative exciton states.

## V. APPLICATION TO COOPERATIVE EXCITATIONS IN THE INFRARED SPECTRA OF SOLIDS

The general formalism of cooperative exciton states can now be readily applied to the interpretation of the infrared spectra of molecular solids in the overtone region.[11] Following the analysis presented in the preceding section, we consider two nearly degenerate excited states of the crystal: the overtone state $\mid 02\rangle$ (or $\mid 20\rangle$) and the doubly excited state $\mid 11\rangle$.[23] These two states are split in zero order because of the finite molecular anharmonocity. In view of the near degeneracy of the crystal states $\mid 02\rangle$ and $\mid 11\rangle$, degenerate perturbation theory must be used in first order, and we seek a representation which is diagonal in the intermolecular electrostatic interaction $\langle 02 \mid V \mid 11\rangle$. This interaction between the two close-lying vibrationally excited configurations in the solid is analogous to the case of Fermi resonance in the vibrational spectra of polyatomic molecules. As is well known,[24] intramolecular Fermi resonance arises from an accidental degeneracy between the vibrational states of a polyatomic molecule. It is the anharmonic terms in the potential energy, i.e., the perturbations between different vibrations which lead to the interaction between close-lying vibrational levels of the same symmetry. In the case of the cooperative excitation to the $\mid 11\rangle$ crystal state, intermolecular interactions lead to a mixing of the double-exciton and the double-excitation states. This interaction may be considered to be an intermolecular Fermi resonance.

The relevant zero-order single-excitation wavefunctions for a pair of molecules can be displayed in the conventional form

$$\eta_\pm=(1/\sqrt{2})(\mid 02\rangle\pm\mid 20\rangle). \quad (30)$$

Only the state $\eta_+$ can interact with the double excitation $\mid 11\rangle$, whereupon the first-order wavefunctions can be displayed in the form

$$\psi_\pm=\alpha_\pm\mid 11\rangle+\beta_\pm\eta_+. \quad (31)$$

The matrix element coupling the states is given by

$$W=\langle 11 \mid V_{\mathrm{ab}} \mid \eta_+\rangle=\sqrt{2}\langle 11 \mid V_{\mathrm{ab}} \mid 02\rangle. \quad (32)$$

Before proceeding to consider the pertinent interaction matrix element, it is useful to display the interaction potential in the dipole approximation, retaining the first term in Eq. (15):

$$V_{\mathrm{ab}}=\frac{(\boldsymbol{\mu}_{\mathrm{a}}\cdot\boldsymbol{\mu}_{\mathrm{b}})}{R_{\mathrm{ab}}{}^3}-\frac{3(\boldsymbol{\mu}_{\mathrm{a}}\cdot\mathbf{R})(\boldsymbol{\mu}_{\mathrm{b}}\cdot\mathbf{R})}{R_{\mathrm{ab}}{}^5}=\gamma\frac{\mu_{\mathrm{a}}\mu_{\mathrm{b}}}{R_{\mathrm{ab}}{}^3}. \quad (33)$$

It is assumed that $R_{\mathrm{ab}}$ is the separation of the centers of gravity of the interacting molecules.[25]

The dipole-moment operators $\boldsymbol{\mu}_i$ are now expanded in power series in the normal coordinates $Q$ with only the first two terms retained. Neglecting interactions between different normal modes, we find

$$\boldsymbol{\mu}_i=\boldsymbol{\mu}_i{}^0+(\partial\boldsymbol{\mu}_i/\partial Q)Q. \quad (34)$$

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[23] In this section, we describe the vibrational wavefunction of a pair of molecules by $\mid v'v''\rangle$, where $v'$ and $v''$ represent the vibrational quantum numbers of Molecules a and b, respectively.

[24] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Co., Inc., New York, 1945).

[25] R. M. Hexter, J. Chem. Phys. **33**, 1833 (1960).

The matrix element of the interaction potential in Eq. (32) can now be displayed in the form

$$W=\frac{\sqrt{2}(\partial\boldsymbol{\mu}/\partial Q)^2\langle 0\mid Q\mid 1\rangle\langle 1\mid Q\mid 2\rangle}{R_{\mathrm{ab}}{}^3}, \qquad (35)$$

where $\langle(M-1)\mid Q\mid M\rangle$ is the transition matrix element. In the harmonic approximation,

$$\langle(M-1)\mid Q\mid M\rangle=(M\hbar/2\omega_0)^{\frac{1}{2}}, \qquad (36)$$

where $\hbar\omega_0$ is the excitation energy corresponding to the $0\longrightarrow1$ excitation.

These results are now applied to the study of the cooperative vibrational excitation in solid HCl. The excitation energy corresponding to the fundamental band is 2800 $\mathrm{cm}^{-1}$. To make a rough estimate of the interaction energy, we set $R_{\mathrm{ab}}=4$ Å. For a diatomic molecule, the normal coordinate and the Cartesian displacement coordinate $r$ are related by $Q=(m_R)^{\frac{1}{2}}r$, where $m_R$ is the reduced mass of the molecule. Hence, in this simple case,

$$(\partial\mu/\partial Q)\langle 0\mid Q\mid 1\rangle=(\partial\mu/\partial r)(\hbar/2m_R\omega_0)^{\frac{1}{2}}.$$

The dipole derivative is markedly enhanced in the solid, leading to an appreciable increase of the infrared absorption of the fundamental band. Using the estimates of Hornig and Hiebert[26] for solid HCl, we set $\partial\mu/\partial r=2$ D/Å. Using all these data, we estimate $W=60$ $\mathrm{cm}^{-1}$. The interaction matrix element $W$ should be of the order of magnitude of the Davydov splitting in the fundamental band of solid HCl. The fundamental band of solid HCl consists of two sharp bands located at $2704\pm3$ $\mathrm{cm}^{-1}$ and $2746\pm3$ $\mathrm{cm}^{-1}$, which are assigned to the Davydov components of the fundamental stretching vibration.[27] Hence, the Davydov splitting in this system is $42\pm6$ $\mathrm{cm}^{-1}$, quite close to the value of $W$ calculated herein.

The zero-order splitting $\delta$ between the states $\mid 11\rangle$ and $(\mid 02\rangle+\mid 20\rangle)$ is readily estimated from the anharmonicity factor. Setting

$$\delta=\tfrac{7}{4}(x_e\omega_e) \qquad (37)$$

and using the gas-phase value $x_e\omega_e=52$ $\mathrm{cm}^{-1}$,[11] we get $\delta=90$ $\mathrm{cm}^{-1}$.

The first-order splitting $y$ between the two states is now obtained from Eq. (9):

$$y=(4W^2+\delta^2)^{\frac{1}{2}}=150\ \mathrm{cm}^{-1}. \qquad (38)$$

This result is in good agreement with the experimental value $y=143$ $\mathrm{cm}^{-1}$,[11] representing the splitting between the overtone and the double-excitation bands. It should be noted at this point that the apparent increase of the anharmonicity factor in the crystal, as noted by Ron and Hornig,[11] is due to the repulsion between two nearly degenerate states.

The first-order wavefunctions can now be obtained from Eqs. (7), (9), and (12). They are

$$\psi_+=0.89\mid 11\rangle+0.45\eta_+,$$
$$\psi_-=0.45\mid 11\rangle-0.89\eta_+. \qquad (39)$$

The states $\psi_+$ and $\psi_-$ are to be identified with the overtone band and the double-exciton state, respectively. Thus, in first order, the intensity of the double-excitation band relative to the overtone band is given by $\rho=(\langle 00\mid\boldsymbol{\mu}\mid\psi_+\rangle/\langle 00\mid\boldsymbol{\mu}\mid\psi_-\rangle)^2$ (where $\boldsymbol{\mu}$ is the transition-moment operator) leading to $\rho=(\beta_+/\beta_-)^2=0.25$. In this first-order calculation, it is assumed that the contribution of other excited states of the crystal to the cooperative excitation is negligible. We now demonstrate that, in this case, a first-order calculation of the intensity of the double-excitation band is sufficient, and that a second-order calculation including the effects of other singly excited configuration leads to a negligible change in the transition probability.

The transition-probability matrix element for the cooperative excitation state can be represented in second order in the form

$$K=\beta_+\langle 00\mid H_{\mathrm{rad}}\mid\eta_+\rangle+\sum_{I;I\neq2}\frac{\beta_+\langle 00\mid H_{\mathrm{rad}}\mid 0I\rangle\langle 0I\mid V\mid\eta_+\rangle+\alpha_+\langle 00\mid H_{\mathrm{rad}}\mid 0I\rangle\langle 0I\mid V\mid 11\rangle}{(2-I)\hbar\omega_0}$$
$$+\sum_{I,J;I,J\neq2}\frac{\beta_+\langle 00\mid V\mid IJ\rangle\langle IJ\mid H_{\mathrm{rad}}\mid\eta_+\rangle+\alpha_+\langle 00\mid V\mid IJ\rangle\langle IJ\mid H_{\mathrm{rad}}\mid 11\rangle}{-(I+J)\hbar\omega_0}. \qquad (40)$$

Within the framework of the harmonic approximation, the relevant intermediate states contributing to the matrix element $K$ in Eq. (40) are the singly excited states $\mid 0I\rangle\equiv\mid 01\rangle$ and $\mid IJ\rangle\equiv\mid 01\rangle$ or $\mid IJ\rangle\equiv\mid 10\rangle$. It should be noted that in the case of a solid consisting of molecules with a permanent dipole moment, the intermolecular electrostatic-interaction potential combines singly excited states, and the second-order contributions of the second and third sums in Eq. (40) exactly cancel, so that the singly excited configurations $\mid 01\rangle$ (or $\mid 10\rangle$) do not contribute to the enhancement of the cooperative excitation. This is a rather peculiar example of crystal-field mixing where, because of a small energy denominator, configuration-interaction effects with the ground state are as important as for the vibrationally excited state. The contributions of crystal-field mixing

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[26] D. F. Hornig and G. L. Hiebert, J. Chem. Phys. **27**, 752 (1957).

[27] D. F. Hornig and W. E. Osberg, J. Chem. Phys. **23**, 662 (1955).

to the ground state $|\,00\rangle$ and to the double-exciton state $|\,11\rangle$ cancels out in the harmonic approximation. When anharmonicity effects are included, a rough calculation shows that second-order effects lead to a contribution of about 1% to the relative intensity.

The results of this calculation indicate that in the infrared spectrum of solid HCl, the intensity of the double-excitation band should be comparable with that of the overtone band, in qualitative agreement with the experimental results of Ron and Hornig.

To complete this discussion, some comments regarding the excitation spectrum (the line shape of the double excitation) are in order. It was observed by Ron and Hornig[11] that the overtone band in solid HCl is rather narrow (bandwidth 20 $\mathrm{cm}^{-1}$) while the double excitation band is broad (bandwidth of 90 $\mathrm{cm}^{-1}$). The line-shape function for a double excitation on Atoms a and b is related to the line shapes $\alpha_{\mathrm{a}}(E)$ and $\alpha_{\mathrm{b}}(E)$, corresponding to the single excitations of the two components, by the convolution integral

$$\int \alpha_{\mathrm{a}}(E)\alpha_{\mathrm{b}}(2\hbar\omega_0-E)\,dE.$$

If we assume Gaussian band shapes for the single excitations, the bandwidth for the double excitation $B_{\mathrm{ab}}$ is related to the bandwidths corresponding to the single excitations $B_{\mathrm{a}}$ and $B_{\mathrm{b}}$ by the expression $B_{\mathrm{ab}}=(B_{\mathrm{a}}+B_{\mathrm{b}})^{\frac{1}{2}}$. In the case of solid HCl, we note that the total width of the fundamental band (including the two Davydov components) is about 60 $\mathrm{cm}^{-1}$. Hence the width of the double-excitation bands should be (qualitatively) about 85 $\mathrm{cm}^{-1}$, in good agreement with the experimental value of Ron and Hornig.

In the present discussion, we do not consider the detailed structure of solid HCl (crystalline HCl has two molecules per unit cell).[26,27] In principle, the double-exciton state in this system will be split into four components, the splitting being determined by the interaction potential between excited states. It is clear that further experimental studies of the double-exciton band shape are of considerable interest.

From the analysis of the double vibrational excitation states we conclude that:

(1) Theoretical arguments lend strong support to the proposal of Ron and Hornig that the appearance of double-excitation bands in the infrared spectra of molecular solids is a general phenomenon which accounts properly for the structure in the overtone region.

(2) A considerable contribution to the intensity of the double-excitation band arises from an intermolecular Fermi resonance effect between the overtone and the double-excitation states. The first-order interaction accounts properly for the splitting between these two states. The calculated intensity ratio of the cooperative excitation band and the overtone band $\rho(\mathrm{calc})=0.25$ is lower than the approximate experimental value[11] $\rho(\mathrm{exptl})=1$–$2$. This discrepancy may indicate that the present formalism, involving only neutral-exciton states, is not complete, and that charge delocalization between neighboring molecules should be considered. These charge-transfer effects may enhance the transition probability to the cooperative exciton state, and might also be of considerable importance in enhancing the intensity of the infrared fundamental band in the solid. Indeed, it is now well established[25–27] that the dipole derivatives for the fundamental band in the solid state range from more than one to almost five times the values in the gas phase. Since relatively small changes in the charge density in the periphery of the molecule in the condensed phase may strongly affect the dipole derivative,[25] changes in charge density induced by intermolecular charge transfer may be important.[28] The intensity changes of the infrared bands of "hydrogen-bonded" solids are closely related to the remarkable enhancement of the infrared-band intensity in molecular charge-transfer complexes, which can be rationalized in terms of vibronic interactions.[29,30]

(3) The repulsion between the $|\,02\rangle$ and $|\,11\rangle$ states provides an explanation for the apparent increase of the anharmonicity factor $(x_e\omega_e)$ in the crystal. It should be noted that recent spectroscopic studies of the cage effect on vibrational states, by Schnepp and Dressler,[31] lead to conclusive evidence for a negative anharmonicity contribution arising from intermolecular repulsions in the condensed phase.

(4) Intensity stealing from the overtone band by intermolecular interaction may provide an explanation for the dilemma posed by the observed relative intensities of the overtone bands in the infrared spectra of solids.[28] In contrast to the enhancement of the fundamental band in the solid, the intensity of the overtone band is generally not increased in the solid and, in certain cases, is even decreased relative to the gas-phase intensity. Crystal-field mixing of single excitations (i.e., $|\,10\rangle$) into the overtone band cannot account for this effect, as the contribution of the ground-state mixing again cancels out the contribution to the overtone state. The interaction between the overtone and the double-excitation states may be responsible for the decrease in the overtone-band intensity. It is also important to consider changes in intensity due to changes in the anharmonicity on going from the free molecule to the solid.

(5) The large width of the double-excitation band is qualitatively understood.

## VI. RADIATIVE ANNIHILATION OF DOUBLE-EXCITON STATES

The implications of the existence of cooperative excitations for the understanding of the radiative

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[28] S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964).

[29] R. S. Mulliken and W. B. Pearson, Ann. Rev. Phys. Chem. **14**, 723 (1964).

[30] G. C. Pimentel and A. L. McLellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, Calif., 1960).

[31] O. Schnepp and K. Dressler, J. Chem. Phys. **42**, 2482 (1965).

annihilation of exciton states in molecular crystals are of considerable interest. It was suggested by Dexter[5] that the inverse of the double-excitation process to the state $|fg\rangle$ can give rise to two photons $\hbar\omega_{0\to f}$ and $\hbar\omega_{0\to g}$. Although this linear optical effect, involving photon multiplication, is of considerable interest, no experimental evidence for such a process is at present available. Recent experimental studies of photon multiplication in $\mathrm{Tl}^+$-doped alkali halide crystals[32] can be interpreted in terms of resonance energy transfer from the exciton band of the ionic crystal to the impurity.

Radiative annihilation of the double-exciton state $|fg\rangle$, produced by the absorption of two photons $\hbar\omega_{0\to f}$ and $\hbar\omega_{0\to g}$, may also lead to the emission of a single photon $\hbar\omega=\hbar\omega_{0\to f}+\hbar\omega_{0\to g}$. This nonlinear radiative process, proceeding through an intermediate state (which does not conserve energy), is just the inverse of the cooperative excitation process. In a very recent paper, Knox and Swenberg[33] have pointed out the possibility of direct emission of a photon from a pair of excitons and estimated the efficiency of this decay channel for triplet–triplet annihilation in crystalline anthracene.[34] For comparative purposes, it is also interesting to consider the transition probability for the radiative annihilation of a double-exciton pair, and then to examine the possibilities inherent in the vibrational and electronic exciton states of molecular crystals.

The probability for the emission of a photon $\hbar\omega$ by radiative decay of a pair of localized excited atoms or molecules is given by the conventional expression

$$T_{fg\to 00}=(4\omega^3/\hbar c^3)K^2, \tag{41}$$

where $K$ is the radiative transition-probability matrix element combining the initial state $|fg\rangle$ with the final state $|00\rangle$. The recipe for calculating this matrix element is presented in Sec. II.

We are now able to estimate the rate of the radiative annihilation of a double-exciton state in molecular crystals. We limit our discussion to exciton states with a relatively small bandwidth (of the order 1–10 $\mathrm{cm}^{-1}$ such as is characteristic of vibrational excitons in molecular crystals and triplet excitons in organic crystals). In this case, the frequency of excitation transfer is small relative to the frequency of intermolecular lattice vibrations, so that there is strong scattering of the excitons by the lattice phonons. In the strong-scattering limit, we assume that the mean free path of the exciton wave is of the order of magnitude of the intermolecular spacing in the crystal. The motion of the excitation can then be described as a random-walk process. The hopping model for exciton motion has been discussed in detail in another paper.[18]

Within the framework of the random-walk model, a simple kinetic scheme leads to the following formula for the reaction rate for radiative annihilation of the double exciton state:

$$RR=\frac{\Gamma n^2}{1+(\gamma/T)}, \tag{42}$$

where $n$ is the exciton concentration, $\Gamma$ the rate of collision of two excitons, and $\gamma$ the excitation transfer rate in the crystal. When the rate of dissociation of the exciton pair (where two excitations are located on neighboring molecules) is large compared with the radiative annihilation rate (i.e., $\gamma\gg T$), the annihilation rate is determined by the radiative transition rate to the final state

$$RR=(\Gamma T/\gamma)n^2, \tag{42a}$$

while, on the other hand, when the transition to the final state is fast on the time scale of exciton migration (i.e., $\gamma\ll T$), the radiative annihilation rate is diffusion controlled, being determined by the rate of collision of the excitons

$$RR=\Gamma n^2. \tag{42b}$$

Consider the application of these general considerations to the study of some specific cases where radiative annihilation of a double-exciton state can occur.

(a) The radiative annihilation of a vibrational double-exciton state: Irradiation of a molecular solid in the fundamental vibrational band (energy $\hbar\omega_0$) may lead to the emission of a photon with energy $2\hbar\omega_0$ arising from the radiative annihilation of the $|11\rangle$ state. The transition probability in solid HCl can be readily estimated from the results of Sec. V, setting $T_{11\to 00}\approx T_{20\to 00}\approx T_{10\to 00}/100$. The radiative lifetime of the single excitation $|10\rangle$, calculated from the dipole derivative data in solid HCl,[26] is $10^{-5}$ sec. Therefore, $T_{11\to 00}=10^3\ \mathrm{sec}^{-1}$. The rate of excitation transfer of two vibrational excitons can be estimated from the expression $\gamma=W/\hbar$, where $W=50\ \mathrm{cm}^{-1}$ is the vibrational-exciton bandwidth. We find $\gamma=10^{13}\ \mathrm{sec}^{-1}$. The rate of the encounter of two excitons is easily estimated from the random-walk model,[18] setting

$$\Gamma=8\pi DR_{\mathrm{ab}}, \tag{43}$$

where $D$ is the diffusion coefficient of the excitons in the strong scattering limit,

$$D\approx\gamma R_{\mathrm{ab}}^2. \tag{44}$$

Setting $R_{\mathrm{ab}}=4$ Å, we find $D=1.6\times10^{-2}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$, so that $\Gamma=10^{-8}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$ which leads to $RR=10^{-18}n^2\ \mathrm{cm}^{-3}\cdot\mathrm{sec}^{-1}$. The very small magnitude of the bimolecular radiative annihilation rate for vibrational excitons indicates that there is no hope of observing this process in molecular crystals, where the channel for direct radiative or nonradiative annihilation of single vibrational states (characterized by a lifetime of $\sim10^{-5}$ sec) provide the dominant decay mode.

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[32] E. R. Ilmas, G. G. Liidya, and Ch. B. Lusshchik, Opt. Spectry. **18**, 255 (1965) [Opt. i Spektroskopiya **18**, 453 (1965)].

[33] R. S. Knox and C. E. Swenberg (private communication), "Direct Radiative Exciton–Exciton Annihilation," J. Chem. Phys. (to be published).

[34] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters **10**, 400 (1963).

(b) The radiative annihilation of a double triplet-exciton state in crystalline anthracene[33,34]: This problem was recently treated in considerable detail by Knox and Swenberg and we limit ourselves to a few general comments. Triplet–triplet annihilation in crystalline anthracene leads to delayed fluorescence on the time scale of milliseconds.[34] This process has been satisfactorily interpreted[18] in terms of a diffusion-controlled interaction between triplet excitons, the triplet-exciton migration being treated in the strong scattering limit. These calculations[18] lead to the numerical values: $\Gamma = 10^{-12}$ cm$^{+3}$ sec$^{-1}$ and $\gamma = 10^{10}$ sec$^{-1}$. The radiative annihilation rate constant for a pair of triplet excitations located on adjacent molecules can be roughly estimated from Eq. (6a). The result is $T \approx T_a(\nu/W)^2$, where $T_a$ is the radiative lifetime of singlet anthracene, $\nu$ is an electron-exchange matrix element combining the double-exciton state and the intermediate singlet state, and $W$ is the energy difference between the double triplet-exciton state and the singlet-exciton state. We set $W=0.5$ eV, which is the energy difference between the double triplet-exciton state (populated by a ruby laser) and the 0–0 band of the $^1B_{2u}$ state in anthracene and also set $T_a = 3\times10^8$ sec$^{-1}$. The exchange matrix element is about $\nu = 10$ cm$^{-1}$, based on the theoretical calculations of Jortner, Rice, Choi, and Katz.[18] (A striking confirmation of this theoretical estimate has been obtained very recently from a direct experimental determination of the Davydov splitting in the first triplet state of crystalline naphthalene.[35]) Using the quoted values, we obtain $T = 10^3$ sec$^{-1}$. Thus it follows immediately that, for radiative triplet–triplet annihilation in crystalline anthracene, $\gamma \gg T$, and the reaction rate is dominated by the transition probability to the final state, the annihilation rate being $RR = 10^{-19}n^2$ cm$^{-3}\cdot$sec$^{-1}$. This rate is seven orders of magnitude smaller than that in the diffusion-controlled channel which involves the direct transition to the singlet state. These conclusions are in general agreement with the recent results of Knox and Swenberg.[33]

The major conclusions of this discussion are basically negative. The direct observation of the radiative annihilation of an exciton pair is conceivably possible (if at all) only with extremely large exciton concentrations, when a large fraction of the crystal molecules are excited, and provided that no direct channel for exciton–exciton annihilation is available. The radiative annihilation channel provides an additional mode of decay of exciton states which will make the interesting process of Bose condensation in a dense exciton gas inaccessible to experimental observation.

## VII. DISCUSSION

In the present work we consider cooperative exciton states in molecular crystals within the framework of the tight-binding approximation. An alternative approach, based on the use of Wannier exciton states, has been presented by Miyakawa[4] and by Ovander.[3] Ovander's work leads to the prediction that the ratio of matrix elements for the single and double excitations is of the order of $(L/R_{ab})^3$, in agreement with the contribution from the dipole interactions obtained in the Frenkel scheme. Miyakawa[4] attributes the intense band in LiF located at 25 eV [9] to a double excitation of the fundamental exciton band. But the selection rules for a double excitation of two allowed transitions show that the transition-probability matrix elements in this case should involve quadrupole and electron-exchange interactions. It is to be expected, then, that the transition probability to the double-exciton state in LiF should be of the order of 1% of the transition probability to the single-exciton state, making Miyakawa's assignment of the 25-eV band subject to question.

Further extensions of the experimental and theoretical study of cooperative excitations should lead to some extremely interesting information about the excited states of molecular crystals. The pertinent problems are:

(a) The present formalism, including only neutral-exciton states, is not complete, and intermolecular electron-transfer effects should be included to obtain a better understanding of the nature of vibrational and electronic cooperative exciton states.

(b) The approximate selection rules for cooperative electronic excitations imply that the allowed transitions, in this case, involve one final state which is allowed and another final state which is forbidden in the dipole approximation. This selection rule ought to be quite general, and should be extremely useful in the study and the location of symmetry-forbidden electronic transitions of molecules. An immediate example that comes to mind is the location of the $^1E_{2g}$ state of benzene. Thus, studies of (linear optical effect) cooperative excitation should be complementary to studies (nonlinear effect) of double-photon transitions in locating excited states which are connected to the ground state by symmetry-forbidden transitions.

(c) A careful study of the matrix elements governing the transition probability to cooperative exciton states may yield interesting information concerning exciton–exciton interactions in molecular crystals.

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