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COMMUNICATIONS

Optical observation of "band-to-band" scattering by time-resolved phosphorescence line narrowing: Exciton dephasing in a quasi-one-dimensional solid[a)b)]

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(Received 9 July 1979; accepted 8 August 1979)

We wish to report our preliminary measurements of (optical) "k-to-k" state scattering in the triplet exciton band of a molecular crystal using time-resolved phosphorescence line narrowing. We chose the system, 1,4-dibromonaphthalene (DBN) since it approximates a quasi-1-D solid quite well and the salient *steady state* spectral features are well characterized. The experiments reported here yield the following: (a) They give the time required for the $k \approx 0$ region to reach complete thermal equilibrium with the rest of the k states following the *direct* optical preparation by a laser; (b) they provide a way for testing the mechanisms of the scattering by exciton–phonon and exciton–photon couplings[1]; and (c) they separate the inelastic contribution to the overall dephasing of the exciton at different temperatures. temperatures.

In perfect and static 1-D solids it is relatively easy to understand the ideas of band transport, simply because of the existence of well-defined states indexed according to the wave vector k of the band and because scattering among them is absent. In disordered systems, however, the picture is more complicated because these k states are mixed by phonons and/or impurities. Since a photon has a wavevector close to zero, primarily the "$k \approx 0$" region of the band can be optically excited leaving other k states unexposed. After the preparation, communication among k states dephases the $k \approx 0$ group, e.g., by scattering the prepared group to all other states (inelastic process) causing complete or incomplete thermalization of population in the band. Elastic scattering events are also possible and will lead to pure dephasing. Our experiments shine some light on these ideas and provide the optical (not magnetic)[2] scattering time for DBN excitons.

The experiments can be described as follows: Using a narrow-band laser we pump the $k \approx 0$ level of DBN to perform phosphorescence line narrowing (PLN) following laser excitation. The emission from the *entire* band to a vibrational exciton in the ground state (wave vector q; see Fig. 1) is then detected as a function of the delay time after the pulse (<8 nsec duration). We also vary the temperature to examine the scattering from the prepared $k \approx 0$ region to other k states in the band. Disorder is introduced by doping the DBN crystals (grown from the melt) with a small fraction of DBN-d_6 (~5%–16%).

Figure 2 shows the PLN spectra obtained at different delay times and temperatures. The short-time behavior clearly shows a narrow spectral band around the $k \approx 0$ region. This implies an incomplete thermalization between the laser-excited $k \approx 0$ group and the k states at the top of the band[3] (width ~ 24 cm^{-1})[4], i.e., at π/c, where c is the crystallographic direction along which molecules

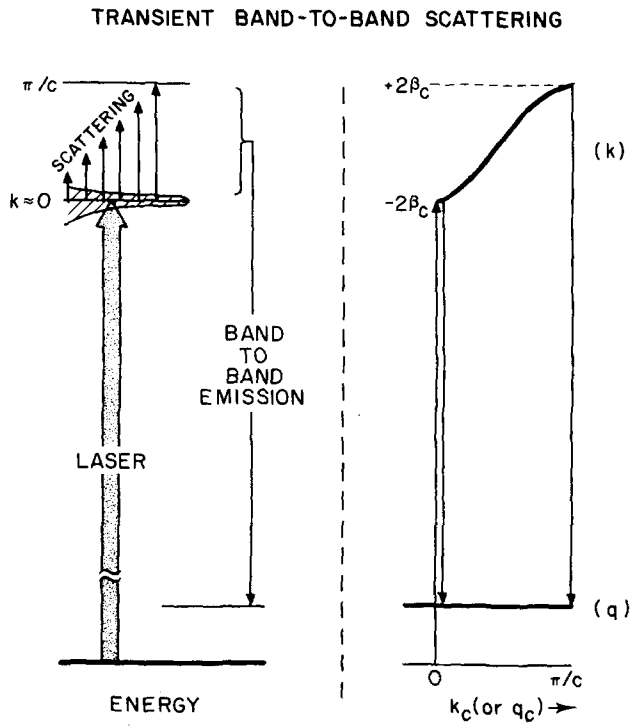

FIG. 1. A scheme for observing *transient* band-to-band optical transitions. The exciton has a k wave vector and the phonon (vibrational exciton) has a q wave vector.

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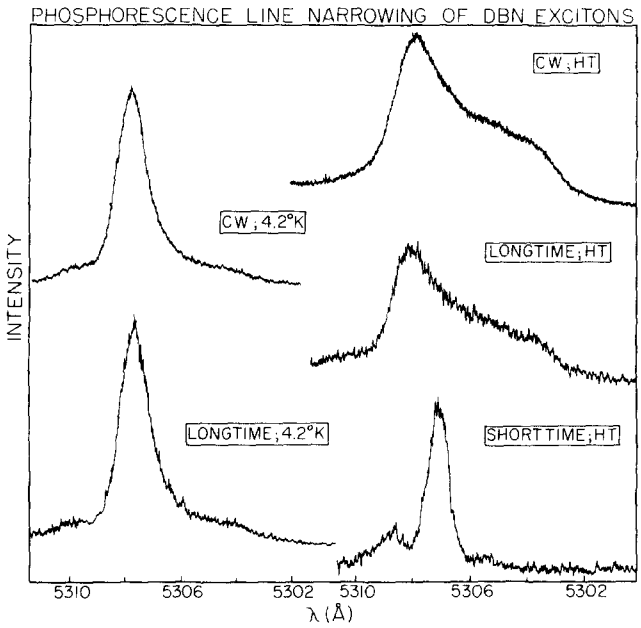

FIG. 2. Phosphorescence line narrowing and cw spectra (moderate resolution) of impure DBN at different temperatures and delay times: HT means high temperature (16.8 °K). A helium flow system was used in these experiments so the absolute temperature is uncertain at the moment, *but* is regulated to 10 m°K during the entire scan.

stack. On the other hand, at times >10 μsec, the band is sampled and we see the characteristic band (electronic exciton)-to-band (vibrational) transition observed under steady state[5] irradiation with an arc lamp (see also Fig. 2). From our preliminary study we conclude that at $T \simeq 20$ K we have two time scales for the optical scattering; the time (~2 μsec) for shifting the population from the bottom-to-the-top of the dressed or disordered exciton and the pure dephasing time of the $\mathbf{k} \approx 0$ group.

In a simple picture, the total dephasing time τ of the *near* $\mathbf{k} \sim 0$ exciton may be expressed as $\tau^{-1} = [T_2'^{-1} + + (\sum T_{1k}^{-1})]$ where T_2' is the time constant for the elastic scattering that contributes to the overall dephasing rate (pure dephasing) and T_{1k}^{-1} is the rate for the population transfer. Using the measured T_{1k} and the fastest emission to the ground state (~100 μsec) we conclude from our line width measurements that the pure dephasing time is ≥ 5 psec[6] and that the exchange of population among k states is relatively slow. This lower limit for the dephasing time is close to that measured by cw absorption.[4,7] Also, it appears that T_{1k} has a uniform distribution in that the $\mathbf{k} \neq 0$ band states receive population in almost a uniform way. However, we must detail these studies before obtaining such a distribution function. Furthermore, the relative importance of "coherent" Raman scattering vs emission must be sorted out. Preliminary studies of these processes were carried out by tuning the laser on-resonance, near-resonance, and off-resonance at different temperatures. On resonance and using system time constants (RC's) that do not distort the intensity profile of the signal, the ratio of the $\mathbf{k} \sim 0$ to $\mathbf{k} \sim \pi/c$ intensities decreases as we change the delay time from 0.1 to 100 μsec.[8] As shown in Fig. 2, this ratio is also temperature dependent.[8] If we use the analysis for a two-level system at different times we obtain a dephasing time that is dominated by T_2' and not T_1 due to the decay to the ground state or T_{1k}. Obviously this is a rather simple picture because there are more than two levels involved in the dephasing. We have also observed similar T_{1k} when the laser was tuned to the other sublattice $\mathbf{k} \simeq 0$ of DBN.

As previously discussed[10] T_2'-type processes have larger cross sections than T_1-type processes, especially at high temperatures. This is due to the fact that T_2' processes involve a larger number of phonons that cause phase (not population) changes in the exciton state. Thus the phase interruptions of the k state can lead to line broadening that is much larger than lifetime broadening. We hope to be able to separate all these scattering events including the coherent Raman-type scattering.[9]

In conclusion, the reported experiments provide a way for measuring exciton scatterings using PLN. The experiments unravel detailed structure hidden under the *inhomogeneously* broadened resonance made of the different k states.

[a] This work was supported by a grant from the National Science Foundation.

[b] Part of this work was announced in the Proceedings of the Second Conference on Dynamical Processes in the Excited States of Ions and Molecules in Solids (DPC-79), University of Wisconsin, Madison, Wisc., 18–20 June 1979.

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[8] D. D. Smith, D. P. Neikirk, and A. H. Zewail (to be published). A high resolution Raman double monochromator with holographic gratings was used to obtain the transient spectra with a *total* system response of ~5 nsec. The emission to the vibronic level is ~1350 cm^{-1} away from the laser. Due to the wavelength difference and detection sensitivity we discriminated against Raman effects from the near $t = 0$ region of the laser. An etalon setup is being incorporated in these experiments in order to quantify the effect and to obtain T_2' directly.

[9] F. A. Novak, J. M. Friedman, and R. M. Hochstrasser, in *Laser and Coherence*, edited by J. Steinfeld (Plenum, New York, 1978), p. 451.

[10] T. E. Orlowski and A. H. Zewail, J. Chem. Phys. 70, 1390 (1979).