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Exciton dynamics
Impurity assisted $k \rightarrow k'$ scattering in a one-dimensional triplet exciton system

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The observed $k \rightarrow k'$ scattering in the linear chain triplet exciton system of 1,2,4,5-tetrachlorobenzene at low temperature is explained by assuming that the scattering takes place at an impurity site via single phonon emission or absorption. The model is supported by a study of the temperature dependence of the scattering rate and the time evolution of the population distribution over the whole band.

1. INTRODUCTION

In the past decade many papers have appeared dealing with the problem of exciton motion in molecular crystals. A common element in the different viewpoints is that one usually tries to understand exciton motion in real space. It is generally agreed that at high temperatures the motion is 'incoherent' and that it can be described by a hopping model, but the various authors use different approaches [1–8] for the low temperature wave-like motion. However, in all the theories exciton–phonon coupling is considered to be the dominant mechanism responsible for exciton scattering. Consequently, two selection rules must be taken into account, the conservation of energy and the conservation of quasi-momentum. Both of these set severe restrictions on the probability of the exciton–phonon scattering process.

In two experimental studies Burland *et al.* [9, 10] measured the optical absorption lineshapes of linear chain triplet excitons in 1,4-dibromonaphthalene and 1,2,4,5-tetrachlorobenzene (TCB) as a function of temperature. They applied the formalism developed by Davydov [1] and Sumi [11] for exciton–phonon scattering to explain the observed lineshapes. Later, Harris [12] attempted to explain these data with the help of an exchange model. The interpretation of these experiments, however, has to be considered with great

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care, especially since it appears from findings by Port *et al.* [13] that the absorption lineshapes are extremely sensitive to sample preparation and handling.

The TCB system is of particular interest because it also enables one to observe the magnetic resonance transitions between the triplet exciton sublevels in zero magnetic field via optical detection (ODMR). Since the exciton k states have slightly different zero-field frequencies, the resulting lineshape 'mirrors' the dispersion of the triplet exciton band [14]. Harris and Fayer [15] and Wieting and Fayer [16] have tried to make an estimate for the scattering rates from an analysis of the zero-field lineshapes. In a more recent paper, Breiland and Saylor [17] introduce a scattering matrix in the momentum representation to fit the ODMR lineshapes. To obtain the best fit with their results they have to assume that the scattering occurs preferentially to nearby k states. They do not discuss their results in terms of existing exciton–phonon scattering theories, in which the conservation laws of energy and quasi-momentum must be obeyed. In the case of TCB, where the dispersion of the triplet exciton band is much smaller than the dispersion of acoustic phonons, this would only lead to scattering in a very limited range in k space [15].

In a recent paper we describe an experiment which makes the direct observation of $k \rightarrow k'$ scattering in the triplet exciton system of TCB possible [18]. The experiment has been performed in the following way. A short laser flash with a duration of 15 ns excites the system selectively from the S_0 ground state into the $k=0$ region of the triplet exciton band. The T_x–T_y zero-field lineshape is then inspected via electron spin echo (ESE) signals. The signals show that initially a strong overpopulation has resulted for the $k \approx 0$ excitons at the top of the exciton band. By varying the delay of the ESE signal with respect to the laser flash, one can follow the evolution of the population of the various k states via the time dependence of the ESE signal at the corresponding zero-field frequency. The results prove that the probability that there will be scattering is not restricted to small ranges in k space. This contrasts very sharply with the prediction based on the existing theories for exciton-phonon scattering and also with the previous conclusions of Breiland and Saylor [17] and Botter *et al.* [19].

In this paper we present two new experimental results on exciton–phonon scattering in TCB. First, we have measured the temperature dependence of the scattering rate T_S^{-1} from the $k \approx 0$ excitons to all other k states. Secondly, we give the results of spin-locking experiments, which support the idea that the principle of detailed balance applies to scattering amongst the k states. To explain these data we propose that the exciton–phonon scattering proceeds via impurities, thus eliminating the selection rule for conservation of quasi-momentum. With the help of this model we have derived expressions for the k dependence and the temperature dependence of the scattering rates in the region of low temperatures, where only one-phonon processes are expected to occur. The resulting expressions give a very good account of the observed low temperature dependence of the scattering rate T_S^{-1}. In addition, we are able to fit the observed scattering pattern amongst the exciton k states with a computer simulation based on our expressions for this impurity-assisted scattering. At high temperatures where $k_B T$ is large compared with the exciton bandwidth, the temperature dependence of the scattering rate deviates strongly from the behaviour predicted on the basis of one-phonon processes. We think that two-phonon type processes dominate the exciton k scattering here.

2. Theory

As we already mentioned in the introduction, the experimentally observed $k \to k'$ scattering in the triplet exciton band of TCB does not indicate any restriction in the scattering probabilities. This might give rise to doubts as to whether direct exciton–phonon coupling is responsible for the observed scattering process, since according to the laws of conservation of energy and quasi-momentum scattering should occur solely in limited regions of k space. However, in this section we shall present a theory which can account for the experimental observations. It is based on impurity-assisted scattering by one-phonon processes and is therefore only valid at low temperatures where $k_B T$ is small compared with the exciton bandwidth.

We start by considering an unperturbed chain of N molecules with an exchange interaction β between nearest neighbours. The hamiltonian describing the excited states of the chain is given by

$$H_0 = \sum_k E_k |k\rangle\langle k| + \sum_q \omega_q (\hat{n}_q + \tfrac{1}{2}). \tag{1}$$

Here $|k\rangle$ describes the exciton state with energy E_k and quasi-momentum k, and $\hat{n}_q$ is the phonon number operator for the mode frequency ω_q and quasi-momentum q. We assume that, under the influence of an impurity, a molecule at site n (most likely a neighbour of the impurity) is displaced from its equilibrium position to a new position defined by the coordinate Q_n. This leads to a perturbation

$$V = \left(\frac{\partial E}{\partial Q_n}\right)_0 Q_n |n\rangle\langle n|, \tag{2}$$

where $|n\rangle$ describes an excitation localized at site n and E is the site energy. If we change (2) from the site representation to the momentum representation we have

$$V = N^{-1} N_{\mathrm{ph}}^{-1/2} \sum_{k,k'} \sum_q |k\rangle\langle k'| \left(\frac{\partial E}{\partial Q_n}\right)_0 Q_q \exp\left[i(k-k'+q)n\right]. \tag{3}$$

Here we have used the fact that there are N_{ph} sites which participate in the phonon state with N_{ph} in the order of magnitude of the total number of molecules in the crystal. This takes into account that while the exciton is one dimensional, the phonons, though anisotropic, are three dimensional. In order to find a form for the coupling constant $(\partial E/\partial Q_n)_0$ we apply the deformation potential approximation for acoustic phonons [20] and write

$$\left(\frac{\partial E}{\partial Q_n}\right)_0 = \lambda \omega_q. \tag{4}$$

Low frequency phonons are expected to contribute negligibly to the site perturbation V; this is assured by taking λ a constant in (4). We obtain

$$V = N^{-1} N_{\mathrm{ph}}^{-1/2} \lambda \sum_{k,k'} \sum_q |k\rangle\langle k'| \omega_q Q_q \exp\left[i(k-k'+q)n\right]$$

$$\equiv \sum_{k,k'} V_{kk'} |k\rangle\langle k'|, \tag{5}$$

with

$$V_{kk'} = N^{-1} N_{\mathrm{ph}}^{-1/2} \lambda \sum_q \omega_q Q_q \exp\left[i(k-k'+q)n\right]. \tag{6}$$

We now apply Fermi's golden rule to get the transition probability for scattering from state k to k' [21]

$$W^n{}_{k'\leftarrow k} = \int_{-\infty}^{\infty} \langle V_{kk'}(t) V_{k'k}(0)\rangle \exp\left[i(E_k - E_{k'})t\right] dt$$

$$= N^{-2} N_{\mathrm{ph}}{}^{-1} \lambda^2 \sum_{q,q'} \omega_q \omega_{q'} \int_{-\infty}^{\infty} \langle Q_q(t) Q_{q'}(0)\rangle \exp\left[i(E_k - E_{k'})t\right] dt. \quad (7)$$

The autocorrelation function $\langle Q_q(t) Q_{q'}(0)\rangle$ for a harmonic oscillator is

$$\langle Q_q(t) Q_{q'}(0)\rangle = \omega_q{}^{-1}[(\bar{n}_q + 1)\exp(-i\omega_q t) + \bar{n}_q \exp(i\omega_q t)]\delta_{q'q} \quad (8)$$

where $\bar{n}_q$ is the occupation number of a phonon q. This leads to

$$W^n{}_{k'\leftarrow k} = N^{-2} N_{\mathrm{ph}}{}^{-1} \lambda^2 \sum_q \omega_q \{[\bar{n}_q + 1]\delta(E_k - E_{k'} - \omega_q) + \bar{n}_q \delta(E_k - E_{k'} + \omega_q)\}. \quad (9)$$

Here the first term corresponds to phonon creation and the second to phonon destruction. We assume that the lattice phonon spectrum is given by a Debye density of states function, that is $\rho(\omega)d\omega = A\omega^2\, d\omega$, and therefore

$$W^n{}_{k'\leftarrow k} = N^{-2} \lambda^2 \int_0^{\omega_D} \rho(\omega)\omega\{[\bar{n}(\omega) + 1]\delta(E_k - E_{k'} - \omega) + \bar{n}(\omega)\delta(E_k - E_{k'} + \omega)\}\, d\omega \quad (10)$$

$$\left.\begin{aligned} W^n{}_{k'\leftarrow k} &= A\lambda^2 N^{-2}[\bar{n}(\Delta E) + 1](\Delta E)^3 \;;\; E_k > E_{k'}, \\ W^n{}_{k'\leftarrow k} &= A\lambda^2 N^{-2}\bar{n}(\Delta E)(\Delta E)^3 \;;\; E_k < E_{k'}, \end{aligned}\right\} \quad (11)$$

with $\Delta E = |E_k - E_{k'}|$. The first part of (11) corresponds with one-phonon emission, and the second part with one-phonon absorption. With m uncorrelated impurities present in the chain we find for the total scattering probability

$$W_{k'k} = \sum_{n=1}^{m} W^n{}_{k'\leftarrow k} = m W^n{}_{k'\leftarrow k}. \quad (12)$$

Since the impurity concentration $c = m/N$, we finally obtain for the total scattering probability using $W = A\lambda^2 c$

$$W_{k'k} = \frac{W}{N}(\Delta E)^3[\bar{n}(\Delta E) + 1] = \frac{W}{N}(\Delta E)^3 \frac{\exp(\Delta E/k_{\mathrm{B}}T)}{\exp(\Delta E/k_{\mathrm{B}}T) - 1} \quad (13)$$

for $E_k > E_{k'}$ and

$$W_{k'k} = \frac{W}{N}(\Delta E)^3 \bar{n}(\Delta E) = \frac{W}{N}(\Delta E)^3[\exp(\Delta E/k_{\mathrm{B}}T) - 1]^{-1} \quad (14)$$

for $E_k < E_{k'}$.

The expressions (13) and (14) have been derived assuming only one-phonon processes to occur. In the next section it is shown that they account nicely for the observed low temperature dependence of the scattering rate $T_S{}^{-1}$. At temperatures where $k_{\mathrm{B}}T$ is large compared with the width of the triplet exciton band this is no longer the case, as two-phonon Raman type processes then have

to be considered. In the above formalism this can be done either by considering quadratic terms in the perturbation V, or by second order perturbation theory.

The impurity may also perturb the near neighbour transfer integrals β due to the change in equilibrium position at site n, so that we must add

$$\left(\frac{\partial\beta}{\partial Q_n}\right)_0 Q_n\{|n\rangle\langle n+1| + |n\rangle\langle n-1| + \text{h.c.}\} \tag{15}$$

to V in equation (2). By proceeding as before and again using the deformation potential approximation, this adds to $V_{kk'}$ in equation (6) a term of identical form except that λ will be different. This will give rise to the same final temperature dependence for $W_{k'k}$ as before and can thus be included in the present formulation.

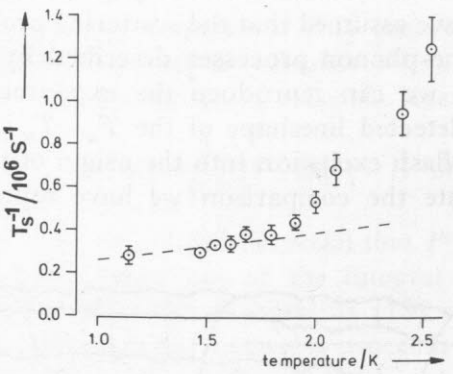

Figure 1. The experimentally observed temperature dependence of the scattering rate $T_S^{-1}(k\approx 0)$, as obtained from the decay of the excess population of the $k\approx 0$ excitons at various temperatures. The dashed line indicates the calculated temperature dependence of $T_S^{-1}(k\approx 0)$ using the impurity assisted exciton–phonon scattering model.

3. Experimental results

In figure 1 we have plotted the temperature dependence of the decay rate $T_S^{-1}(k\approx 0)$ of the initial excess population of the $k\approx 0$ triplet excitons in TCB after selective laser excitation in the 0–0 band of the $T_0 \leftarrow S_0$ absorption. The results have been obtained by measuring the decay of the electron spin echo signal at 3572·5 MHz (the frequency in the $T_x - T_y$ zero-field transition corresponding with the $k\approx 0$ excitons) as a function of the delay after the laser flash. The rate T_S^{-1} therefore represents the total scattering rate from $k\approx 0$ to all the other exciton k states.

The scattering rates from other regions of the exciton band cannot be found directly from the above experiments. However, in the following we present the results of spin-locking experiments which, in principle, allow one to obtain the scattering rates from any part of the band. In the spin-locking experiment a $\pi/2$ microwave pulse is applied, followed immediately by a $\pi/2$ phase shift of the driving microwave field. In this way the direction of the microwave magnetic induction $\mathbf{B}_1$ is made parallel to the macroscopic magnetization in the horizontal plane of the rotating frame. Since at 1·15 K spin-lattice relaxation is slow [18, 19], this magnetization can only decay via jumps in the resonance

frequency, which differ from the microwave frequency by an amount larger than $\gamma_e B_1$. When tuning the spectrometer to 3582·5 MHz (the frequency in the $T_x - T_y$ transition corresponding to the $k \approx \pm \pi/a$ excitons) we find at 1·15 K $T_{1\rho}(k \approx \pm \pi/a) = 10 \pm 1\ \mu s$. At 3572·5 MHz we find $T_{1\rho}(k \approx 0) = 2{\cdot}2 \pm 0{\cdot}2\ \mu s$.

The fact that $T_{1\rho}^{-1}(k \approx 0)$ is almost equal to the scattering rate $T_S^{-1}(k \approx 0) = (2{\cdot}7 \pm 0{\cdot}2\ \mu s)^{-1}$ indicates that the spin-locking experiment indeed measures the scattering rate from $k \approx 0$ to the other k states. This supports the idea that $T_{1\rho}^{-1}(k \approx \pm \pi/a)$ is a good measure for the scattering rate from the $k \approx \pm \pi/a$ excitons to the other k states. In particular the ratio $T_{1\rho}^{-1}(k \approx 0)/T_{1\rho}^{-1}(k \approx \pm \pi/a) = 4{\cdot}6$ is close to the Boltzmann factor $\exp(\Delta E/k_B T) = \exp(4\beta/k_B T) = 5{\cdot}5$ ($4\beta = 1{\cdot}36\ cm^{-1}$ and $T = 1{\cdot}15$ K). This finding shows that the principle of detailed balance applies to scattering in the band.

As a first test of our model presented in the preceding section, we performed computer calculations of the evolution of the population distribution over the exciton k states. We have assumed that the scattering probability is determined by impurity assisted one-phonon processes described by (13) and (14). Our aim is to see whether we can reproduce the experimentally observed time evolution of the ESE detected lineshape of the $T_x - T_y$ zero-field transition at 1·15 K, following laser flash excitation into the origin of the $T_0 \leftarrow S_0$ absorption band [18]. To facilitate the comparison we have reproduced this curve in figure 2.

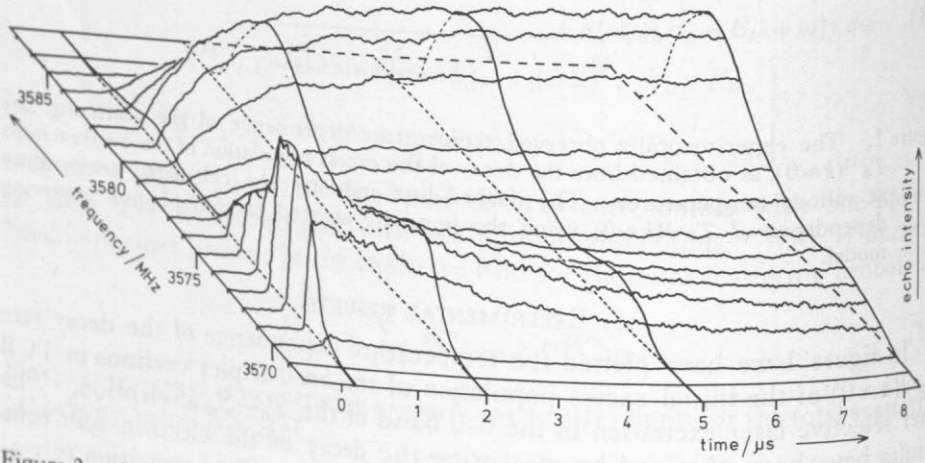

Figure 2. A three-dimensional representation of the time evolution of the ESE detected lineshape of the T_x–T_y triplet exciton zero-field transition in TCB following laser flash excitation into the absorption origin at 374·8 nm. The laser bandwidth is 0·2 cm^{-1} and the pulse energy 3 mJ. The microwave pulses have a peak power of 1 W and a duration of 250 ns. The delay time t indicates the time interval between the laser flash and the first microwave pulse. The interval τ between the microwave pulses is 1·5 μs. The $k \approx 0$ excitons have a resonance frequency of about 3572·5 MHz, and the $k \approx \pm \pi/a$ excitons about 3582·5 MHz. The temperature is 1·15 K.

In the numerical calculation it is convenient to adopt a slightly different notation for k [7, 17]. We write the dispersion relation for the energy E_k of exciton state k in a chain of N molecules, $E_k = E_0 + 2\beta \cos k\theta$ with $\theta = \pi/(N+1)$ and $k = 1, 2, \ldots, N$. For TCB $\beta = +0{\cdot}34\ cm^{-1}$ and the optically accessible state (in this notation $k = 1$) is at the top of the band.

The Pauli master equation [22] governing the population $P^k(t)$ of exciton state k is given by

$$\frac{dP^k(t)}{dt} = \sum_{k'=1}^{N} P^{k'}(t) W_{kk'} - P^k(t) \sum_{k'=1}^{N} W_{k'k}, \tag{16}$$

where $W_{k'k}$ is the probability for scattering from k to k'. We assume that the markovian approximation is valid, that is each scattering event is independent of the preceding ones, which implies that the $W_{k'k}$ are time independent [5]. The solution of (16) is found with the help of laplacian transformation techniques

$$P^k(t) = P^k(0) \exp(-W^k t) + \sum_{k'=1}^{N} W_{kk'} \int_0^t \exp(W^k[t'-t]) P^{k'}(t')\, dt', \tag{17}$$

where $W^k = \sum_{k'=1}^{N} W_{k'k}$ is the total scattering rate from state k to all the other k' states. Since the convolution integral in (17) cannot be solved analytically, we have used a numerical method to calculate $P^k(t)$. To this end we have developed an iterative computer program using the linear approximation of (17)

$$P^k(t+\delta t) = P^k(t) \exp(-W^k \delta t) + \frac{1}{W^k}[1 - \exp(-W^k \delta t)] \sum_{k'=1}^{N} W_{kk'} P^{k'}(t). \tag{18}$$

This approximation is valid only if δt is so small that $P^{k'}(t')$ can be considered a constant and consequently taken out of the integral in (17). To solve the $P^k(t)$, we have taken for $W_{k'k}$ the expressions (13) and (14) derived in the preceding section, assuming that the scattering proceeds via processes where one phonon with an energy $\Delta E = |2\beta(\cos k\theta - \cos k'\theta)|$ is absorbed or emitted.

Figure 3 depicts the three-dimensional representation of the time evolution of the $T_x - T_y$ zero-field lineshape, resulting from the computer calculation. To relate a given exciton k state to a particular zero-field frequency, we have used the dispersion relation $\nu(k) = \nu_0 + 2\mu \cos k\theta$ [14], with $\mu = -2{\cdot}5$ MHz and $\nu_0 = 3577{\cdot}5$ MHz. In addition we have used $N = 50$ for the number of molecules in the chain and a gaussian inhomogeneous broadening of 1·5 MHz for the spin

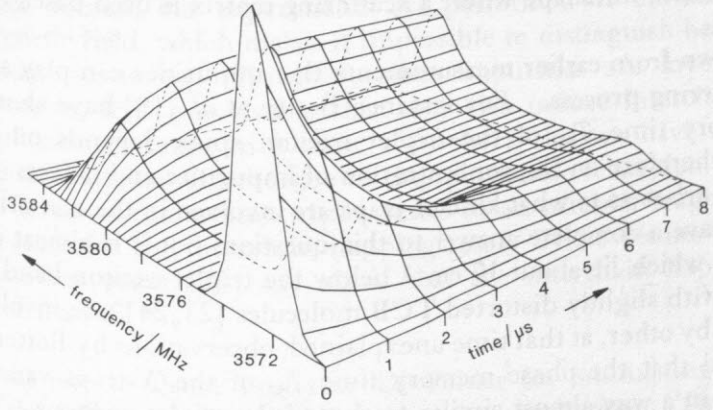

Figure 3. A three-dimensional representation of our computer simulation of the experiment depicted in figure 2, using the impurity assisted exciton–phonon scattering model described in the text.

packet related to a particular k state. The value of $N=50$ seems to be a reasonable estimate for the actual average chain length. (An estimate of the average chain length may be obtained from the dependence of the phase memory time on the zero-field frequency, that is on the particular value of k. An account of this experiment will be presented in a forthcoming paper. The results of the computer simulations, however, turn out to be independent of the chain length since W^k becomes independent of N for $N>15$.) The inhomogeneous width of 1·5 MHz is larger than the homogeneous spin packet linewidth of about 0·1 MHz as derived from spin-echo measurements [18]; it has been estimated from the overall zero-field lineshape and from the variation of the initial ESE detected lineshape with the bandwidth of the exciting laser [18]. The only adjustable parameter in the fit is the constant W in the expressions (13) and (14), which is given a value such that the computed decay rate $T_S^{-1}(k\approx 0)$ is the same as the experimentally observed one. It is seen that on the basis of the assumptions given above, a very good reproduction is obtained of the experimentally observed time evolution of the T_x-T_y lineshape.

As a second and perhaps even more important test of the validity of our model, we calculated the temperature dependence of the scattering patterns as presented in figure 3 to obtain the temperature dependence of $T_S^{-1}(k\approx 0)$. The result is indicated in figure 1 by the dashed line, which very nicely reproduces the experimentally observed temperature dependence of $T_S^{-1}(k\approx 0)$ up to 2 K (where $k_B T$ is almost equal to the bandwidth 4β of the triplet exciton band). We see this as an important support for the validity of our one-phonon impurity assisted scattering model, which seems to apply up to a temperature where $k_B T$ is equal to the bandwidth.

4. Discussion

We have shown that the temperature dependence of the scattering rate $T_S^{-1}(k\approx 0)$ between 1·15 and 2 K can be explained very well by our model for impurity assisted exciton-phonon scattering which takes only one-phonon processes into account. Further support is provided by the close fit between the experimentally observed and computer simulated time dependence of the T_x-T_y zero-field lineshape where a scattering matrix is used based on the same process.

It is known from earlier measurements that impurities can play a role in the exciton scattering process. For instance Botter *et al.* [19] have shown that the phase memory time T_M of the triplet exciton spins depends on the crystal quality and therefore on the concentration of impurities and defects. Naturally the question arises as to what kind of traps are involved in the scattering process. We do not have a complete answer to this question, but it is almost certain that the X-traps, which lie about 17 cm^{-1} below the triplet exciton band and which correspond with slightly distorted TCB molecules [23, 24], are involved. This is supported by other, at that time unexplained, observations by Botter *et al.* [19]. It was found that the phase memory time T_M of the X-traps varies with the temperature in a way almost similar to that of the triplet excitons. This effect cannot be explained by trapping or detrapping mechanisms, because the related rate constants are much too slow. Moreover phonon assisted excitation exchange between trap and band can be excluded. We think that in the exciton scattering

process the X-trap molecule changes its position slightly, resulting in a small change in its zero-field splitting frequency. This modulation of the resonance frequency results in a shortening of the phase memory time of the X-traps with increasing temperature as observed experimentally.

The scattering model discussed above cannot account for the temperature dependence of T_S^{-1} above $T \approx 2$ K. This is not very surprising since above this temperature two-phonon Raman type processes are possible. Such processes are expected to induce a uniform scattering probability over the band, since they are roughly independent of the energy separation ΔE of the two k states involved. Furthermore, a strong temperature dependence is predicted, usually of the order of T^5 to T^7. In the limited temperature range between 2 and 2·5 K it is difficult to ascertain the exact temperature dependence. However, we do have an important additional piece of information, which is also from the work of Botter *et al.* [19]. At 5 K it was observed that a motional averaging of the whole $T_x - T_y$ zero-field lineshape sets in. This indicates that at this temperature the scattering rate must be of the order of the total linewidth, that is $\approx 2\pi \times 10^7\ s^{-1}$. Comparing this value with the estimated contribution of two-phonon processes to the scattering rate T_S^{-1} at 2·5 K, we derive a temperature dependence between these two temperatures $\sim T^{(6\cdot4 \pm 0\cdot6)}$. We are therefore led to believe that Raman-type processes dominate the scattering in this temperature range. Whether impurities also play an important part here remains an open question. In principle, Raman-type processes, without involving impurities, can fulfil both the conditions for the conservation of energy and quasi-momentum. However, impurities again eliminate the second condition and this may facilitate the scattering process.

Another two-phonon process is the Orbach process, where a third, intermediate level is involved. At low temperatures any of the exciton states can in principle act as an intermediate, facilitating the scattering to nearby k states for which the one-phonon process only gives a very low probability. At present we are uncertain about the importance of the Orbach processes ; however preliminary work [24] indicates that the major effects are included in equations (13)–(15).

Finally, we like to mention that our observations may be explained by intra- as well as inter-chain scattering processes. This has not been discussed in the present paper because our experiments are performed in the absence of an external magnetic field, which makes it impossible to distinguish between intra- and inter-chain scattering. However, since impurities are involved in the scattering process, it is conceivable that they also induce interchain hopping with a simultaneous change in k state. To check this we have completed a study of the orientational dependence of the spin-lattice relaxation rates among the Zeeman levels of the exciton triplet states in an external magnetic field to obtain a measure for the interchain hopping rate. These results will be presented in another paper [25] and show that the interchain hopping rate is slightly lower than T_S^{-1}.

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