TRIPLET EXCITON SPECTRAL LINE SHAPES IN MOLECULAR CRYSTALS: 1,2,4,5-TETRACHLOROBENZENE

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Triplet exciton optical absorption line shapes, widths, and positions have been measured as a function of temperature in the molecular crystal 1,2,4,5-tetrachlorobenzene (1CB). At temperatures above 20 K the absorption line has a gaussian shape and increases in width with temperature. At 14 K the line becomes lorentzian. This change in line shape with temperature is discussed in terms of a model first suggested by Toyozawa. The lorentzian line is taken to be evidence of a delocalized exciton state, while the gaussian high temperature line shape implies the localization of the exciton by lattice phonons. The nature of the difference between the optical line width and the previously reported TCB ESR line width is also briefly discussed.

1. Introduction

Energy transport via triplet Frenkel excitons in molecular crystals is a topic of considerable current interest although it has been the subject of extensive investigation for many years [1]. Much experimental [2–5] and theoretical [6–8] attention has been directed towards understanding the role that exciton scatterers such as phonons, impurities, and lattice defects play in the exciton transport process. The difficulty lies in finding experiments with observables that can unambiguously be placed in a theoretical framework to yield insight into the nature of exciton transport. To date, the mode of long range exciton transport at low temperatures (4 K), coherent (wave-like) versus incoherent (diffusive), is still a matter of controversy. It is not even clear at this juncture that the term "coherence" has been defined precisely enough in terms of an experimental observable to make the distinction between incoherent and coherent transport possible.

One experimental method for investigating exciton scattering processes that has considerable theoretical basis is the measurement of exciton absorption line shapes, widths, and positions [5,9]. For triplet excitons both optical and electron spin resonance (ESR) spectral lines have been investigated in this way [4,5]. Here we report temperature dependent optical absorption experiments on the triplet exciton origin of 1,2,4,5-tetrachlorobenzene (TCB). TCB is a particularly interesting compound to study for several reasons. First, it is an example of a basically one-dimensional exciton transport system [3]. As such, investigations of many of its properties are simplified. Furthermore, it may serve as a useful prototype for other one-dimensional systems, such as biopolymers. Second, extensive ESR line shape experiments have been conducted on this system [3,10], and it is of interest to compare the correlation times measured in ESR experiments with the corresponding times measured optically. Third, unlike systems in which triplet absorption line shapes have been measured previously [5], TCB has the interesting features that: (1) the optically accessible $k \approx 0$ level is at the top rather than at the bottom of the band [10], and (2) the TCB triplet exciton bandwidth is only 1.4 cm^{-1} compared to bandwidths of > 10 cm^{-1} in previously measured systems [3,10].

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2. Experimental

The purification and growth of the TCB single crystals have been described previously [8]. During an experiment the crystal was immersed in He vapor and its temperature varied by varying the rate of flow of cooled He gas past the sample in a variable temperature cryostat. The temperature was monitored near the sample with a Si diode, and the quoted temperatures are estimated to be accurate to within ± 0.3 K.

The spectra were recorded using a spectrometer (Jobin–Yvon THR 1500) with a measured resolution of better than 300000. In no case did the instrumental line width contribute significantly to the observed line widths or line shapes. A log amplifier was employed to give absorption curves directly and care was taken to ensure that the absorption was small enough so that the measured line shape indeed reflected the true absorption line shape [5].

Crystals from several different boules were examined. In addition, the crystals were treated to very different temperature cycling processes. In some cases the crystals were cooled to below 77 K in minutes; in others this process took over 24 hours. In only one case were we able to detect any effect of either the origin of the crystal or the manner of cooling on the line shape, position, or width. It was observed that if a particular sample was taken to low temperatures, allowed to warm and then again cooled, significant distortion of both the optical and ground state Raman [11] line shapes resulted. Crystals subjected to this temperature cycling process were not used to obtain the results cited below.

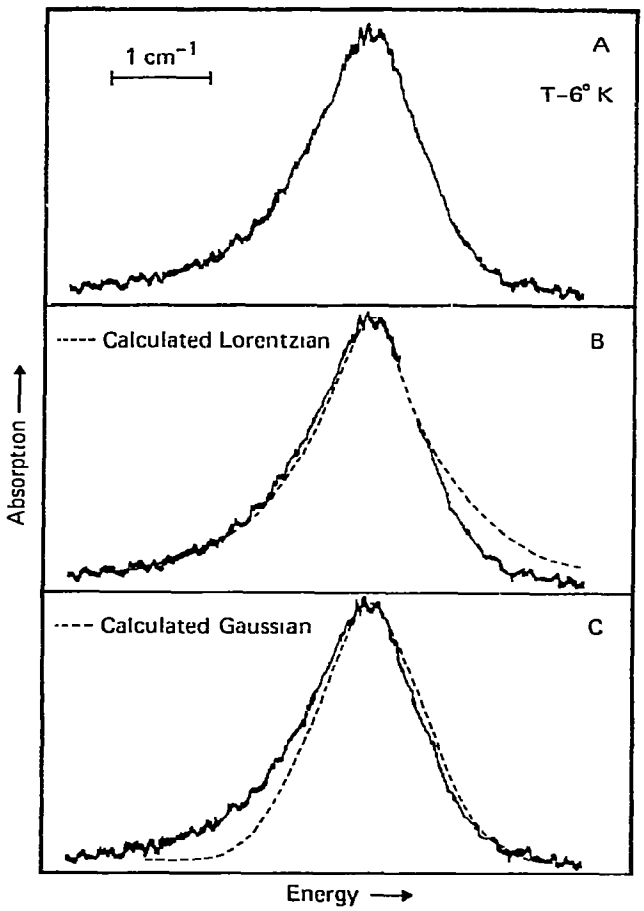

Fig. 1. TCB triplet exciton absorption line shape at 6 K. (a) Absorption line only. (b) Data and calculated lorentzian. (c) Data and calculated gaussian to high energy side. The procedure in (b) and (c) was to measure the absorption peak height and the full width at half height and to construct a lorentzian or gaussian from these two parameters only.

3. Results

3.1. The absorption line shape

In fig. 1a the low temperature absorption line shape is shown. The first important point to note is that the line is an asymmetric lorentzian. Asymmetric exciton absorption line shapes have been previously reported and discussed for the triplet exciton in 1,4-dibromonaphthalene (DBN) [5,12]. The asymmetry is attributed to the asymmetric position of the $k \approx 0$ level at one edge of the exciton band. Unlike DBN, the lorentzian broadening in TCB is on the low energy side of the line (fig. 1b), due to the fact that the $k \approx 0$ level is at the top of the band in TCB. The high energy side of the line falls off like a gaussian (fig. 1c).

As the temperature increases the line becomes more symmetric until, at around 14 K, it has become a symmetric lorentzian as indicated in fig. 2a. Upon further increasing the temperature, the line shape changes and at 22 K it has a gaussian shape as shown in fig. 2b.

3.2. Temperature dependence of the width and position

Fig. 3 shows the temperature dependence of the full width at half maximum for the TCB triplet exciton. At

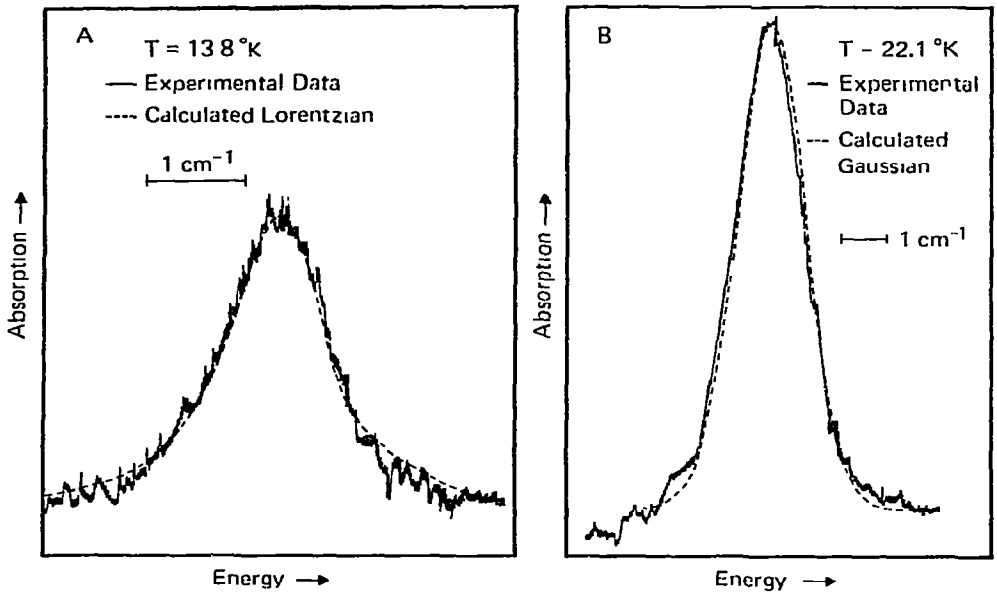

Fig. 2. TCB triplet exciton absorption line shape at (a) 13.8 K and at (b) 22.1 K. The procedure for the calculated curves is described in the caption to fig. 1.

low temperatures (below 12 K) the width is constant within experimental uncertainty and equal to 1.3 ± 0.2 cm^{-1}. Note that while the overall width remains constant in this temperature region, the shape of the line as discussed in the previous subsection begins to change. Above 20 K the width begins to broaden rapidly. The position of the line is also temperature dependent as shown in fig. 4. Comparing figs. 3 and 4 it can be seen that the width and position of the line change with temperature in basically the same manner.

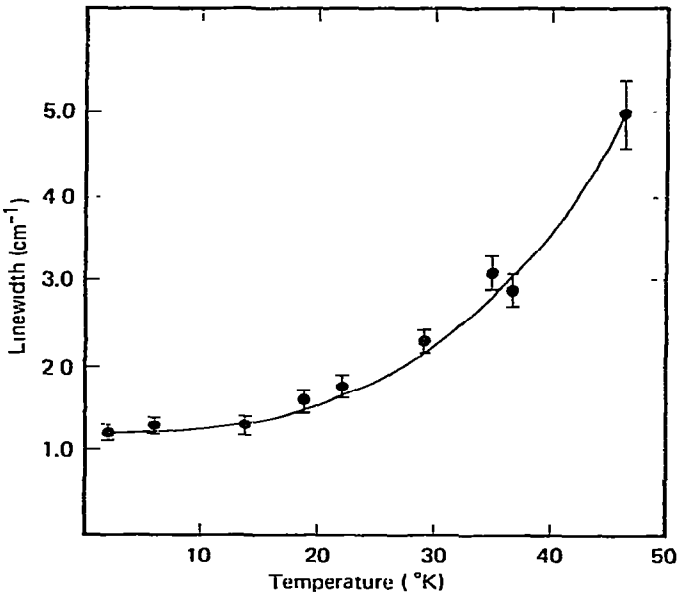

Fig. 3. Absorption line width, that is, the full width at half maximum as a function of temperature.

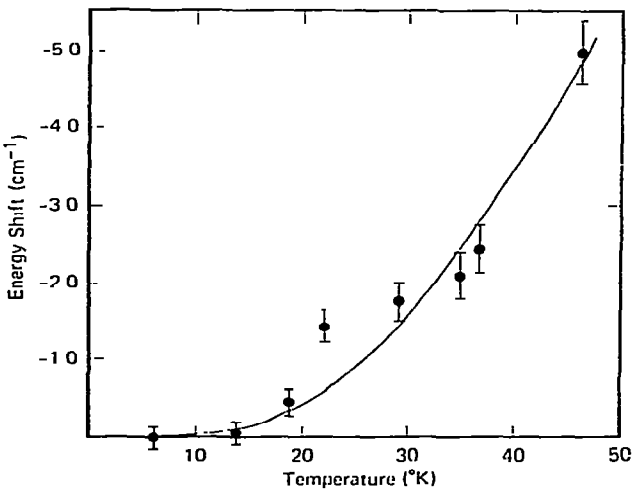

Fig. 4. Energy shift in the absorption line as a function of temperature.

4. Discussion

The origin of the low temperature asymmetric lorentzian line shape has been previously described for the DBN triplet exciton system [5,12]. The asymmetry arises from the asymmetric position of the optically accessible $k \approx 0$ level at one edge of the exciton band. In the DBN triplet exciton the $k \approx 0$ level is known to be at the bottom of the band [12] and the asymmetric lorentzian broadening occurs on the high energy side of the absorption line. Dlott and Fayer [10] have shown that for TCB the $k \approx 0$ level occurs at the top of the band. We thus expect and in fact observe that the asymmetry in TCB occurs on the low energy side of the absorption line.

As shown in fig. 1c, the high energy side of the absorption line is gaussian in appearance. In the DBN system, the overall line is considerably narrower and the non-lorentzian side falls off extremely sharply. The line appears as if it is almost one half of a lorentzian. It has been suggested that DBN molecules containing one or more ^{13}C atoms results in isotopic impurities that are amalgamated into the DBN band and are responsible for an exciton scattering process which makes a major contribution to the *homogeneous* line width [5]. However, similar calculations for the TCB triplet exciton system indicate that scattering by ^{13}C impurities will, in this case, make a negligible contribution when compared to the observed TCB line width. This fact, and the gaussian "high energy" shape, strongly suggest that the low temperature line is to some extent inhomogeneously broadened. If this is the case, it is reasonable to consider the possibility that the TCB absorption line is composed of a gaussian distribution of half-lorentzian lines. Computer simulation studies show that if the half-lorentzians have a width 40 to 50% of the gaussian width, the observed line shape, "low energy" lorentzian and "high energy" gaussian, could be reproduced. Thus, as a rough estimate, the optical homogeneous line width is between 0.4 and 0.5 of the observed 1.3 cm^{-1} width. This corresponds to an optical T_2 on the order of 15 to 20 ps.

As in the DBN case, the TCB triplet exciton absorption line shape becomes more symmetric as the temperature increases and at 14 K the line is a lorentzian with full width at half maximum of 1.3 cm^{-1}, corresponding to a T_2 of 8 ps for the processes responsible for dephasing the $k \approx 0$ exciton.

It is important to compare the 15–20 ps low temperature optical T_2 we have observed in TCB with the 0.9 μs T_2 obtained for this exciton system from ESR line widths [10]. Several points need to be made here. First, optical and magnetic resonance experiments measure different consequences of the exciton scattering process. The optical experiment measures the electric dipole correlation function and the magnetic resonance experiment the magnetic dipole correlation function [13]. In principle there is no reason to believe that the two functions are affected in the same way by these scattering processes, or that they will yield identical correlation times. Second, even if this were the case, the relationship between the correlation time associated with a particular scattering process and line width or T_2 is not straightforward [14]. One requires a model of the exciton scattering process to obtain such a relationship. Models relating optical line widths with microscopic exciton scattering processes have been proposed in the past [7,9,15]. These models all relate the optical line width to the scattering of the $k \approx 0$ exciton into other optically inaccessible k-states, although the models do not yield values for the extent to which k itself is changed. The interpretation of the ESR experiments is more complicated since a direct relationship between the exciton scattering mechanism and the ESR line width has not been established. The line widths have been ascribed to scattering between magnetically inequivalent molecules [6] and to changes in spin–orbit coupling with k [3,16].

Perhaps the most interesting aspect of the TCB absorption line shape is its change from lorentzian to gaussian in the region around 20 K. This behavior has been predicted theoretically [15], but as far as the authors are aware, this is the first experimental observation of such a line shape change. The change corresponds to what Toyozawa has called the transition from weak to strong coupling. Its origin can best be seen by considering first the high temperature gaussian line shape. This line shape arises from the effect of a Boltzmann distribution of lattice coordinates on the energy of the electronic excited state. The line shape in this temperature region is given by the expression

$$I(E) = C \exp[-(E - E_a)^2/2D^2] , \qquad (1)$$

where E_a is the position of the absorption maximum and C is a constant. D is the thermally averaged value of the change in the exciton energy due to random lat-

tice fluctuations. Note that for the gaussian lines the width cannot in any way be related to exciton scattering times.

Toyozawa [15] has shown that eq. (1) will describe the exciton line shape provided $D \gg B$, where B is the exciton band half width (0.7 cm^{-1} for TCB). In the other extreme, where $B \gg D$, exciton transport is sufficiently rapid so that motional narrowing occurs, i.e., the exciton is not affected by the details of the local potential fluctuations. In this case the line shape should be lorentzian.

In fig. 5, we have extracted the values of D from the gaussian absorption lines. It is clear from this figure that in the region where $B \approx D$, the line changes shape from gaussian to lorentzian as predicted by theory. This change may be seen as a transition between the high temperature self-trapped exciton and the low temperature delocalized exciton.

The temperature dependence of the gaussian width has been discussed by Sumi and Toyozawa [17]. In the low temperature regime in which we are working, that is where kT is not much larger than the frequencies of the phonons involved in the exciton localization, the temperature dependence of D is complex. All we can say is that theory predicts an increase in D with temperature, and such an increase is observed.

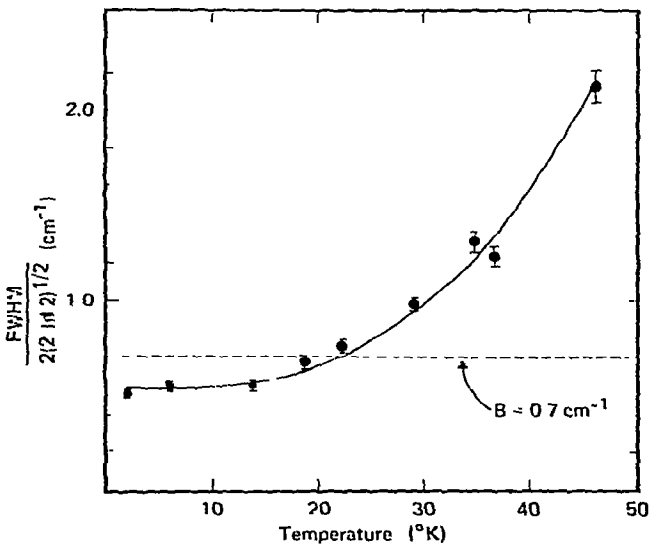

Fig. 5. The full width at half maximum (fwhm) divided by $2(2 \ln 2)^{1/2}$ as a function of temperature. The ordinate is thus equal to the parameter D in eq. (1) when the line shape is gaussian, that is, above the dotted line in the figure. The dotted line locates the energy of the exciton band half width B.

No discussion of a temperature dependent energy shift has been given for the localized exciton. In fact, within the approximations made by Sumi and Toyozawa [17], no such shift is expected. We of course observe an energy shift with approximately the same temperature dependence as the line width. It is noteworthy that when one subtracts out the low energy temperature independent line width, the temperature dependent full width at half maximum and the level shift are equal within experimental error.

5. Conclusions

The TCB triplet exciton optical absorption line shape and position have been measured as a function of temperature from 2–45 K. The exciton line shape is asymmetric to the low energy side at low temperatures, a manifestation of the position of the optically accessible $k \approx 0$ level at the top of the band. As the temperature is increased, the line becomes more symmetric until at 14 K it has become lorentzian.

At 20 K the line shape changes from lorentzian to gaussian which, within the theoretical framework of Toyozawa [15], indicates that the exciton has become localized by the lattice phonons. As far as we are aware, this is the first observation of the effect on an optical spectrum of such a transition from a localized to a delocalized exciton regime.

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