The Journal of Chemical Physics

Triplet exciton dynamics: Exciton phonon scattering at low temperature

Bret Jackson and R. Silbey

Α

Citation: J. Chem. Phys. **77**, 2763 (1982); doi: 10.1063/1.444212 View online: http://dx.doi.org/10.1063/1.444212 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v77/i6 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



Triplet exciton dynamics: Exciton phonon scattering at low temperature^{a)}

Bret Jackson and R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received 7 April 1982; accepted 3 June 1982)

In this paper, we calculate the $k \rightarrow k'$ scattering rates of excitons by acoustic phonons. We consider twophonon processes only, having considered one-phonon processes in an earlier paper. We treat one-phonon events and a single two-phonon event in both pure and impure crystals. We apply these results to the recent experimental work on tetrachlorobenzene and discuss the dependence of the rates on energy mismatch.

I. INTRODUCTION

In the last few years, it has been possible to observe experimentally the effect of phonon scattering on the transfer of resonance excitation energy from one molecule to another. In a series of beautiful experiments, the Leiden group has observed the decay of electron spin-echo signals in the triplet states of dimers of naphthalene^{1,2} and in the triplet states of linear stacks of tetrachlorobenzene (TCB) molecules.³⁻⁵ In the last set of experiments, they observed the populations of the exciton states (with wave vector k) as a function of time after a laser flash which populated the k=0 state (the top of the exciton band in TCB). The populations n_k of the various k states obey the master equation

$$\dot{n}_{k} = \sum_{k^{*} \neq k} W_{kk} \cdot n_{k^{*}} - \sum_{k^{*} \neq k} W_{k^{*}k} n_{k} . \qquad (1.1)$$

The jump rates W_{kk} , were found from the experimental data to be simple functions of temperature from the lowest temperature up to $T \sim 2 \text{ K}^5$:

$$W_{kk'} \propto \{ \exp[\beta(E_k - E_{k'})] - 1] \}^{-1} , \qquad (1.2)$$

and this is successfully explained by an impurity induced one-phonon scattering mechanism. The exciton is scattered from k to k' with a single phonon absorption or emission, but the k selection rule on the phonon is not obeyed due to the presence of impurities.

Above 2 K, the rate at which excitons are scattered out of k = 0 increases much faster with T than given by Eq. (2). Another phonon scattering mechanism must therefore become important at this temperature. A strong possibility are two phonon processes which we explore theoretically in this paper. There are a variety of such processes which have been discussed before principally for the spin relaxation of impurity ions in crystals⁶⁻⁸ but also for exciton scattering.⁹ These processes can be broken down into twophonon absorption, two-phonon emission, and a combined absorption and emission process. We will see that the latter is most important for our study and we concentrate on that. This process can be further broken down into nonresonant Raman processes and resonant Raman processes. Furthermore, two-phonon processes can occur by two one-phonon events (i.e.,

second order perturbation theory of a linear phonon coupling) or a single two-phonon event (first order perturbation theory of a quadratic phonon coupling). All of these will be discussed fully in this paper which is laid out in the following way: in Sec. II, we discuss the quadratic coupling perturbation for both the pure systems (i.e., k conservation preserved) and the impurity induced case; in Sec. III, we discuss linear phonon coupling taken to second order, including the off resonance case and the resonant case; in Sec. IV, we calculate W_{kk} as a function of temperature and $E_k - E_{kr}$ and discuss the experimental implications of these dependences.

Two final comments are in order. First, this discussion shows the close connection between the excitonphonon scattering theory we treat and the theory recently presented for resonant and nonresonant fluorescence.¹⁰ Second, the present theory should be applicable to the recent experiments by Zewail and his co-workers on the excitons in dibromonaphthalene (DBN).¹¹ In DBN, the exciton band is much broader than in TCB so that impurity induced two-phonon absorption and emission should be more important than in TCB. In addition, the presence of another exciton band close in energy to the lowest, as well as the low lying librational mode should also be important in the scattering processes. The methods of this paper will allow a theoretical discussion of the results in DBN also.

II. QUADRATIC COUPLING TO FIRST ORDER

A. Pure crystals

The zeroth order Hamiltonian describing the excitations in our TCB system can be written

$$H_0 = \sum_{k} \epsilon_k a_k^* a_k + \sum_{\lambda} \omega_{\lambda} (b_{\lambda}^* b_{\lambda} + \frac{1}{2}) , \qquad (2.1)$$

where $\epsilon_k = 2J \cos k$, with J being the exchange interaction between nearest neighbors. The operators a_k^* and $a_k (b_\lambda^* \text{ and } b_\lambda)$ create and destroy excitons (phonons) of quasimomentum $k(\lambda)$, respectively. A local linear coupling between the excitons and the bath, taken to first order, gives a negligible contribution to the scattering rate W_{k^*k} , because the steepness of the phonon dispersion curve prevents the conservation of both energy and momentum for the event. We can write the next term, the quadratic coupling, as⁹

J. Chem. Phys. 77(6), 15 Sept. 1982

0021-9606/82/182763-05\$02.10

^{a)}Supported by NSF (CHE81-00407).

$$V = \frac{1}{N} \sum_{\substack{k,k'\\\lambda,\lambda'}} \eta(\lambda,\lambda') a_{k'}^* a_k (b_\lambda + b_{-\lambda}^*) (b_{\lambda'} + b_{-\lambda'}^*)$$
$$\times \delta(k' - k - \lambda - \lambda') , \qquad (2.2)$$

where $N = N_x N_y N_z$ is the number of sites in the crystal.

Due to the very low temperatures involved in these experiments, we consider interactions with the acoustic modes only. η is a deformation potential coupling, ¹² where $\eta^2(\lambda, \lambda') = \eta^2 \omega_\lambda \omega'_\lambda$.

The scattering rate to lowest order in V can be written

$$W_{k'-k} = \int_{0}^{\infty} \langle V_{kk'}(t) V_{k'k} \rangle \exp[i(\epsilon_{k} - \epsilon_{k'})t] dt , \qquad (2.3)$$

$$= \frac{4\pi}{N^{2}} \sum_{\lambda,\lambda'} \eta^{2}(\lambda,\lambda') \left[(n_{\lambda}+1)(n_{\lambda'}+1) \delta(\epsilon_{k} - \epsilon_{k'} - \omega_{\lambda} - \omega_{\lambda'}) \delta(k-k'-\lambda-\lambda') + n_{\lambda}n_{\lambda'} \delta(\epsilon_{k} - \epsilon_{k'} + \omega_{\lambda} + \omega_{\lambda'}) \delta(k-k'+\lambda+\lambda') + (n_{\lambda}+1)n_{\lambda'} \delta(\epsilon_{k} - \epsilon_{k'} - \omega_{\lambda} + \omega_{\lambda'}) \delta(k-k'-\lambda+\lambda') + n_{\lambda}(n_{\lambda'}+1) \delta(\epsilon_{k} - \epsilon_{k'} + \omega_{\lambda} - \omega_{\lambda'}) \delta(k-k'+\lambda-\lambda') \right], \qquad (2.4)$$

where $n_{\lambda} = [\exp(\beta \omega_{\lambda} - 1)^{-1}]$, and the brackets in Eq. (2.3) denote an average over the bath variables.

The first two terms above describe the simultaneous emission and absorption of two phonons, respectively. For these processes $\omega_{\lambda} + \omega_{\lambda}$ can at most equal the exciton bandwidth. For TCB, 4J = 1.36 cm⁻¹, and such events utilize only a small portion of the available phonon spectrum. Also, the phonon density of states and the coupling are very small in this region. We therefore ignore these processes and combine the last two terms, which can utilize any available phonons provided $\Delta \omega$ = $-\Delta \epsilon_{b}$.

We should also note that for the TCB system, the exciton band is flat in two dimensions (x and y). This quasi-one dimensionality is due to the coupling J being larger between adjacent sites on a chain than between sites on different chains. Therefore, $\epsilon_k = \epsilon_{k_x} = 2J \cos k_x$ and the quantity we are actually measuring in these experiments is

$$W_{k'_{g} - k_{g}} = \sum_{\substack{k_{X}, k_{y} \\ k_{X} \neq k'_{y}}} W_{k' - k} , \qquad (2.5a)$$

which essentially eliminates the momentum restrictions in the x and y directions. In addition, the impurities in the stack along the z direction will cut this stack into a number of noninteracting segments. Because of this, the populations measured in the experiment will be those of a number of segments. To take this into account, we will coarse-grain the master equation for the system by summing the rates for the pure system over a small range (α) of final k's. Thus,

$$W_{k'_{z}-k_{z}} = \sum_{\alpha} \sum_{\substack{k_{x}k_{y} \\ k'_{x}k'_{y}}} W_{k'-k}^{(\alpha)}$$
 (2.5b)

Let us assume that the average segment length is N_{ex} in units of the lattice spacing, then the number of impurities per chain in the z direction is approximately N_x/N_{ex} . This is also equal to the average number of pure k states in the small range around a k state of a segment. As an approximation, we will then take

$$W_{k'_{x}-k_{x}} = \sum_{\alpha} \sum_{\substack{k_{x}k_{y} \\ k'_{x}k'_{y}}} W_{k'-k}^{(\alpha)} \cong \frac{N_{g}}{N_{ex}} \sum_{\substack{k_{x},k_{y} \\ k'_{x},k_{y}}} W_{k'-k}^{(\alpha)} . \qquad (2.5c)$$

To change the sums in Eq. (2.4) to integrals, we introduce the phonon density of states $\rho(\omega)$. We need to calculate the density of states of the absorbed (ω) and emitted (ω') phonons, under the momentum conservation restriction, i.e.,

$$\rho(\omega)\rho(\omega')\,\delta(k_{z}+\lambda_{z}-k'_{z}-\lambda'_{z})$$

$$=\frac{1}{N^{2}}\sum_{\lambda,\lambda'}\,\delta(\omega-\omega_{\lambda})\,\delta(\omega'-\omega'_{\lambda})\,\delta(k_{z}+\lambda_{z}-k'_{z}-\lambda'_{z}) \,.$$
(2.6)

For an acoustic phonon

$$\omega_{\lambda} = \left[C_{11}^2 \lambda_{x}^2 + C_{1}^2 \lambda^2 \right]^{1/2} , \qquad (2.7)$$

where $\lambda^2 = \lambda_x^2 + \lambda_y^2$. The phonons which are important here (in the range $2K \rightarrow 10$ K) are well within the Debye part of the spectrum. Eq. (2.7) is reasonably valid in this region, which extends out to about 50 cm⁻¹ in most molecular crystals.

Using Eq. (2.7) to calculate Eq. (2.6), we arrive at

$$\rho(\omega)\rho(\omega')\delta(k_x+\lambda_x-k'_x-\lambda'_x)=\frac{\omega\omega'}{(2\pi)^3N_xC_1^4}\left(\lambda_x^a-\lambda_x^b\right).$$
 (2.8)

This calculation sets the upper and lower bounds on λ_{z} by requiring

$$C_{11} \left| \lambda_{\mathbf{z}} - \Delta k_{\mathbf{z}} \right| \leq \omega' , \quad C_{11} \left| \lambda_{\mathbf{z}} \right| \leq \omega .$$

This not only defines the limits on λ_s ,

$$\lambda_{x}^{a} = \frac{\omega}{C_{11}}$$
, $\lambda_{x}^{b} = \left| \Delta k_{x} \right| - \frac{\omega'}{C_{11}}$,

but also sets a lower bounds on the usable phonons, i.e.,

$$\omega + \omega' \ge C_{11} \left| \Delta k_{\mathbf{z}} \right|$$

or

$$\omega', \omega \ge D \equiv \frac{1}{2} (C_{11} |\Delta k_s| - |\Delta \epsilon|) , \qquad (2.9)$$

where D is always positive due to the steepness of the phonon line $(C_{11} > 2J)$ and $\Delta \epsilon = \epsilon'_k - \epsilon_k$.

We now have

$$W_{k'_{z}-k_{z}} = \frac{\eta^{2}}{\pi^{2}N_{ex}C_{\perp}^{4}} \int_{D}^{\omega_{D}} \int_{D}^{\sigma_{D}} d\omega d\omega' \ \omega^{2}(\omega')^{2}n(\omega)[n(\omega')+1] \\ \times \left[\frac{\omega+\omega'}{C_{11}} - |\Delta k_{z}|\right] \delta(\omega-\omega'-\Delta\epsilon) .$$
(2.10)

For $\Delta \epsilon < 0$,

$$W_{k_{g}^{*}k_{g}} = \frac{2\eta^{2}}{\pi^{2}N_{ex}C_{\perp}^{4}C_{11}} \int_{D}^{\infty} d\omega \,\omega^{2}(\omega + |\Delta\epsilon|)^{2}n(\omega)$$
$$\times (n(\omega + |\Delta\epsilon|) + 1) [\omega - D] . \qquad (2.11)$$

We set the Debye frequency ω_D equal to ∞ , which is valid at these low temperatures, and we find that

$$W_{k_{g}^{*}k_{g}} = \frac{2\eta^{2}}{\pi^{2}C_{\perp}^{4}C_{11}N_{ex}} \exp(-D/kT) \left[120(kT)^{6} + (96D + 48 | \Delta\epsilon|)(kT)^{5} + [36D^{2} + 36D | \Delta\epsilon| + 6 | \Delta\epsilon|^{2}) \times (kT)^{4} + (8D^{3} + 12D^{2} | \Delta\epsilon| + 4D | \Delta\epsilon|^{2})(kT)^{3} + (D^{4} + 2D^{3} | \Delta\epsilon| + D^{2} | \Delta\epsilon|^{2})(kT)^{2} \right].$$
(2.12)

For $\Delta \epsilon > 0$, we get the same result preceded by the Boltzmann factor $\exp[-(|\Delta \epsilon|/kT)]$. These rates are influenced by the factor $\exp(-D/kT)$, which favors a higher temperature and should weight the scattering considerably toward a smaller $|\Delta k|$.

B. Impurity induced transitions

We will now compute the impurity induced scattering rate, quadratic in the phonon interaction, but momentum nonconserving due to the loss of periodicity near an impurity. Our methods parallel those of Ref. 4, where a linear coupling was considered.

Consider a site *n*, in a segment of TCB molecules N_{ex} sites long. An impurity in a neighboring stack, which is adjacent to site *n*, will bring about a displacement in its equilibrium position (Q_n) and a change in its site energy *E*, giving rise to a perturbation

$$V = (\partial^2 E / \partial Q_n^2)_0 Q_n^2 a_n^* a_n .$$

$$V = \frac{1}{N_{ex}N} \sum_{k,k'} a_k^* a_{k'} Q_\lambda Q_{\lambda'} (\partial^2 E / \partial Q_n^2)_0 \exp[i(k - k' + \lambda + \lambda')n] .$$
(2.13)

Again using the deformation potential approximation for the coupling

$$(\partial^2 E/\partial Q^2)_0 \exp[i(\lambda+\lambda')n] = \gamma \omega_\lambda \,\omega'_\lambda, \qquad (2.14)$$

we arrive at the following:

$$W_{k'-k} = \sum_{\lambda,\lambda'} \omega_q \omega_{q'} \omega_\lambda \omega_{\lambda'} \int_0^\infty dt \langle Q_q(t) Q'_q(t) Q_\lambda Q_{\lambda'} \rangle$$

$$\stackrel{q,q'}{\times} \exp[i(\epsilon_k - \epsilon_{k'})t]$$

$$= \frac{8\pi\gamma^2}{N_{ex}^2 N^2} \sum_{q,q'} \omega_q \omega_{q'} (n_{q'} + 1) n_q \,\delta(\epsilon_k - \epsilon_{k'} + \omega_q - \omega_{q'}) , \qquad (2.15)$$

where we have again omitted the terms corresponding to absorption and emission of two phonons. We convert the sums to integrals, calculating the density of states from Eq. (2.7),

$$\rho(\omega) = \frac{1}{N} \sum_{\lambda} \delta(\omega - \omega_{\lambda}) = \frac{\omega^2}{2\pi^2 C_1^2 C_{11}}$$
(2.16)

to obtain (for $\Delta \epsilon_k < 0$),

$$W_{k'-k} = \frac{\gamma^2}{\pi^3 C_{\perp}^4 C_{11}^2 N_{ex}^2} \left[1452(kT)^7 + 732(kT)^6 \left| \Delta \epsilon \right| + 150(kT)^5 \left| \Delta \epsilon \right|^2 + 12(kT)^4 \left| \Delta \epsilon \right|^3 \right]$$
(2.17)

having again set $\omega_D = \infty$ in the final integration. The $\Delta \epsilon > 0$ rate is the same, multiplied by $\exp(-|\Delta \epsilon|/kT)$. Equations (2.12) and (2.17) both have the high temperature dependence which shows up in the TCB experiments above 2 K. We will compare these terms in Sec. IV.

III. LINEAR COUPLING TO SECOND ORDER

In this section we take both the pure linear phonon coupling, and the impurity induced linear coupling to second order in perturbation theory. Since we are linking two first order processes via some intermediate state, we can have both resonant and nonresonant scattering, corresponding to the transitions to and from the intermediate being energy conserving and nonconserving, respectively.

Consider the process where an exciton of wave vector k absorbs a phonon ω , scattering to some state λ . It then emits ω' , scattering to k'. One proper way to connect these two events¹³ is through the propagator

$$\langle k', \omega' | U^{(2)} | k, \omega \rangle$$

$$= \sum_{\lambda} \int_{0}^{t} dt_{1} \int_{0}^{t_{1}} dt_{2} \exp[i(\epsilon_{k'} + \omega')(t - t_{1})]$$

$$\times V_{k'\lambda} \exp[-i\epsilon_{\lambda}(t_{1} - t_{2})] V_{\lambda k} \exp[-i(\epsilon_{k} + \omega)t_{2}],$$

which gives the usual second order transition rate

$$W_{k'-k} = \lim_{t \to \infty} \frac{\partial}{\partial t} |\langle k', \omega' | U | k, \omega \rangle|^{2}$$
$$= 2\pi \left\langle \left| \sum_{\lambda} \frac{V_{k'\lambda} V_{\lambda k}}{\epsilon_{\lambda} - \epsilon_{k} - \omega} \right|^{2} \right\rangle \delta(\epsilon_{k} + \omega - \epsilon'_{k} - \omega') .$$
(3.1)

Toyozawa¹⁰ has taken a density matrix approach, retaining only the terms $\rho\alpha\beta$ corresponding to the three states involved. Solving for the rate of population change in the final state (as $t - \infty$) provides the same result [Eq. (3.1)], which contains both the resonant and nonresonant contributions.

A. Resonant case

In the resonant case $(\epsilon_{\lambda} = \epsilon_{k} + \omega)$, to avoid the divergence in the denominator of Eq. (3.1), we must recognize the finite lifetime or width of the state λ by introducing the term $i\gamma_{\lambda}/2$, where γ_{λ} is the scattering rate out of the intermediate. Toyozawa's derivation introduces γ_{λ} naturally if one includes terms higher than second order in V.¹⁰

One can also take a semiclassical approach, similar to the density matrix derivation, by using a master equation, as Scott and Jeffries have done.¹⁴ We can write expressions for the populations of the initial, intermediate, and final states $(N_k, N_\lambda, N_{k'})$ as follows:

$$N_{k} = -N_{k} (W_{\lambda-k}^{(1)} + W_{k'-k}^{(1)}) + N_{\lambda} W_{k-\lambda}^{(1)} + N_{k'} W_{k-k'}^{(1)} , \qquad (3.2)$$

where the $W^{(1)}$'s are first order transition rates. This approach is semiclassical in that it treats the various absorption and emission processes as separate uncorrelated events. Therefore, this method can only give the resonance contribution, where energy is conserved in going to and from λ . Since we do not properly connect

J. Chem. Phys., Vol. 77, No. 6, 15 September 1982

the two events in terms of the time spent in the intermediate, we lose the quantum mechanical effect of being able to make off-resonance transitions due to the uncertainty in ϵ_{1} .

The long time or steady state assumption on the intermediate $(\dot{N}_{\lambda} = 0)$ allows us to solve the above for \dot{N}_{μ} ,

$$\dot{N}_{k} = N_{k} \left(W_{k'-k}^{(1)} + \frac{W_{\lambda-k}^{(1)} W_{k'-\lambda}^{(1)}}{2\gamma_{\lambda}} \right) - N_{k'} \left(W_{k-k'}^{(1)} + W_{\lambda-k'}^{(1)} - \frac{W_{k-\lambda}^{(1)} W_{\lambda-k'}^{(1)}}{2\gamma_{\lambda}} \right) , \qquad (3.3)$$

where $2\gamma_{\lambda} = W_{k-\lambda}^{(1)} + W_{k-\lambda}^{(1)}$ is the inverse scattering lifetime of the intermediate. We see that in addition to the first order rate from k to k', we get a second order rate via λ , which is equivalent to the resonant solution of Eq. (3.1).

If we were to start with a full Paul Master Equation in terms of these first order rates $W^{(1)}$,

$$\dot{P}_{k}(t) = \sum_{k'} P_{k'}(t) W_{k-k'}^{(1)} - P_{k}(t) \sum_{k'} W_{k'-k}^{(1)}, \qquad (3.4)$$

where the k's cover all values in the exciton band, and somehow solve it numerically, we will have included all *n*th order on-resonance transitions via all possible intermediates. This is exactly what van Strien *et al.*⁴ have done in analyzing their experiments.

For the momentum conserving one-phonon perturbation taken to second order, we have no resonance contribution due to an inability to conserve energy and momentum $(W^{(1)}=0)$.

The resonant second order impurity assisted contribution does not have the high temperature dependence of the quadratic perturbations as can be seen from Eq. (3.3), using the first order impurity induced rates calculated in Ref. 4,

$$W_{b-a}^{(1)} = \frac{\lambda^2}{N_{ex}^2 2\pi C_{\perp}^2 C_{11}} \left| \Delta \epsilon_{ab} \right|^3 n(\Delta \epsilon) , \quad \text{for } \Delta \epsilon > 0 , \quad (3.5)$$

Also, since the intermediates lie within the exciton band, ω and ω' are always less than 1.36 cm⁻¹ (for TCB), limiting them to a part of the phonon band with weak coupling and low density of states. These terms are therefore insignificant when compared with the quadratic cases, which access all or most of the available phonon spectrum.

B. Off-resonant case

The off-resonance case is similar to the quadratic coupling case to first order, except that: (1) the process is not simultaneous, and we must distinguish between absorbing ω first or emitting ω' first. (2) the contribution from each pair of ω 's is weighted by how far the initial process is off-resonance to the intermediate. Therefore, one would expect that these processes contribute little to $W_{k'_{2}-k_{2}}$ when compared with the quadratic rates. Also, the impurity induced resonant rates are down by another factor of $1/N_{ex}$ than the quadratic impurity rates, because they are a higher order process.

Solving Eq. (3.1) for the usual linear phonon per-

turbation (with deformation potential coupling),

$$V = \frac{1}{\sqrt{N}} \sum_{k,k',\lambda} a_{k'}^* a_k g \sqrt{\omega_{\lambda}} (b_{\lambda} + b_{-\lambda}) \delta(k + \lambda - k') \qquad (3.6)$$

gives, for absorption of ω , followed by emission of ω' ,

$$W_{k'_{g}-k_{g}} = 8\pi g^{4}/N^{2}$$

$$\times \sum_{\lambda,\lambda'} \frac{\omega_{\lambda}\omega_{\lambda'} n_{\lambda}(n_{\lambda'}+1) \delta(k_{g}-\lambda'_{g}-k'_{g}) \delta(\omega-\omega'-\Delta\epsilon)}{[2J\cos(k_{g}+\lambda_{g})-2J\cos k_{g}-\omega]^{2}}$$
(3.7)

This can be simplified by realizing that the major contribution to the sum is from the region $\omega > 2kT > 2J$. Therefore, we set $(\Delta \epsilon - \omega)^2 = \omega^2$. Proceeding exactly as before, we have for $\Delta \epsilon < 0$,

$$W_{k_{g^*}k_{g}} = \frac{2g^4 \exp(-D/kT)}{\pi^2 N_{\bullet x} C_{\perp}^4 C_{11}} \left[6(kT)^4 + (4D+4 | \Delta \epsilon |)(kT)^3 + (D^2+2D | \Delta \epsilon | + | \Delta \epsilon |^2)(kT)^2 \right].$$
(3.8)

For $\Delta \epsilon > 0$, ω' being emitted first,

$$W_{k_{z}-k_{z}} = \frac{2g^{4}}{\pi^{2}N_{\bullet x}C_{\perp}^{4}C_{11}} \exp(-D/kT) \left[6(kT)^{4} + 4D(kT)^{3} + D^{2}(kT)^{2}\right].$$
(3.9)

The reverse of these processes, where $\Delta \epsilon > 0$, are the same except for the Boltzmann factor $\exp(-|\Delta \epsilon|/kT)$.

For the impurity induced rates, we use a perturbation similar to Eq. (2.13), which is discussed elsewhere.⁴ That is,

$$V = \frac{1}{N_{\text{ex}}} - \frac{1}{\sqrt{N}} \sum_{k, k', q} \lambda a_k^* a_{k'} \omega_q Q_q \exp[i(k-k')n] .$$
(3.10)

For $\Delta \epsilon < 0$, with absorption of ω first, the same methodology as before leads to

$$W_{k'-k} = \frac{2\lambda^4}{N_{ox}^3 C_{\perp}^4 C_{11}^2 \pi^3} \left[25(kT)^5 + 19 \right| \Delta \epsilon \left| (kT)^4 + 7 \right| \Delta \epsilon \left| {}^2(kT)^3 + 2 \right| \Delta \epsilon \left| {}^3(kT)^2 \right], \qquad (3.11)$$

and for $\Delta \epsilon < 0$, with ω' being emitted first,

$$W_{k'-k} = \frac{2\lambda^4}{N_{\bullet x}^3 C_1^4 C_{11}^2 \pi^3} \left[25(kT)^5 + 6 \left| \Delta \epsilon \right| (kT)^4 \right].$$
(3.12)

As before, the reverse rates differ only by the Boltzmann factor.

IV. CONCLUSIONS

As mentioned earlier, the off-resonance rates of Sec. III are similar in form to the quadratic first order equations, but are much smaller in magnitude because of the weighting. They become even less significant as the temperature increases, due to a lower order temperature dependence. The resonant second order impurity induced case has already been included in the master equation calculation of van Strien *et al.* and is also small in magnitude and temperature dependence. Therefore, the scattering in these experiments (above 2 K) is probably described by the quadratic rates. To compare Eqs. (2. 12) and (2. 17), we must generalize the latter to the case of *n* impurities and determine reasonable values for C_{11} and N_{ex} . These resonance experiments involve a crystal containing a large number of excitons in many TCB chains of varying lengths. An impurity defines the end of a chain (i.e., we assume no transport through an impurity site). Most of the signal received can be thought of as coming from a set of most probable or average chains, estimated to be approximately 50 sites in length.⁴ Each of these average chains has an impurity at each end and approximately four impurity affected sites in between, due to the impurities in the four neighboring chains (we are assuming one impurity every 50 sites on the average). Repeating the derivation of Eq. (2.17) for a random set of *n* impurity affected sites, we get Eq. (2.17) times *n*, plus a string of cross terms which average to zero. We therefore estimate $n/N_{ex} \approx 1/8$.

Values for C_{11} were extracted from the slopes of experimentally determined phonon dispersion curves¹⁵ for molecular crystals similar to TCB. For the three acoustic branches, we get values of approximately 10, 20, and 30 cm⁻¹.

Taking $C_{11} = 10 \text{ cm}^{-1}$, and assuming the coupling constants are approximately the same $(\eta \approx \gamma)$, we see that the pure phonon rate is dominant, although the impurity induced process may contribute as much as 15%-20% of the scattering.

It would be useful to be able to estimate the coupling constants η (the pure two-phonon constant), γ (the impurity induced two-phonon constant), and λ (the impurity induced one-phonon constant). Unfortunately, it is very difficult to calculate these quantities accurately. We can however estimate these by comparing our theoretical results to the experiment. From our earlier work⁴ we can estimate that $\lambda^2 \sim 0.05$ cm⁻¹, assuming that the low T experimental results are due to the impurity induced one phonon processes. It is likely that γ^2 is smaller, or the same magnitude, since

$$\lambda \propto \left(\frac{\partial E}{\partial Q_n}\right)_0$$
 and $\gamma \propto \left(\frac{\partial^2 E}{\partial Q_n^2}\right)_0$.

Thus, we expect the impurity induced two-phonon processes to be small. If we assume then that the higher temperature experimental results⁴ are due to pure twophonon processes, we estimate that $\eta^2 \sim 0.005-0.01$.

Also, there is some doubt as to the correct value for N_{ex} . Dlott, Fayer, and Wieting, ^{16,17} in a set of experiments monitoring trap emission in TCB, estimate $N_{ex} \sim 2.2 \times 10^4$. This would make the pure two-phonon process considerably more dominant, and we should consider $N_{ex} = 50$ to be a lower limit.

At low temperatures, the pure phonon rate heavily

favors a small Δk (small $\Delta \epsilon$) due to the prefactor exp(-D/kT). The effect diminishes as the temperature increases. For the steeper acoustic bands ($C_{11} \approx 20$, 30 cm⁻¹) the weighting is even more significant, since *D* is approximately two and three times larger. In more realistic systems, where the phonon dispersion curves become less steep near the Brillouin zone edges, this effect should be somewhat less pronounced.

The impurity assisted case very slightly favors a larger $|\Delta \epsilon|$ (large Δk), an effect which also diminishes with higher temperature. It also favors less steep acoustic bands. Both rates exhibit the rapid increase with temperature indicated by the experiments $(T^{6.4\pm0.06})^4$.

To sum up, the pure quadratic phonon interaction seems to be the dominant mechanism for the scattering of excitons in these low temperature (2 to ~10 K) onedimensional systems, favoring a small change in k_x . The impurity induced rates, however, may not be small enough to neglect, and become even more important with higher temperature, greater impurity concentration, and steeper acoustic bands.

- ¹B. Botter, C. Nonhof, J. Schmidt, and J. van der Waals, Chem. Phys. Lett. **43**, 210 (1976).
- ²B. Botter, A. van Strien, and J. Schmidt, Chem. Phys. Lett. **49**, 39 (1977).
- ³A. van Strien, J. van Kooten, and J. Schmidt, Chem. Phys. Lett. **76**, 7 (1980).
- ⁴A. van Strien, J. Schmidt, and R. Silbey, Mol. Phys. 46, 151 (1982).
- ⁵A. van Strien, Ph.D. thesis, University of Leiden, Leiden, (1981).
- ⁶D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).
- ⁷(a) R. Orbach, Proc. R. Soc. London Ser. A **264**, 458 (1961); (b) R. Orbach and A. Mankov, *Spin Lattice Relaxation in Ionic Solids* (Harper and Row, New York, 1966).
- ⁸A. Abraham and B. Bleaney, *EPR of Transition Metal Ions* (Clarendon, Oxford, 1970).
- ⁹R. Munn and R. Silbey, J. Chem. Phys. 68, 2439 (1979).
- ¹⁰See, e.g., Y. Toyozawa, J. Phys. Soc. Jpn. 41, 400 (1976).
- ¹¹D. Smith and A. Zewail, J. Chem. Phys. 71, 3533; J. LeMaistre and A. Zewail (private communication, 1981).
 ¹²C. Kittel, *Quantum Theory of Solids* (Wiley, New York,
- 1963). ¹³See, e.g., P. Dirac, The Principles of Quantum Mechanics
- (Clarendon, Oxford, 1978).
- ¹⁴P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962). ¹⁵See, e.g., for *p*-dichlorobenzene, P. A. Reynolds, J. K.
- Kjems, and J. W. White, J. Chem. Phys. 60, 824 (1974). ¹⁶D. D. Dlott and M. D. Fayer, Chem. Phys.. Lett. 41, 305 (1976).
- ¹⁷D. D. Dlott, M. D. Fayer, and R. D. Wieting, J. Chem. Phys. **69**, 2752 (1978).