Chemical Physics

Exciton-phonon scattering and exciton trapping in onedimensional exciton systems@fa@f)

Hartmut Benk@f@f and Robert Silbey

Al

Citation: J. Chem. Phys. **79**, 3487 (1983); doi: 10.1063/1.446200 View online: http://dx.doi.org/10.1063/1.446200 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v79/i7 Published by the American Institute of Physics.

Additional information on J. Chem. Phys.

Journal Homepage: http://jcp.aip.org/ Journal Information: http://jcp.aip.org/about/about_the_journal Top downloads: http://jcp.aip.org/features/most_downloaded Information for Authors: http://jcp.aip.org/authors



Exciton-phonon scattering and exciton trapping in onedimensional exciton systems^{a)}

Hartmut Benk^{b)} and Robert Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received 26 May 1983; accepted 24 June 1983)

We calculate the $k \rightarrow k'$ scattering of excitons by phonons when impurities play a role. This is important for very narrow one-dimensional exciton bands as in tetrachlorobenzene. Three mechanisms are discussed and the dependence on impurity concentration and jump size are considered for all three.

I. INTRODUCTION

In a recent set of experiments, Schmidt and co-workers¹ have carefully studied the scattering of triplet excitations in tetrachlorobenzene (TCB) crystals at low temperature using electron spin echo experiments. These excitations are one-dimensional exciton states trix elements. Other workers, notably Fayer and coworkers² and Breiland and Saylor³ have also studied this system using ODMR measurements. Another quasione-dimensional system, dibromonaphthalene (DBN), has been studied by optical spectroscopy by Zewail⁴ and others.⁵ Both systems have been studied by spin resonance by Wolf and co-workers.⁶

All these systems are characterized by rather narrow exciton bands (~1.36 cm⁻¹ in TCB, ~20 cm⁻¹ in DBN), much narrower than the acoustic phonon bands. This means that one phonon scattering processes are excluded in the limit of infinitely long, pure exciton systems where k conservation must hold. However, these one phonon processes can occur if there are impurities or structural dislocations in the crystal. For example, if there are a finite number (N) of TCB molecules in a one-dimensional array (due to impurities or structural dislocations at each end of the array), then k (quasimomentum) conservation is not necessary, at least to order 1/N. In addition, if an impurity is present on an adjoining chain, it may induce one phonon scattering by breaking the translational invariance [e.g., by changing the site diagonal exciton-phonon coupling of one (or a few) molecules on the chain]. Finally, if an impurity is in the chain, it changes all the electronic states (and may lead to trapping states), which also leads to the breakdown of the k selection rules. This also makes one phonon processes allowed. These three mechanisms are the subject of this paper. In Sec. II, we state the general formulation of the problem. In Sec. III, we compute the microscopic exciton scattering rates.

written $\hat{H}_{ex} = \sum_{n=1}^{N_{ex}} \epsilon_n a_n^* a_n + \sum_{n=1}^{N_{ex}} J_{nm} a_n^* a_m .$ due to the large anisotropy in the excitation transfer ma-

The operators a_n^* and a_n create and destroy a localized electronic excitation of energy ϵ_n at the molecular site n. J_{nm} is the energy exchange matrix element between molecules n and m. N_{ex} is assumed to be the total number of electronically excitable molecules, say linearly arranged in the z direction, whereas the whole threedimensional molecular crystal under consideration (in which the linear chain is embedded) consists of $N = N_p$ $= N_x N_y N_z$ molecules, where obviously always $N_{ex} \le N_z$. The intermolecular vibration energy of the crystal is described by a pure harmonic Hamiltonian of the form

II. BASIC EQUATIONS OF THE GENERAL PROBLEM

The electronic Hamiltonian of an arbitrary linear aggre-

(2.1)

gate of N_{ex} molecules (in particular a linear chain) can be

A. The Hamiltonian

$$\hat{H}_{\mathrm{yh}} = \sum_{q} \hbar \omega(q) b_{q}^{*} b_{q} . \qquad (2,2)$$

The operators b_a^* and b_a create and destroy a phonon of frequency $\omega(q)$ and wave vector q, where q is a threedimensional vector.

We will assume that as far as the phonon states are concerned, all the molecules in the crystal are identical. Thus there is complete translation invariance for the phonon variables (in contrast to the exciton variables), and so

$$q_i = \frac{2\pi}{N_i d_i} v_i$$
, $i = x, y, z$ (2.3a)

with

$$-N_i/2 \le v_i \le N_i/2$$
, (2.3b)

where d_i is the lattice unit in *i* direction. The coupling between the electronic variables and the phonon bath is represented by the linear exciton-phonon Hamiltonian:

$$\hat{H}_{ex-ph} = (N_p)^{-1/2} \sum_{q,n=1}^{N_{ex}} e^{i \, qn} \chi_n(q) a_n^* a_n (b_{-q}^* + b_q) + (N_p)^{-1/2} \sum_{q,n,m} e^{i \, qn} F_{nm}(q) a_n^* a_m (b_{-q}^* + b_q) .$$
(2.4)

^{a)}Supported by National Science Foundation (Grant CHE81-00407). ^{b)}On leave from Inst. für Theoretische Physik, Teil 1, Universität Stuttgart, Germany; recipient of a Postdoctoral Fellowship from the Deutsche Forschungsgemeinschaft (DFG).

J. Chem. Phys. 79(7), 1 Oct. 1983

0021-9606/83/193487-09\$02.10

The coupling constants $\chi_n(q)$ and $F_{nm}(q)$ determine the strength of the local and nonlocal exciton-phonon coupling coming from the modulation of the molecular energies ϵ_n and the energy exchange integrals J_{nm} due to the intermolecular vibrations.⁷

For our problem of exciton-phonon scattering the electronic Hamiltonian in the local representation [Eq. (2.1)] is not convenient. Therefore we first diagonalize it in the so-called delocalized ρ representation. By means of the unitary transformation

$$a_{n}^{\star} = \sum_{\rho} c_{n}^{(\rho)} a_{\rho}^{\star}$$
, (2.5)

we deduce from the Eqs. (2, 1), (2, 2), and (2, 4) the corresponding crystal Hamiltonian:

$$\hat{H}_{cr} = \sum_{\rho} E(\rho) a_{\rho}^{*} a_{\rho} + \sum_{q} \hbar \omega_{q} b_{q}^{*} b_{q}$$

$$+ \sum_{\rho, \rho', q} G_{\rho\rho'}(q) a_{\rho}^{*} a_{\rho'}(b_{-q}^{*} + b_{q}) .$$
(2.6)

The new operators $a_{\rho}^{*}(a_{\rho})$ create (destroy) an electronic crystal excitation in the exact energy eigenvalues $E^{(\rho)}$ of the arbitrarily composed molecular aggregate (or linear chain of molecules) which can be electronically excited.

The last term in Eq. (2.6) describes the exciton-phonon coupling in the ρ representation and induces inelastic scattering $(|\rho'\rangle + |\rho\rangle)$ of the excitons by phonons (both pure scattering and trapping are possible as we will see below). The scattering parameter in Eq. (2.6) is

$$G_{\rho\rho}(q) = (N_{\rho})^{-1/2} \left\{ \sum_{n} c_{n}^{(\rho)*} c_{n}^{(\rho^{*})} e^{iqn} \chi_{n}(q) + \sum_{n,m} c_{n}^{(\rho)*} c_{m}^{(\rho^{*})} e^{iqn} F_{nm}(q) \right\}.$$
(2.7)

The important transformation coefficients $c_n^{(\rho)}$ in the above equation correspond physically to the probability amplitudes of the exact wave functions $|\psi^{(\rho)}\rangle$ with energy eigenvalues $E^{(\rho)}$ at molecular sites *n* of the crystal, i.e.,

$$\left|\psi^{(\rho)}\right\rangle = \sum_{n} c_{n}^{(\rho)} \left|n\right\rangle , \qquad (2.8)$$

where $|n\rangle$ describe the local molecular wave functions with molecule *n* excited.

In the case of arbitrarily doped molecular crystals or aggregates the ρ space is divided into a ϕ space which consists of perturbed delocalized excitons $E^{(\phi)}$ and an x space which consists of impurities induced quasilocalized exciton states $E^{(x)}$, called trap states, outside the exciton band. The transformation coefficients $c_n^{(\rho)}$ [Eq. (2.5)] can be calculated by means of a Green's function formalism as was shown by one of the authors.⁸ Only in the limiting case of an unperturbed, infinite (this means translational invariant) molecular crystal does the ρ space reduce into the usual k space (Bloch space) with $c_n^{(k)} = (N_{ex})^{-1/2} e^{ikm}$. Here k is an accurately defined quantum number equal to the quasimomentum of the pure delocalized excitons with the energies $E^{(k)}$,

$$E^{(k)} = \sum_{n,m} J_{nm} \exp[ik(n-m)] . \qquad (2.9)$$

B. Dynamics of the system-derivation of an effective density matrix equation

The dynamics of the coupled total system (excitons and phonons) described by the crystal Hamiltonian \hat{H}_{cr} [Eq. (2.6)] obeys the known Liouville equation

$$\dot{\hat{\rho}} = \frac{-i}{\hbar} \left[\hat{H}_{\rm cr}, \hat{\rho}(t) \right]. \tag{2.10}$$

In order to focus on the electronic system, we find an equation of motion for the reduced density matrix $\hat{\sigma}(t)$,

$$\hat{\sigma}(t) = \operatorname{tr}_{\mathfrak{p}\,\mathfrak{h}} \hat{\rho}(t) \tag{2.11}$$

which describes the dynamics of the excitonic subsystem. tr_{ph} means the trace over the phonon (lattice) states.

Since the derivation of the equation of motion of the reduced density matrix $\hat{\sigma}$ has been described by others,⁹ the procedure [an approximation equivalent to second order time dependent perturbation theory in the exciton-phonon coupling $G_{\rho\rho}(q)$] is not outlined explicitly here.

One finds that the diagonal elements of the density operator $\sigma_{\rho\rho} = \langle \rho | \hat{\sigma} | \rho \rangle$ obey the following equation of motion:

$$\dot{\sigma}_{\rho\rho} = -\sigma_{\rho\rho} \sum_{\rho^{\bullet}} A_{\rho\rho^{\bullet}} + \sum_{\rho^{\bullet}} A_{\rho^{\bullet}\rho} \sigma_{\rho^{\bullet}\rho^{\bullet}} \,. \qquad (2.12)$$

 $\sigma_{\rho\rho}(t)$ describes the probability to find an exciton in the state $|\rho\rangle$ with energy $E^{(\rho)}$ at time t. At this point we want to emphasize that the diagonal elements of the density operator $\sigma_{\rho\rho}(t)$ decouple from their nondiagonal elements $\sigma_{\rho\rho'}$ only in this ρ -energy eigenrepresentation (in contrast to the alternative local $|n\rangle$ representation). Therefore, this ρ representation is the most convenient representation for our system under investigation and leads to a closed equation of motion [Eq. (2.12)] for the occupation probabilities $\sigma_{\rho\rho}$ of the exact exciton energy eigenstates $E^{(\rho)}$. Equation (2.12) is therefore a Pauli master equation.

The phonon-induced transition rates $A_{\rho\rho}$, between two different states $|\rho\rangle$ and $|\rho'\rangle$ can be written

$$A_{\rho\rho^{\bullet}} = 2 \operatorname{Re} \int_{0}^{\infty} \exp[-(i\hbar)^{-1} (E^{(\rho)} - E^{(\rho^{\bullet})})\tau] \times \operatorname{tr}_{\mathfrak{ph}} [B_{\rho\rho^{\bullet}}(0) B_{\rho^{\bullet}\rho}(\tau) \hat{\sigma}_{\mathfrak{ph}}] d\tau \qquad (2.13)$$

with

$$B_{\rho\rho^{\bullet}}(t) = \sum_{q} G_{\rho\rho^{\bullet}}(q) \{ b^{*}_{-q} \exp[+i\omega(q)t] + b_{q} \exp[-i\omega(q)t] \} .$$
(2.14)

 $\hat{\sigma}_{\rm ph}$ means the equilibrium distribution of the phonons at a fixed temperature T,

$$\hat{\sigma}_{ph} = z^{-1} \exp(-\hat{H}_{ph}/k_B T)$$
 (2.15a)

with

$$z = \operatorname{tr}_{\mathfrak{ph}} \exp(-\hat{H}_{\mathfrak{ph}}/k_B T)$$
 (2.15b)

where k_B is the Boltzmann's constant.

Taking into account Eqs. (2.7) and (2.14) we evaluate the integral equation (2.13) to give the following microscopic transition rates in the ρ space:

$$A_{\rho\rho^{\bullet}} = 2\pi \sum_{q} |G_{\rho\rho^{\bullet}}(q)|^{2} \{ [1 + n(q)] \delta [E^{(\rho)} - E^{(\rho^{\bullet})} - \omega(q)] + n(q) \delta [E^{(\rho)} - E^{(\rho^{\bullet})} + \omega(q)] \}, \qquad (2.16)$$

where

$$n(q) = \{ \exp[h\omega(q)/k_B T] - 1 \}^{-1}$$
 (2.17)

is the average number of phonons in the thermal equilibrium.

The first contribution of $A_{\rho\rho}$, [Eq. (2.16)] describes one-phonon-emission processes, the second one-phononabsorption processes.

From Eq. (2.16) we deduce for all transition rates $A_{\rho\rho'}$ the following relation with respect to their inverse rates $A_{\rho'\rho}$,

$$A_{\rho\rho^{*}}/A_{\rho^{*}\rho} = \exp[(E^{(\rho)} - E^{(\rho^{*})})/k_{B}T]. \qquad (2.18)$$

By means of this relation we find from Eq. (2.12) the stationary equilibrium occupation probabilities $\sigma_{\rho\rho}(t \rightarrow \infty)$:

$$\sigma_{\rho\rho}^{eq} = \sigma_{\rho'\rho'}^{eq} \exp[-(E^{(\rho')} - E^{(\rho')})/k_B T]$$
(2.19)

which means that at equilibrium there is a Boltzmann distribution in the ρ states.

In the following we have to evaluate the microscopic transition rates $A_{\rho\rho'}$ [Eq. (2.16)] exactly. In this paper we limit ourselves to the case of the interaction of one-dimensional excitons with three-dimensional phonons. In addition, we distinguish two types of exciton phonon interactions. For *pure exciton-phonon interaction* if we look at pure unperturbed excitons (k) and phonons (q) in an infinite molecular crystal, the Hamiltonians $\hat{H}_{ex}(\epsilon_n = \epsilon, J_{nm} = J_{n-m})$, \hat{H}_{ph} and $\hat{H}_{ex-ph}(X_n = X, F_{nm} = F_{n-m})$ are all translational invariant $(N_{ex} = N_{x} \rightarrow \infty)$.

As we will show below in the cases of one-dimensional triplet exciton systems, with bandwidths much smaller than the Debye frequency, the corresponding scattering rates A_{pp} , due to this pure exciton-phonon coupling mechanism are identically zero

$$A_{kk'}(\text{pure}) = 0$$
 . (2.20)

An experimentally detected finite nonzero scattering rate in these cases (for example $TCB^{1(a)}$) must therefore come from other scattering mechanisms which we will discuss now. These form a second class which will be called the *impure exciton-phonon interaction*. In this case we define (a) two *impurity assisted exciton scattering* mechanisms and (b) one *impurity induced exciton scattering* mechanism (where the impurities are directly involved).

In the two impurity-assisted mechanisms, the impurities do not create perturbed exciton states (ϕ) or trap states (x). In the first mechanism, the exciton states are defined only over a finite number of sites, N_{ex} , because there are *disruptive* impurities preventing the excitation from getting past. That is, there are impurites at each of the stack of N_{ex} molecules. We can write

$$\langle N_{di} \rangle = \langle N_x \rangle / \langle N_{ex} \rangle$$
, (2.21a)

where N_{di} is the number of disruptive impurities and as

before N_x is the number of molecules in the z direction in the crystal. This gives for the average concentration of disruptive impurities, C_{di} ,

$$C_{\rm di} = \frac{\langle N_{\rm di} \rangle}{\langle N_{\rm s} \rangle} = \frac{1}{\langle N_{\rm ex} \rangle} \quad .$$
 (2.21b)

In the second mechanism, we allow N_{ex} to go to infinity, but allow an impurity on a neighboring stack to interact with a few (perhaps one) molecule on the stack under consideration. This breaks the translational invariance of the exciton-phonon interaction and allows one phonon processes to occur. We call this the *interstitial* mechanism. Let us suppose that the molecule at site n_0 is affected by the interstitial impurity; this gives rise to an exciton-phonon Hamiltonian [see Eq. (2.4)]

$$\hat{H}_{ex-ph} = N_{p}^{-1/2} \sum_{q} \{ \tilde{\chi}_{0}(q) \exp(iqn_{0}) a_{n_{0}}^{*} a_{n_{0}}(b_{q} + b_{-q}^{*}) + (\tilde{F}_{0,\pm 1} \exp(iqn_{0}) a_{n_{0}}^{*} a_{n_{0}\pm 1} + j.c.)(b_{q} + b_{-q}^{*}) \} .$$
(2.22)

In this case the proportionality parameter turns out to be the concentration of the interstitial impurities C_{ii} with

$$C_{ii} = \langle N_{ii} \rangle / \langle N_{ex} \rangle . \tag{2.23}$$

In contrast to the above mechanisms, in the *impurity* induced exciton scattering mechanism the impurities are substitutional impurities in the molecular chain and are directly involved in the exciton states. The impurity molecules generate perturbed exciton waves $(\phi \neq k)$ as well as quasilocalized exciton-trap states (x) resulting in nonzero exciton scattering rates $A_{\rho\rho}$, $\equiv A_{\phi\phi}$, as well as exciton trapping rates $A_{\rho\rho}$, $\equiv A_{\phi\phi}$. In this case the important proportionality parameter turns out to be the concentration of the trapping impurities C_{tip} .

$$C_{\rm ti} = \langle N_{\rm ti} \rangle / \langle N_{\rm ex} \rangle . \qquad (2.24)$$

In the following section we calculate all nonzero microscopic scattering rates $A_{\rho\rho}$, and their dependence on the concentration of disruptive, interstitial, and trapping impurities C_{d1} , C_{11} , and C_{11} . Special importance is drawn to the microscopic ρ selectivity of the scattering rates leading to the prediction of whether the excitons undergo *nearby jumps* ($\Delta \rho \rightarrow 0$) or *long jumps* in the ρ space of the corresponding band.

III. MICROSCOPIC EXCITON-SCATTERING RATES

A. Pure exciton-phonon interaction

In this case the exciton wave functions [Eq. (2.8)] represent unperturbed Bloch waves. Therefore,

$$\left|\psi^{(k_{g})}\right\rangle = \sum_{n} c_{n}^{(k_{g})} \left|n\right\rangle$$
(3.1a)

with

$$c_n^{(k_g)} = (N_{ex})^{-1/2} e^{ik_g n}$$
 (3.1b)

It is important to notice that only for the infinite unperturbed crystal $(N_{ex} = N_x = N)$ do we have well defined exciton and phonon quasimomenta with the following values:

$$k_{g} = 2\pi v_{ex}/Nd_{g}$$
, $-N/2 \le v_{ex} \le N/2$, (3.2a)

$$q_{z} = 2\pi v_{p}/Nd_{z}$$
, $-N/2 \le v_{p} \le N/2$. (3.2b)

The general scattering parameter $G_{\rho\rho'}(q)$ [Eq. (2.7)] can now be written

$$G_{\rho\rho\sigma}(q) \equiv G_{k_{g}k_{g}'}(q) = N^{-1/2} \exp(iq_{\perp}n_{\perp}) \sum_{n=1}^{N} N^{-1} \\ \times \exp[i(k_{g} - k_{g}' + q_{g})n] \left\{ \chi(q) + \sum_{\alpha = \pm 1} \exp(ik_{g}'\alpha) F_{\alpha}(q) \right\}.$$
(3.3)

Taking into account Eqs. (3, 2) we have

$$\left|G_{k_{z}k_{z}'}(q)\right|^{2} = N^{-1}\delta(k_{z} - k_{z}' + q_{z})\left\{\chi(q) + 2F_{1}(q)\cos k_{z}'\right\}.$$
 (3.4)

For the q dependence of the local (χ) and nonlocal (F_{α}) exciton-(acoustic) phonon coupling we take the Davydov form⁷:

$$\chi(q) = \chi^{ac} \sqrt{\omega(q)} \tag{3.5a}$$

and

$$F_{\alpha}(q) = F_{\alpha}^{\text{ac}} \sqrt{\omega(q)}$$
 (3.5b)

For the acoustic phonon frequencies we assume the following anisotropic dispersion relation¹⁰:

$$\omega(q) = \left\{ C_{\perp}^2 q_{\perp}^2 + C_{\perp}^2 q_{\perp}^2 \right\}^{1/2} \,. \tag{3.6}$$

Taking into account Eqs. (3, 4)-(3, 6) we deduce from Eq. (2, 16) the following integral expression for the scatter-ing rate $A_{kk'}$:

$$\begin{aligned} A_{kk'} &= \{\chi^{ac} + 2F^{ac}\cos k_{s}'\}^{2} \cdot \frac{1}{2\pi} \int dq_{s} \int q_{1}dq_{1} \{C_{\parallel}^{2}q_{s}^{2} + C_{1}^{2}q_{1}^{2}\}^{1/2} \\ &\times \{(1 + n[\{C_{\parallel}^{2}q_{s}^{2} + C_{1}^{2}q_{1}^{2}]^{1/2}])\delta(E^{(k)} - E^{(k')} - \{C_{\parallel}^{2}q_{s}^{2} + C_{1}^{2}q_{1}^{2}\}^{1/2}) \\ &+ n[\{C_{\parallel}^{2}q_{s}^{2} + C_{1}^{2}q_{1}^{2}\}^{1/2}]\delta(E^{(k)} - E^{(k')} + \{C_{\parallel}^{2}q_{s}^{2} + C_{1}^{2}q_{1}^{2}\}^{1/2})\}. \end{aligned}$$

$$(3.7)$$

Evaluating the integral (3, 7) we end up with the exact result

$$A_{kk^{*}}^{\text{pure}} = \frac{1}{2\pi} \left(\frac{2J}{C_{\perp}} \right)^{2} (\cos k - \cos k')^{2} (\chi^{\text{ac}} + 2F_{1}^{\text{ac}} \cos k'_{z})^{2} f_{T}(\Delta E_{kk^{*}})$$
$$\times \theta [(\Delta E_{kk^{*}})^{2} - C_{\parallel}^{2} (k_{z} - k_{z^{*}})^{2}], \qquad (3.8)$$

where

$$\Delta E_{kk'} = E^{(k)} - E^{(k')} ,$$

$$f_T(x) = [1 + n(x)] \theta(x) + n(|x|)\theta(-x) .$$

Due to this $(\cos k - \cos k')^2$ dependence of the scattering rate the excitons prefer long range jumps (when "temperature allowed") rather than nearby jumps $(k \approx k')$ within the exciton band because the latter are of the order N^{-4} weaker. This statement is only of relevance in case where we deal with exciton bands $E^{(k)}$ which are larger than the corresponding phonon bandwidths $\omega(q)$. This is normally the case of singlet(S) excitons (Fig. 1). For the opposite case in which the phonon dispersion exceeds the exciton dispersion (and in which we are particularly interested in this paper) the last factor in Eq. (3.8), the Heaviside function θ , is zero and so thus are all the $A_{kk'}$. This case holds for triplet (T) excitons which have bandwidths of the order of 1 cm^{-1} , whereas characteristic phonon energies are greater than 10 cm⁻¹. Therefore in all these special cases of flat exciton bands and steeper phonon bands nonzero scattering rates A_{kk} .



FIG. 1. Typical dispersion curves for singlet excitons $[E^{(k)}(S)]$, triplet excitons $[E^{(k)}(T)]$, and phonons $(\omega^{(q)})$.

cannot be obtained with the usual pure exciton-phonon interaction. However, the impure exciton-phonon mechanisms do give rise to nonzero scattering rates.

B. Impure exciton – phonon mechanisms

The first impurity assisted exciton scattering mechanism we discuss can be thought of as due to the finite size of our exciton system (N_{ex}) in comparison with the phonon system $(N_x \gg N_{ex})$. Given a finite chain of N_{ex} molecules the corresponding exciton probability amplitudes are given by

$$c_n^{(k)} = \{2/(N_{\text{ex}} + 1)\}^{1/2} \sin kn$$
(3.9a)

with

$$k = \pi v / (N_{\text{ex}} + 1)$$
, $v = 1, 2, 3, \dots, N_{\text{ex}}$ (3.9b)

Now the scattering parameter [Eq. (2, 7)] becomes

$$G_{kk'}(q) = (N_{p})^{-1/2} \frac{2}{(N_{ex} + 1)} \exp(iq_{\perp}n_{\perp}) \sum_{n} \sin kn \sin k'n$$
$$\times \exp(iq_{\pi}n) [\chi(q) + 2\cos k' F_{1}(q)] . \qquad (3.10)$$

Taking very carefully into account the different values of the k [Eq. (3.9b)] and q [Eq. (3.2b)] vectors we can sum up the geometric series and find for the scattering rate (2.16) (after an integration similar to that in the pure exciton-phonon interaction case) the exact result

$$A_{kk'}^{i\,\mathrm{mp}} = \frac{2}{3\pi} C_{d\,i}^2 \left(\frac{2J}{C_{\perp}}\right)^2 \left(\frac{2J}{C_{\parallel}}\right)^3 \sin^2 k \sin^2 k' \\ \times \left|\cos k - \cos k'\right| (\chi^{\mathrm{ac}} + 2\cos k' F_1^{\mathrm{ac}})^2 f_T(\Delta E_{kk'}) ,$$
(3.11)

where C_{di} is the average concentration of disruptive impurities which limit our molecular chains in exciton space. First of all we see that the absolute values of the scattering rates due to the different mechanisms (pure-impure) are very different from one another by the amount

J. Chem. Phys., Vol. 79, No. 7, 1 October 1983

$$A_{kk'}^{imp}(T)/A_{kk'}^{pure}(S) \sim C_{di}^2 \left(\frac{2J_T}{C_{\parallel}}\right)^3 \left(\frac{2J_T}{2J_S}\right)^2 \ll 1$$
 (3.12)

To have a concrete idea in the case of TCB for example we have $(2J_T/C_{11})^3 \sim 10^{-3}$ and assuming $C_{di} \sim 10^{-2}$ ^{1(b)} then we have

$$A_{kk'}^{imp}(T)/A_{kk'}^{pure}(S) \sim \ll 10^{-7}$$
 (3.12a)

Therefore, exciton-phonon scattering in the triplet system should be usually much slower than a similar singlet system. This conclusion is compatible with the experimental observances. The selectivity of the scattering rate [Eq. (3, 11)] is strong. Since the usual experiment^{1(a)} has an overpopulation of the $k \approx 0$ exciton level at t = 0 due to a laser flash, we compute from Eq. (3.11) the values of the corresponding scattering rates $A_{\mu\nu}$. out of the $k \approx 0$ level, and show these in Fig. 2. In this scattering path diagram, as in the others to follow, only the dominant path, i.e., that which maximizes individual jumps, is shown. From this we see that the k=0excitons will be scattered first with high probability to the $k = 0.606\pi$ level carrying out a long jump process $(\sim C_{di}^4)$ dominating the slower nearby-jump processes $(\sim C_{di}^8)$ and then the excitons undergo successively smaller jumps with decreasing scattering rates A_{kk} . toward the final $k = \pi$ level. Hence, the detected $k = \pi$ exciton have usually arrived there by a multistep process. Summarizing we see that during the whole impurity assisted scattering process both long and small jumps occur.



FIG. 2. Scattering path diagram for the disruptive mechanism. The scattering rates for the jumps with the largest rates are given. The dashed lines become important for concentrations $c \equiv c_{d1} > 0.2$, leading to the long jumps being preferred, in contrast to the low concentration path.



FIG. 3. Scattering path diagram for the interstitial mechanism. One or two step long jumps are important for all concentrations.

Now let us consider the second impurity assisted exciton-phonon mechanism due to a nontranslational excitonphonon Hamiltonian as described in Eq. (2.22). In this case we assume the excitons are an infinite system like the phonons (N_x) corresponding to the case of the pure exciton-phonon interaction $(N_x = N_{ex})$. Taking into account the exciton-phonon Hamiltonian in Eq. (2.22), the scattering parameter can be written

$$G_{kk'}(q) = N_{p}^{-1/2} N_{ox}^{-1} \exp[i(k_{x} - k'_{x} + q_{x})n_{0}] \exp(iq_{1}n_{1}) \\ \times [\tilde{\chi}_{n0}(q) + 2\cos k' \tilde{F}_{1}(q)]$$
(3.13)

and from Eq. (2.16) we deduce the exact expression

$$A_{kk'}^{i\,\mathrm{mp}} = \frac{1}{\pi} C_{ii}^{2} \left(\frac{2J}{C_{i}}\right)^{2} \left(\frac{2J}{C_{u}}\right) (\left|\cos k - \cos k'\right|)^{3} \\ \times [\tilde{\chi}^{ac} + 2\cos k' \tilde{F}_{1}^{ac}]^{2} f_{T}(\Delta E_{kk'}) .$$
(3.14)

Comparing this expression with the corresponding expression A_{kk}^{imp} (3.11) based on the finiteness of the exciton system then we have

$$\frac{A_{kk'}(\text{interstitial})}{A_{kk'}(\text{disruptive})} \sim \left(\frac{C_{\parallel}}{2J}\right)^2 \gg 1$$
(3.15)

which means that the exciton-phonon scattering mechanism due to this nontranslational coupling is more effective than the finite size mechanism considered before. How long is the range of the exciton jumps in this case? As before we start with an exciton at k = 0 and follow its evolution by calculating the different competitive scattering rates A_{kk} . (3.14) now in orders of C_{11} . We end up with the scattering path shown in Fig. 3. This scattering path diagram shows clearly, that the exciton now carries out as a one or two step process. In addition to a last transferent the lower half of the band with a slower transference tions into the lower half of the band with a slower transition to the final $k = \pi$ level to follow. Finally, we want to point out that the overall scattering rate out of k = 0is further enhanced [compare Eq. (3.15)] by noting that for the finite size chain $\sin^2 k \sim C_{d1}^2$ near k = 0; thus

$$\frac{A_{k=0,k'}(\text{interstitial})}{A_{k=0,k'}(\text{disruptive})} \sim \frac{C_{11}^2}{C_{41}^4} \gg 1.$$
(3.16)

J. Chem. Phys., Vol. 79, No. 7, 1 October 1983

We now turn to the last mechanism: *impurity induced* exciton-phonon scattering. In this case we no longer deal with unperturbed exciton states as before but instead, use perturbed band excitons (ϕ) and quasilocalized trap states (x). We take the following model for dilute impurities: a linear chain of 2N molecules with a substitutional impurity at one site, say n=0. The site energy of the guest differs from that of the host molecules by the amount ΔU_0 and the nearest neighbor interaction between guest and host is J' rather than J, the host-host interaction. Within a Green's function formalism, it has been shown that the exact eigenfunctions of such a system have coefficients^{8(a)}

$$c_{n}^{(\bullet)} = (\gamma^{1/2}) \left(\cos n\phi + \alpha^{(\bullet)} \sin \left| n \right| \phi \right) c_{0}^{(\bullet)}$$
 (3.17a)

(symmetric modes), with

$$\beta = (\Delta U_0)/2J , \quad \gamma = (J'/J)^2 , \qquad (3.17b)$$

$$\alpha^{\vee \bullet \prime} \equiv -\left[\beta + (\gamma - 1)\cos\phi\right]/\gamma \sin\phi = \tan N\phi , \quad \phi \le \pi$$
(3.17c)

representing the secular equation of the system; from normalization, it is found that

$$c_0^{(\phi)} = (N\gamma)^{-1/2} \left[1 + \alpha^{(\phi)2} + N^{-1} \alpha^{(\phi)} \cos \phi - N^{-1} + (N\gamma)^{-1} \right]^{-1/2}$$
(3.17d)

The antisymmetric mode is not influenced, therefore

$$c_n^{(k)} = N^{-1/2} \sin kn$$
, $k = \pi v/N$, $v = 1, 2, 3, \dots, N-1$.
(3.17e)

From the exciton amplitudes [Eq. (3, 17)] we can find the scattering parameters $G_{\phi\phi}(q)$ from Eq. (2, 7) to obtain

$$G_{\phi\phi}(q) = c_0^{(\phi)} c_0^{(\phi')} (2N_{ph})^{-1/2} [(1 - \cos q) \\ \times \{a_{\phi\phi}(\cos \phi - \cos \phi')^{-2} + b_{\phi\phi}\} + c_{\phi\phi'}], \quad (3.18a)$$

where

$$a_{\phi\phi'} = \left\{\beta(\cos\phi + \cos\phi') + 2(\gamma - 1)\cos\phi\cos\phi'\right\}$$
$$\times \left\{\chi + 2F_1\cos\phi'\right\}, \qquad (3.18b)$$

$$b_{\phi\phi'} = 2F_1 \gamma^{-1/2} (\gamma^{-1/2} - 1) (\cos \phi - \beta) , \qquad (3.18c)$$

and

$$c_{\phi\phi'} = 2F_1 \gamma^{-1/2} (\gamma^{-1/2} - 1) [2\beta - (\cos \phi + \cos \phi')] - 2\beta F_1 .$$
(3.18d)

Inserting these into Eq. (2.16), we find the scattering rate $A_{\phi\phi}$, due to a single impurity molecule within our chain:

$$A_{\phi\phi'} = \pi^{-1} c_0^{(\phi)2} c_0^{(\phi')2} \left(\frac{2J}{c_\perp}\right)^2 \left(\frac{2J}{c_\parallel}\right) (\cos\phi - \cos\phi')^3 \\ \times \left\{ \frac{1}{20} \left(\frac{2J}{c_\parallel}\right)^4 [a_{\phi\phi'} + b_{\phi\phi'} (\cos\phi - \cos\phi')^2]^2 + \frac{1}{3} \left(\frac{2J}{c_\parallel}\right)^2 \\ \times [a_{\phi\phi'} + b_{\phi\phi'} (\cos\phi - \cos\phi')^2] c_{\phi\phi'} + c_{\phi\phi'}^2 \right\} f_T(\Delta E_{\phi\phi'}).$$
(3.19)

It is sufficient to discuss only two limiting cases: (a) purely diagonal disorder of the guest with $|\beta| \gg 1$, $\gamma = 1$, and the exciton-phonon coupling ratio $\chi/2F_1 \gg 1$; and (b) purely off-diagonal disorder with $\gamma \neq 1$, $\beta = 0$, and the same exciton-phonon coupling ratio $\chi/2F_1 \gg 1$. In case (a), the general formula, Eq. (3.19) reduces to



FIG. 4. Scattering path diagram for the impurity induced mechanism, type (a): pure diagonal disorder, $|\beta| > 1$, $\gamma = 1$. Long jumps (dashed lines) become important at high concentrations, $c \equiv c_{ti} > 0.2$.

$$A_{\phi\phi}^{(a)} = C_{ti}^{2} (\chi^{2}/5\pi) (2J/C_{\perp})^{2} (2J/C_{\parallel})^{5} \beta^{-2} \sin^{2} \phi \sin^{2} \phi' \\ \times (|\cos \phi - \cos \phi'|)^{3} (\cos \phi + \cos \phi')^{2} f_{T} (\Delta E_{\phi\phi'}) .$$
(3.20)

Comparing this in turn to the rate due to the other mechanisms we have considered (the disruptive impurity or finite chain and the interstitial impurity or nontranslational exciton phonon coupling), we find

$$\frac{A_{\phi\phi}^{(a)}}{A_{kk'}(\text{disruptive})} \sim \left(\frac{2J}{C_{\mu}}\right)^2 \ll 1 , \qquad (3.21a)$$

and

$$\frac{A_{\phi\phi}^{(a)}}{A_{kk'}(\text{interstitial})} \sim \left(\frac{2J}{C_{\parallel}}\right)^4 \ll 1 , \qquad (3.21b)$$

where the inequalities are for narrow triplet exciton band. We see that the scattering rates are smaller than those for the other mechanisms. In Fig. 4, we show the scattering path diagram for $\phi = 0$ excitons at very low temperature. We see that the $\phi = 0$ exciton first undergoes a long jump to the middle of the band (ϕ $\approx 0.55\pi$) followed by a faster jump to $\phi \approx 0.82\pi$. There then follow a succession of smaller jumps with smaller rates towards $\phi = \pi$. Note that the exciton tends to avoid $\phi = \pi$. Note that direct transfer (long jumps) gets more probable as the impurity concentration increases. Finally, this mechanism is fourth order in impurity concentration (see Fig. 4) as is the disruptive or finiteness mechanism; both of which are slower than the interstitial or nontranslational mechanism which is second order in impurity concentration.

Turning now to case (b), off-diagonal disorder, the scattering rate reduces to

$$A_{\phi\phi}^{(b)} = C_{ti}^2 \chi^2 \frac{4}{5\pi} \left(\frac{\gamma - 1}{\gamma}\right)^2 \left(\frac{2J}{C_{\perp}}\right)^2 \left(\frac{2J}{C_{\parallel}}\right)^5 \sin^2\phi \cos^2\phi$$
$$\times \sin^2\phi' \cos^2\phi' (\cos\phi - \cos\phi')^3 f_T(\Delta E_{\phi\phi'}) . \quad (3.22)$$

In contrast to $A_{\phi\phi}^{(a)}$, this has a minimum at $\phi' = \pi/2$, which is reflected in the corresponding scattering path

J. Chem. Phys., Vol. 79, No. 7, 1 October 1983



FIG. 5. Scattering path diagram for impurity induced mechanism, type (b): pure off-diagonal, $\gamma \neq 1$, $\beta = 0$. Long jumps are preferred at higher concentrations $c \equiv c_{ti} > 0.02$.

diagram, Fig. 5. In contrast to case (a), the first jump is from $\phi = 0$ to $\phi \simeq 0.4\pi$ (upper half of band and then to 0.8 π (lower half of band). Successively smaller jumps with decreasing scattering rates follow before finally ending up at $\phi \simeq \pi$. Note that the final slower *multistep approach* to $\phi \simeq \pi$ is a general characteristic of almost all our mechanisms, as is evidenced in the scattering path diagrams, Figs. 2, 4, and 5 but is nearly absent in Fig. 3.

Thus far, we have only discussed scattering between the perturbed states $(\phi - \phi')$, but there are an equal number of unperturbed states (k) with $c_n^{(k)}$ given by Eq. (3.17e).

The scattering rate $A_{kk'}$ between such unperturbed levels will be zero as in the pure scattering, while the scattering parameter $G_{k\phi'}(q)$ between an unperturbed k state and a perturbed state labeled by ϕ' is given as

$$G_{k\phi}(q) = c_0^{(\phi')} \gamma^{1/2} (2N_{ph})^{-1/2} N^{-1/2} \sin k \left\{ 2\alpha^{(\phi')} \sin \phi' \sin q \right.$$

 $\times (\cos k - \cos \phi')^{-2} (\chi + 2F_1 \cos \phi') + 2\cos qF_1(\gamma^{-1/2} - 1) \right\}$
(3.23)

and the scattering rate $A_{k\phi}$, is found to be $(\chi/2F \gg 1)$

$$A_{k\phi} = (4/3\pi)c_{t1}^2 \frac{\gamma^2 \chi^2 [2\beta + 2(\gamma - 1)\cos\phi']^2}{\gamma^2 \sin^2\phi' + [\beta + (\gamma - 1)\cos\phi']^2} \left(\frac{2J}{C_1}\right)^2 \left(\frac{2J}{C_1}\right)^2 \times \sin^2k \sin^2\phi' |\cos k - \cos\phi'| f_T(\Delta E_{k\phi}) .$$
(3.24)

First, we see that $A_{k\phi}$, $>A_{\phi\phi}$, in either case (a) or (b):

$$\frac{A_{ko}}{A_{\phi\phi}} \sim \left(\frac{2J}{C_{\parallel}}\right)^{-2} \gg 1 \quad . \tag{3.25}$$

Second, in the quasidiagonal disorder case $(|\beta/\gamma| \gg 1)$ we find exactly the same k, ϕ' dependence as in the case of the disruptive or finiteness mechanism [Eq. (3.11)]; therefore, the scattering path diagram for this case is the same as for the finite exciton system (see Fig. 2).

C. Trapping

As we have already mentioned, the impurity not only creates perturbed exciton states but also localized trap states (labeled $\phi^{(x)}$) below the exciton band. The scattering between a ϕ and $\phi^{(x)}$ is called trapping. We can calculate $G_{\phi\phi}(x)$, we use Eq. (3.18) but replace ϕ' by $\pi + i\phi^{(x)}$. Restricting ourselves to pure local disorder $(\beta < 0, \gamma = 1)$, we find [see also Ref. 8(b)]

$$G_{\phi\phi}(\mathbf{x})(q) = (2N_{\phi})^{-1/2} N^{-1/2} \sin\phi (\sin^{2}\phi + \beta^{2})^{-1/2} \\ \times \left\{ (1 - \cos q) \frac{\beta(\cos\phi - \cos\phi^{(\mathbf{x})})}{(\cos\phi + \cosh\phi^{(\mathbf{x})})^{2}} \\ \times (\chi - 2F_{1}\cosh\phi^{(\mathbf{x})}) + 2|\beta|F_{1} \right\}$$
(3. 26)

with

$$\cosh \phi^{(x)} = (1 + \beta^2)^{1/2} \tag{3.27}$$

which follows from the secular equation (3.17c). For deep traps $(|\beta| \gg 1)$, Eq. (3.26) reduces to

$$G_{\phi \phi}(x)(q) = (2N_{\phi})^{-1/2} N^{-1/2} \sin \phi [(1 - \cos q)\chi |\beta|^{-1} + 2F_1 \cos q].$$
(3.28)

Carrying out the integration over the phonon variables, we find for the trapping rate

$$A_{\phi\phi}(x) = \pi^{-1} C_{ti} \sin^2 \phi \left(\frac{\Delta E}{C_1}\right)^2 \left(\frac{\Delta E}{C_0}\right) \frac{3}{2} \frac{\chi^2}{\beta^2} - \frac{2\chi F_1}{|\beta|} + 2F_1^2$$
(3.29)

 $(\Delta E$ is the energy difference between the trap state $[\phi^{(x)}]$ and the band state ϕ). This shows that the trapping rate is proportional to the impurity concentration to the first power, in contrast to the scattering mechanisms. A most interesting result is the $\sin^2 \phi$ dependence^{8(b)} of $A_{\phi\phi(x)}$, (Fig. 6) which predicts a trapping rate which is maximized from the middle of the band, and not out of $\phi = 0$ as predicted by Kenkre.¹¹

D. Exciton density of states

Thus far we have not taken into account the known unusual density of states for one dimensional systems,



FIG. 6. Trapping rate vs exciton wave vector $k(\phi)$. Note the maximum at the band center.



FIG. 7. Cumulative scattering rate out of k=0, for disruptive mechanism $[\Gamma_0^4]$, see Eq. (3.31a)] and for interstitial mechanism $[\Gamma_0^4]$, see Eq. (3.32a)]. The relevant concentration variable is c in both cases (i.e., c_{di} or c_{ii}).

which shows maxima at the band edges and a minimum at the band center. Our discussions have only concerned maximizing the microscopic transition rates. However, these rates should be multiplied by a final density of states. Will this change the picture deduced from the scattering path diagrams? To answer this, we write the cumulative scattering rate out of the k=0 level $\Gamma_0(\Delta E)$ as an integral over the band.

$$\Gamma_0(\Delta E) \equiv \sum_{k'=0}^{k'(\Delta E)} A_{0k'} = \int_0^{\Delta E} dE \,\rho(E) A(E) , \qquad (3.30)$$

where $\rho(E)$ is the density of exciton states. For the disruptive mechanism, we find

$$\Gamma_0^d(\Delta E) = C_{d1}^3 A \int_0^{\Delta E} \frac{E}{8J^3} \left[4J^2 - (E - 2J)^2 \right]^{1/2} dE ,$$

$$0 \le \Delta E \le 4J (3, 31a)$$

$$A = \frac{2}{3\pi^2} \left(\frac{2J}{C_{\perp}}\right)^2 \left(\frac{2J}{C_{\parallel}}\right)^3 , \qquad (3.31b)$$

and for the interstitial mechanism

$$\Gamma_0^{t}(\Delta E) = C_{11}\tilde{A} \int_0^{\Delta E} dE (\Delta E/2J)^3 [4JE - E^2]^{-1/2}, \quad (3.32a)$$

$$\tilde{A} = \frac{1}{\pi^2} \left(\frac{2J}{C_\perp} \right)^2 \left(\frac{2J}{C_\parallel} \right)$$
 (3.32b)

The formula for the impurity induced mechanism reduces to an expression similar to Eq. (3.31a). Note that the singularity in the density of states is removed in all but one mechanism, that of the interstitial impurity. In Fig. 7 we plot the $\Gamma_0(\Delta E)$ of Eqs. (3.31a) and (3.32a). The figure shows that the scattering from k = 0 occurs to levels in the lower half of the band (in the disruptive case) and to states close to the lower edge (interstitial case) leading to the same results or even sharpening the conclusions found from the scattering path diagrams in Figs. 2 and 3. Hence, the effects of the density of states do not contradict the scattering path diagrams.

IV. CONCLUSIONS

In this paper, we have considered three impurity mechanisms of scattering of excitons by phonons. In particular, we have been concerned with the scattering in quasi-one-dimensional exciton states, as exemplified by tetrachlorobenzene (TCB). In this system, the triplet exciton band is too narrow for one phonon processes to occur with k conservation; therefore, impurity effects must be invoked. The three mechanisms we have investigated are (1) "disruptive" impurities, where the impurities cage the exciton in a linear chain of N_{ex} molecules, thus breaking the translation symmetry of the lattice, (2) "interstitial" impurities, where an impurity on one chain interacts with the exciton states on a neighboring chain, (3) "impurity induced" scattering where the impurities in a chain perturb the excitation states of the chain, and creating new states including trap states. We have presented in Figs. 2-5, the scattering paths for excitons initially at the top of the band for these three mechanisms.

We find that, at low impurity concentrations, the interstitial mechanism gives the largest scattering rates of all mechanisms considered. This is the mechanism considered by van Strien et al.^{1(a)} in their fit of their experimental data on the temperature dependence of exciton scattering rates in TCB. This mechanism is largest with respect to impurity concentration ($\sim C^2$) and with respect to the ratio of exciton bandwidth to phonon bandwidths (~ J/C_{\parallel} and J/C_{\perp}). It also favors long jumps, in contrast to the other mechanisms which are more democratic in this regard. Although this mechanism gives the largest rates, the other mechanisms will all contribute to the experimental rates. In their study, Breiland and Saylor³ fit their data with a short jump only mechanism. None of the mechanisms considered here will *prefer* short jumps if the exciton starts at k = 0. However, if the exciton is initially in the center of the band, short jumps may be as probable as long jumps. This indicates the sensitivity to the initial conditions and may explain the contradictory conclusions on this point of Breiland and Saylor³ and those of van Strien et al.^{1(a)} who start in k = 0. At higher temperatures, two phonon processes become important, ¹⁰ and even in TCB, impurities need not be invoked in order to get substantial exciton scattering. At high concentrations of impurities, we expect long jumps $(k = 0 - k = \pi)$ to be dominant, as is evidenced in Figs. 2-5.

In other quasi-one-dimensional systems, like dibromonaphthalene (DBN), the triplet exciton band is wider than in TCB and so $(2J/C_{\rm s})$ and $(2J/C_{\rm s})$ will be closer to unity; therefore the scattering rates produced by the three mechanisms in DBN will be more similar to each other. This will complicate the interpretation of the experimental data.

ACKNOWLEDGMENTS

We would like to thank Professor J. Schmidt for many discussions. H. Benk gratefully acknowledges financial support in the form of a postdoctoral fellowship from the DFG.

- ¹(a) A. van Strien, J. van Kooten, and J. Schmidt, Chem. Phys. Lett. **76**, 7 (1980); (b) A. van Strien, J. Schmidt, and R. Silbey, Mol. Phys. **46**, 151 (1982).
- ²(a) C. B. Harris and M. D. Fayer, Phys. Rev. B 10, 1784 (1974); (b) R. D. Wieting and M. D. Fayer, J. Chem. Phys. 73, 744 (1980).
- ³W. G. Breiland and M. C. Saylor, J. Chem. Phys. **72**, 6485 (1980).
- ⁴(a) D. Smith and A. Zewail, J. Chem. Phys. 71, 3533 (1979);
 (b) A. H. Zewail, D. Smith, and J.-P. Lemaistre, in *Excitons*,

edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), Vol. 2, p. 665 ff.

- ⁵(a) D. M. Burland, U. Konzelmann, and R. M. Macfarlane, J. Chem. Phys. 67, 926 (1977); (b) D. M. Burland, D. E. Cooper, M. D. Fayer, and C. R. Gochanour, Chem. Phys. Lett. 52, 279 (1977); (c) B. Leong and D. M. Hanson, J. Chem. Phys. 78, 1613 (1983).
- ⁶R. Schmidberger and H. C. Wolf, Chem. Phys. Lett. 16, 402 (1972); J. Zieger and H. C. Wolf, Chem. Phys. 29, 209 (1978).
- ⁷A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
- ⁸(a) H. Benk, Diplomarbeit, Universität Stuttgart, 1975; (b) H. Benk, Doktorarbeit, Universität Stuttgart, 1982; (c) H.
- Benk, H. Haken, and H. Sixl, J. Chem. Phys. 77, 5730 (1982).
 ⁹(a) H. Haken, Laser Theory, Encyclopedia of Physics XXV/2C (Springer, Berlin, 1970), p. 51 ff; (b) W. H. Louisell, Quantum Statistical Properties of Radiation (Wiley, New York, 1973), Chap. 6; (c) M. Sargent III, M. O. Scully, and W. E. Lamb, Laser Physics (Addison-Wesley, Reading, Mass., 1974), Chap. 16.
- ¹⁰B. Jackson and R. Silbey, J. Chem. Phys. 77, 2763 (1982).
- ¹¹V. M. Kenkre, Phys. Status Solidi B 89, 651 (1978).