Exciton trapping in molecular crystals by phonon emission at impurity sites

Jai Singh

Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511

(Received 23 April 1985)

A general operator of interaction among excitons, impurities, and phonons is derived for doped molecular crystals. Using the first-order term of the operator, the rate of trapping of an exciton by emitting a single phonon at impurity sites is calculated and found to be in good agreement with previous results. The interaction operator can be applied to study higher-order processes involving multiphonons as well.

I. INTRODUCTION

The transport of charge carriers and excitation energy has received much attention recently.[1-4] The mechanism of exciton trapping at impurity and physical defect sites leads to understanding of the quenching of fluorescence and phosphorescence in crystals. Craig, Dissado, and Walmsley[5] discussed trapping and self-trapping of excitons in molecular crystals. They calculated the trapped lifetime and damping rate of excitons. The rate of trapping of an excitation migrating in a quasi-one-dimensional dilute system was also calculated.[4] However, the rate of trapping of an exciton at impurity sites has not been calculated explicitly as a function of the trap depth and phonon frequency in molecular crystals. The difficulty in calculating the trapping rate of excitons is due mainly to the lack of a suitable Hamiltonian that accounts for exciton, phonon, and impurity interaction. Also, for rigorous calculations the exciton-phonon interaction Hamiltonian in a diagonal form is necessary as it is recognized in formulating the theory of self-trapping[6] of excitons in molecular crystals. However, until recently[7] the exciton-phonon interaction Hamiltonian was not diagonalized appropriately.

In this paper we present the calculation of the rate of trapping of an exciton at impurity sites by emitting a phonon. An exciton moving in the crystal encounters an impurity site which has an excitation energy less than that of its host. The exciton thus gets trapped at the impurity site, and the excess energy excites a phonon. In general, the number of phonons emitted after the exciton is trapped would depend on the trap depth and temperature of the crystal. Here, however, we consider shallow traps in crystals at very low temperatures so that only a single phonon is emitted. The theory can easily be extended to the emission of several phonons, as will be demonstrated elsewhere.

The Hamiltonian for the motion of an exciton in an impure or doped crystal is first derived in order to obtain an exciton-impurity-phonon interaction operator suitable for the calculation. From the derived general interaction operator we consider only the zeroth- and first-order terms which are, respectively, independent and linearly dependent on the lattice displacement vectors. However, we present the derivation of the rate only due to the first-

order interaction here. The derivation of the rate of trapping due to the zeroth-order interaction has been published elsewhere,[8] therefore, we will present only the result here. The rates are obtained as functions of the trap depth and phonon frequency, and their orders of magnitude agree well with previous results.

II. INTERACTION OPERATOR FOR EXCITON TRAPPING

The excitation Hamiltonian of a crystal with one impurity at site p can be written in the real crystal space as

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{imp}} , \tag{1}$$

where

$$\hat{H}_0 = \sum_l \left[\Delta E + \sum_{m\,(\neq l)} D_{l,m} \right] B_l^\dagger B_l + \sum_{l,m\,(\neq l)} M_{l,m} B_l^\dagger B_m , \tag{2a}$$

and

$$\hat{H}_{\text{imp}} = \Delta_p B_p^\dagger B_p , \tag{2b}$$

where ΔE is the energy of excitation of an isolated host molecule and ΔE_p is that of an impurity. The summation over l and m in (2a) runs over all the molecules in a crystal. We define the trap depth as

$$\Delta_p = \Delta E_p - \Delta E + \sum_{m\,(\neq p)} D_{p,m} - \sum_{m\,(\neq l)} D_{l,m} . \tag{3}$$

Here we consider those impurities for which $\Delta E > \Delta E_p$ so that the trap depth Δ_p is negative. It is assumed that the exciton transfer matrix element $M_{l,m}$ does not change significantly due to the substitution of an impurity.

The Hamiltonian $\hat{H}_0$ is the well-known Frenkel exciton Hamiltonian in a pure crystal[9] and is translationally invariant. The excitation operator $B_l^\dagger$ in a pure crystal is expanded in $\mathbf{k}$ space as[9]

$$B_l^\dagger = N^{-1/2} \sum_{\mathbf{k}} \exp(-i\mathbf{k}\cdot l) B_{\mathbf{k}}^\dagger , \tag{4}$$

N is the number of unit cells and expansion (4) is valid for crystals with one molecule per unit cell. For a vibrating lattice of a pure crystal expansion (4) may also be assumed to be valid if the lattice-displacement vectors are small.

This leads to the derivation[9-11] of the exciton-phonon interaction, using (2a) and (4), for a pure crystal.

For the derivation of the exciton-impurity-phonon interaction from $\hat{H}_{imp}$ (2b) we assume that expansion (4) is valid for $B_p^\dagger$ and B_p as well. This assumes that the impurity molecule sits in the same position as a host molecule, and no spatial symmetry is destroyed.[12] This assumption may be quite acceptable, particularly for isotopic impurities when the impurity concentration is not too high. In view of this the Hamiltonian (1) for a crystal with lattice vibration will have $\hat{H}_0$ and $\hat{H}_{imp}$ as

$$\hat{H}_0 = \sum_k E(k)B_k^\dagger B_k + N^{-1/2} \sum_{k,q} S(k,q)B_{k+q}^\dagger B_k(b_{-q}^\dagger + b_q)$$

$$+ \sum_q \hbar\omega(q)(b_q^\dagger b_q + \tfrac{1}{2}), \tag{5}$$

and

$$\hat{H}_{imp} = \Delta_p N^{-1} \sum_{k,k'} B_k^\dagger B_{k'} \exp[i(k'-k)\cdot(p+R_p)], \tag{6}$$

where R_p represents the lattice displacement vector of the impurity from its equilibrium position p. It is to be noted that in (5) the last term of the phonon Hamiltonian is not

derived from (2a); instead it is simply added to (5). Although we have subjected $\hat{H}_0$ and $\hat{H}_{imp}$ to similar assumptions and approximations, there is one significant difference which may be noted in (5) and (6): In (5), as a result of the translational symmetry, the exciton and phonon wave vectors are conserved; i.e., in each term of (5) the sum of the wave vectors of the particles (exciton and phonon) created is equal to that of the particles annihilated. However, this is not true for $\hat{H}_{imp}$ in (6). In this sense the translational symmetry is destroyed in the region where there is an impurity in the crystal. This distinction between $\hat{H}_0$ [Eq. (5)] and $\hat{H}_{imp}$ [Eq. (6)] will be maintained throughout in the following.

In deriving (5) the lattice-displacement vector R is expanded in the reciprocal-lattice space[9] as

$$R_l = N^{-1/2} \sum_q \left[\frac{\hbar}{2I\omega(q)}\right]^{1/2} \hat{e}(q)\exp(iq\cdot l)(b_{-q}^\dagger + b_q), \tag{7}$$

where I is the mass coefficient of hosts. In (5) and (7) the phonon branch index is dropped. Assuming that R_p in (6) can also be expanded like R_l (7) we can write

$$\hat{H}_{imp} = \Delta_p N^{-1} \sum_{k,k'} B_k^\dagger B_{k'} \exp[i(k'-k)\cdot p]\exp\left[i\sum_q (k'-k)\cdot\hat{e}(q)Z(q,p)(b_{-q}^\dagger + b_q)\right]. \tag{8}$$

The form of $Z(q,p)$ is obvious from (7).

$\hat{H}_{imp}$ [Eq. (8)] is an operator representing the interaction between a localized excitation at p [one can use (4) to write $B_p^\dagger B_p$ in (8)] and phonons localized at p as well. The meaning of a localized phonon is used only in the sense of expansion (7), where the right-hand side is associated with a particular lattice-displacement vector of the molecule at l. It does not, however, refer to the intramolecular vibrations. As the phonon operators $(b_{-q}^\dagger + b_q)$ appear in the exponential function, one can use (8) for multiple phonon processes of any order. Here, however, we will consider up to the first order only. For deriving the interaction up to the first order one expands (8) in a Taylor series about the lattice equilibrium. In doing so one must calculate the derivative of (6) with respect to the lattice-displacement vectors at the lattice equilibrium. The derivative of Δ_p will be negligibly small because ΔE and ΔE_p [Eq. (3)] are constants. Although $D_{l,m}$ [Eq. (3)] depends on lattice-displacement vectors, the derivative of the difference $\sum_m'(D_{p,m} - D_{l,m})$ will be negligible. Hence, we can safely assume in (6) that $\partial\Delta_p/\partial R_p = 0$, and then the Taylor series expansion of (6) will be equivalent to expanding the second exponential function of (8) into its series. The first two terms of the series are obtained as

$$\hat{H}_{imp}^{(0)} = \Delta_p N^{-1} \sum_{k,k'} B_k^\dagger B_{k'} \exp[i(k'-k)\cdot p] \tag{9}$$

and

$$\hat{H}_{imp}^{(1)} = i\Delta_p N^{-1} \sum_{k,k',q} (k'-k)\cdot\hat{e}(q)Z(q,p)\exp[i(k'-k)\cdot p]$$

$$\times B_k^\dagger B_{k'}(b_{-q}^\dagger + b_q). \tag{10}$$

$\hat{H}_{imp}^{(0)}$ represents the zeroth-order interaction among excitons, impurities and phonons, and $\hat{H}_{imp}^{(1)}$ is that of the first order. We will use (9) and (10) to calculate the rate of trapping of an exciton at an impurity in the crystal. It is to be noted that the interaction operators (9) and (10) are different from what has been used earlier.[5]

III. EXCITON TRAPPING

Consider that an exciton is created initially by an incident photon in the pure crystal region. Therefore, initially the energy operator of the crystal can be expressed by the Hamiltonian $\hat{H}_0$ as in Eq. (5). However, it is worth writing the Hamiltonian (5) in its diagonal form.[6-11] For the 0-0 phonon transition the diagonalized Hamiltonian representing the energy operator of a composite exciton-phonon state is obtained as

$$\hat{H}_{0-0} = \sum_K \lambda_0(K)A_K^\dagger A_K, \tag{11}$$

with $\lambda_0(K)$ being the energy eigenvalue of the composite exciton-phonon state. The eigenvalue equation of the initial state can be written as

$$\hat{H}_{0-0}|K;n\rangle = \lambda_0(K)|K;n\rangle, \tag{12}$$

where

$$| \mathbf{K};n \rangle = A_{\mathbf{K}}^{\dagger} | 0_{\text{ex-ph}} \rangle , \tag{13}$$

and $| \mathbf{K};n \rangle$ is the eigenvector of the initial state. Equations (12) and (13) imply that instead of exciting an exciton in the pure crystal region we create a composite exciton-phonon state with energy eigenvalue $\lambda_0(\mathbf{K})$. We consider the trapping phenomena at very low temperature assuming $\bar{n}_q = \bar{n}_{-q} = 0$. For acoustic phonons, by setting the initial phonon energy $\sum_q \hbar\omega(q)(\bar{n}_q + \frac{1}{2}) = 0$, we get[12]

$$\lambda_0(\mathbf{K}) = E(\mathbf{K}) \pm \left[E_0^2 [E(\mathbf{K}) - E_0] + B^2 \left[\frac{E(\mathbf{K})}{2} - E_0 \right] \right]^{1/2} t^{-1/2} , \tag{14}$$

where $t = Iv^2$, and v is the velocity of sound in the crystal. E_0 is the energy of the center and $2B$ the bandwidth of the unperturbed exciton band.

In the trapped situation we assume that the impurity $\mathbf{p}$ is excited and one extra phonon is created in the lattice. The eigenvector of such a state can be written as

$$| p;n \rangle = G_q B_p^{\dagger} b_q^{\dagger} | 0;n \rangle \delta_{q,\mathbf{K}} , \tag{15}$$

where $\delta_{q,\mathbf{K}}$ conserves the momentum of the system before and after the trapping, and $G_q = (1 + \bar{n}_q)^{-1/2}$ is the nor-

malization constant of the eigenvector (15). The energy eigenvalue of (15) is obtained from

$$\hat{H}_p | p;n \rangle = W_p | p;n \rangle , \tag{16}$$

where $\hat{H}_p$ is assumed to be

$$\hat{H}_p = E_p B_p^{\dagger} B_p + \sum_q \hbar\omega(q)(b_q^{\dagger} b_q + \frac{1}{2}) , \tag{17}$$

and

$$E_p = \Delta E_p + \sum_{m\,(\neq p)} D_{p,m} , \tag{18}$$

represents the excitation energy of the impurity molecule in the crystal. In writing (18) we assume that the excitation transfer matrix element $M_{p,m}$ is negligible. From (15)–(18) we obtain W_p as

$$W_p = E_p + \sum_q \hbar\omega(q)(\bar{n}_q + \delta_{q,\mathbf{K}} + \frac{1}{2}) . \tag{19}$$

IV. TRAPPING RATE

For calculating the trapping rate we need to calculate the transition matrix element $\langle p,n | H_{\text{imp}}^{(J)} | \mathbf{K};n \rangle$, $J=0$ or 1. Using (9), (13), and (15) the transition matrix element $\langle p;n | \hat{H}_{\text{imp}}^{(0)} | \mathbf{K};n \rangle$ is already calculated.[8] The transition matrix element $\langle p;n | \hat{H}_{\text{imp}}^{(1)} | \mathbf{K};n \rangle$ is obtained using (10), (13), and (15) as

$$\langle p;n | \hat{H}_{\text{imp}}^{(1)} | \mathbf{K};n \rangle = \Delta_p N^{-2} \sum_{\mathbf{k}} \left[\frac{\hbar}{2I_p\omega(-q)} \right]^{1/2} i(\mathbf{K} - \mathbf{k})\cdot\hat{e}(-q) \exp[i(\mathbf{K} - q)\cdot p] C_0(\mathbf{K},0;n)(1 + \bar{n}_q)\delta_{q,\mathbf{K}} , \tag{20}$$

where $\mathbf{k}$ sums over the exciton wave vectors in the whole $\mathbf{k}$ space. Considering that a longitudinal phonon is emitted after the trapping of the composite exciton-phonon state, (23) can be written as

$$\langle p;n | \hat{H}_{\text{imp}}^{(1)} | \mathbf{K};n \rangle = i\Delta_p N^{-1} \left[\frac{\hbar}{2I_p\omega(-q)} \right]^{1/2} | \mathbf{K} | C_0(\mathbf{K},0;n)(1 + \bar{n}_q)\delta_{q,\mathbf{K}} . \tag{21}$$

From the conservation of energy before and after the trapping we get from (14) and (19)

$$\hbar\omega(\mathbf{K}) = \Delta_p + \left[\frac{B^2 E(\mathbf{K})}{2Iv^2} \right]^{1/2} , \tag{22}$$

where it is assumed that $\Delta_p = E(\mathbf{K}) - E_p$. In arriving at (22) the initial phonon energy in (19) is set to zero.

The rate of transition (R) can be calculated using (21) and (22) in (23):

$$R = \frac{2\pi C_p}{\hbar} \sum_{\mathbf{K}} | \langle p;n | \hat{H}_{\text{imp}}^{(1)} | \mathbf{K};n \rangle |^2 \rho(\hbar\omega(\mathbf{K})) , \tag{23}$$

where C_p is the impurity concentration, usually used in the form of a ratio of the impurity and host concentrations.[5,13] At low temperature we consider the contribution of acoustic phonons to be dominant, and hence the Debye model density of phonon states $\rho(\hbar\omega)$ is used:

$$\rho(\hbar\omega) = 6N(\hbar\omega)^2/(\hbar\omega_D)^3 . \tag{24}$$

ω_D is the Debye cutoff frequency. Using (21)–(24) we find the rate of transition (R) per second as

$$R = \frac{6\pi\Delta_p^2 C_p}{\hbar I_p v^2(\hbar\omega_D)^3} \left| \Delta_p^3 - \frac{3\Delta_p^2 B^{3/2}\Gamma(\frac{3}{4})}{4\sqrt{2\pi I v^2}\Gamma(\frac{5}{4})} - \frac{1}{\sqrt{\pi}} \left[\frac{B^3}{2Iv^2} \right]^{3/2} \frac{\Gamma(\frac{5}{4})}{\Gamma(\frac{7}{4})} \right| . \tag{25}$$

The transition rate R in (25) is derived correctly; however, a simpler solution can be obtained. Instead of using the energy conservation (22) we can use, as a good approximation, $\hbar\omega = \Delta_p$. This means that the trap depth is equal to the energy of the emitted phonon. One then obtains

$$R = \frac{6\pi\Delta_p^5 C_p}{\hbar I_p v^2(\hbar\omega_D)^3} . \tag{26}$$

In actual calculations of the rate from (25) or (26) it is

TABLE I. The rate of trapping calculated in naphthalane mixed crystals (Ref. 14) using $\zeta = 1.283$ g/cm^3, $\Omega = 4.74 \times 10^{-22}$ cm^3, $\hbar \omega_D = 90$ cm^{-1}, $B = 100$ cm^{-1}, and the impurity concentration $C_p = 0.5$.

Host	Impurity	Trap depth (cm^{-1})	$M_p = I_p/I$	Rate [Eq. (25)] (sec^{-1})	Rate [Eq. (26)] (sec^{-1})	Rate R_0 [Eq. (28)] (sec^{-1})
$C_{10}H_8$	$C_{10}D_8$	50	1.06	8.3×10^{11}	1.4×10^{12}	7.6×10^{12}
2α-$C_{10}H_6D_2$	$C_{10}D_8$	30	1.04	7.4×10^9	1.1×10^{11}	5.9×10^{11}
$C_{10}H_8$	2α-$C_{10}H_2D_6$	18	1.04	2.3×10^{10}	8.6×10^9	4.6×10^{10}
$C_{10}H_8$	4α-$C_{10}H_4D_4$	8	1.03	5×10^9	3.1×10^8	4×10^9

convenient to use $I = \zeta \Omega$ and $I_p = M_p \zeta \Omega$, where ζ is the mass density of the crystal, Ω is the volume of an unit cell, and $M_p = I_p/I$.

The transition rate R_0 calculated from the zeroth-order interaction (9) is obtained,[8] using $\hbar \omega = \Delta_p$, as

$$R_0 = \frac{6 \pi \Delta_p^5 E(0) C_p}{\hbar B^2 (\hbar \omega_D)^3} , \tag{27}$$

where $E(0)$ is the energy of the unperturbed exciton state at wave vector $\mathbf{k} = 0$. Since $E(0)$ is measured from the center of the unperturbed exciton band, one may expect that $E(0) \sim |B|$. Using this in (27) we obtain

$$R_0 = \frac{6 \pi \Delta_p^5 C_p}{\hbar B (\hbar \omega_D)^3} . \tag{28}$$

In Table I we have shown R calculated from (25) and (26), and R_0 from (28) for naphthalene crystals doped with four impurities, with $\Delta_p = 50$, 30, 18, and 8 cm^{-1}. We have used $B = 100$ cm^{-1} and $\hbar \omega_D \sim 90$ cm^{-1} in the calculations. The transition rates R and R_0 are found to be of the same order of magnitude and in the range of $10^9 - 10^{12}$ sec^{-1}. Any desired value of C_p can be used. Here, however, we have used $C_p = 0.5$.

V. DISCUSSION

A simple approach to study the trapping of an exciton in a doped or impure molecular crystal is presented. The results are quite general and can be applied to any crystal. Results are obtained using a new but rigorously derived interaction operator (8) of the exciton, impurity, and lattice vibrations. It is obvious from the interaction operator, as stated earlier, that such an operator can be applied for multiphonon processes as well. Here, however, we have presented the calculation and derivation of the trapping rate only from the first-order interaction operator. Also, we have presented results from the zeroth-order interaction operator. The first-order interaction (10) is linear in the lattice-displacement vectors, as is the exciton-phonon interaction Hamiltonian in (5). The eigenvector (13) of the composite exciton-phonon state used as the initial state of the crystal is also linear in phonon creation and annihilation operators. It is therefore quite consistent to consider only the zeroth- and first-order interaction operator (10) for the present calculations. Furthermore, it is well established that the traps play an active role at low temperatures which is the case considered here too. Unless the traps are very deep one

may not expect the emission of more than one phonon after the excitation is trapped in the crystal. It may also be expected that only the low-energy phonons can be emitted from shallow traps in the crystal at low temperatures. The present theory considers therefore only the emission of acoustic phonons in the crystal although it can easily be extended for optical phonons as well.

Rates R [Eqs. (25) and (26)] and R_0 [Eq. (27)] are calculated from the first-order [Eq. (10)] and zeroth-order [Eq. (9)] exciton-phonon-impurity interaction operators, respectively. The zeroth-order interaction operator represents interaction between excitons and impurity molecules in a crystal lattice at equilibrium, and the first-order interaction represents that in a vibrating lattice. Therefore, R_0 contributes to the rate of trapping of an exciton at the impurity site when no phonons are involved in the interaction operator and the trapping occurs mainly due to the energy difference between the excited states of host and impurity molecules. The rate R, however, contributes to the rate of trapping when the interaction operator also involves phonons. Both rates obtained here are of the same order of magnitude for naphthaleme crystals, and they would probably be obtained so from the present theory for most crystals because of the assumption that the lattice-displacement vectors are small and the translational symmetry is retained in a vibrating lattice. The rate R_0 using the zeroth-order interaction was not calculated before.

Craig, Dissado, and Walmsley[5] have calculated the trapping rates as a function of the exciton-phonon coupling but not explicitly as a function of the trap depth. However, the present results show that the trapping rates depend not only on the exciton-phonon coupling but also on the trap depth. Intuitively one expects the trap depth to play a role in the trapping process. The difference in approaches is mainly due to the difference in the exciton, impurity, and phonon interaction operators (9) or (10), and that used in Ref. 5. Craig, Dissado, and Walmsley considered only the first-order interaction but in a different form which gives the rate of trapping as independent of the trap depth. In the present trapping rates (25) and (26) the exciton-phonon coupling is present through the velocity of sound for acoustic phonons as well as the Debye cutoff frequency. For $C_p = 10^{-4}$, as used in Ref. 5, and $\Delta_p = 50$ cm^{-1}, we get from Eqs. (25) or (26) and (27) $R \sim 10^8 - 10^9$ sec^{-1}, which is in agreement with the result estimated by Craig, Dissado, and Walmsley[5] for lightly doped crystals.

Recently Argyrakis and Kopelman[13] discussed the

dynamics of the excitation energy in mixed organic solids where they have shown the time dependence of the rate of trapping. Present results are derived for crystals at rather low impurity concentrations[15] and the rates are calculated in units of sec^{-1}, whereas Argyrakis and Kopelman[13] have studied the rate in $nsec^{-1}$. However, as our results are calculated using the golden rule (23) they represent only an average rate over a time of a second. Argyrakis and Kopelman[13] have studied the time dependence of the rate constant over a time span 0—100 $nsec^{-1}$ and at trap concentrations 10^{-4}—10^{-5} in a ternary solid of naphthalane. They have found a rate of 0.02, in a time of a nanosecond which is 2×10^7 sec^{-1} from the direct conversion of nanoseconds into 10^{-9} sec, and after 100 nsec they have found a rate of 0.01 which is likewise equal to 10^5 sec^{-1}. Thus the average rate in a time of 0—100 nsec varies between 10^7 and 10^5 sec^{-1}, which is of about the same order of magnitude as the rates given in Table I provided we use the trap concentrations as 10^{-4}—10^{-5}. The present results are therefore in agreement with those found by Argyrakis and Kopelman as well.

The trapping rates obtained here are derived for crystals with one molecule per unit cell. The theory can easily be extended to multiple molecules per unit cell as well. However, it may be expected that the molecular multiplicity would affect the results only by a factor which would probably not change the order of magnitude of the rate.

From (26) and (28) it is seen that rate of trapping depends on the trap depth as Δ_p^5, and hence it is very sensitive to Δ_p. It is only due to the approximation $\hbar\omega = \Delta_p$ otherwise, as it can be seen from the Table I, that the rate calculated using (25) is not so sensitive to Δ_p. Moreover, one has to be careful in varying Δ_p because the results are obtained for processes emitting only a single low-energy acoustic phonon at very low temperature. For deep traps involving large Δ_p and multiple phonons, the results are expected to be considerably different.

Rates of trapping R_0 and R are calculated here considering a situation when a moving exciton encounters an impurity site and becomes trapped there. Therefore, this mechanism of trapping excludes the contribution to the trapping rates from the possibility of exciton hopping towards the impurity. Inclusion of such a possibility is expected to increase the trapping rates of both R_0 and R, and the increase may be expected to be proportional to the hopping velocity.

In deriving the zeroth- and first-order interaction operator (9) and (10) we have terminated the exponential series in (8) at the first-order term. Instead, if one first uses

$$\exp(b_q^\dagger + b_q) = \exp(b_q^\dagger)\exp(b_q)\exp(-\tfrac{1}{2}[b_q^\dagger, b_q]) \; ,$$

and then expands the exponential factor in (8) up to the first-order terms, one gets an exponential factor independent of the phonon operators in (9) and (10). This factor is similar to the Debye-Waller factor, and it tends to reduce the transition rate of exciton trapping in molecular crystals by 1—2 orders of magnitude. This has recently been discussed by Singh.[16]

ACKNOWLEDGMENT

[1]A. Blumen and R. Silbey, J. Chem. Phys. **69**, 3589 (1978).

[2]C. R. Gochanaur, H. C. Anderson, and M. D. Fayer, J. Chem. Phys. **70**, 4254 (1978).

[3]A. Blumen and R. Silbey, J. Chem. Phys. **70**, 3707 (1979).

[4]J. Klafter and R. Silbey, J. Chem. Phys. **72**, 849 (1980).

[5]D. P. Craig, L. A. Dissado, and S. H. Walmsley, Chem. Phys. Lett. **46**, 191 (1977).

[6]D. P. Craig and L. A. Dissado, Chem. Phys. Lett. **44**, 419 (1976).

[7]D. P. Craig and J. Singh, Chem. Phys. Lett. **82**, 405 (1981).

[8]J. Singh, Singapore J. Phys. **2**, 33 (1985).

[9]A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).

[10]J. Singh, Chem. Phys. **75**, 371 (1983).

[11]J. Singh, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1984), Vol. 38, p. 295.

[12]J. Singh, Phys. Rev. B **30**, 7267 (1984).

[13]P. Argyrakis and R. Kopelman, Chem. Phys. **78**, 251 (1983).

[14]K. P. Meletov, E. I. Rashba, and E. F. Sheka, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 184 (1979) [JETP Lett. **29**, 165 (1979)].

[15]In Eq. (1) the presence of a single impurity is considered and the impurity-impurity interaction is ignored. The theory presented here is therefore applicable for crystals with low-impurity concentration.

[16]J. Singh, in Proceedings of the Dynamical Processes in the Excited States of Solids Conference—85, Lyon, France, July 1985 [J. Phys. (Paris) (to be published)].