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PROPOSAL FOR EXPERIMENTS FOR THE INVESTIGATION OF EXCITON COHERENCE

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We present a theoretical analysis of proposed Ronchi grating experiments directed specifically at transport coherence and vibrational relaxation of triplet excitons in molecular crystals.

Although coherence in exciton transport in molecular crystals has occupied experimentalists and theorists for many years, and although the major theoretical problems appear to have been resolved, a clear demonstration of coherence or an unambiguous measurement of its degree are conspicuously absent. Years ago, it had been thought that the temperature dependence of the energy transfer rate in doped crystals gave evidence of coherence[1]. However, it is now realized that (i) incoherent transport is equally able to produce that dependence and that (ii) energy transfer data could very well be capture-limited and contain little or no information concerning exciton motion. Recently, spin echo experiments[2] appeared to have shown that triplet motion in TCB at low temperatures is highly coherent. And yet, optical lineshape measurements in the same system point to incoherent transport. A detailed reanalysis[3] of trapping (phosphorescence) data[4] in TCB, undertaken specifically to resolve this issue, shows that the situation is quite inconclusive: the data is compatible with coherent as well as incoherent motion.

Even if exciton trapping were motion-limited, it has been shown[5] that coherence would not have a highly discernible effect on trapping. The characteristic length for trapping experiments is the distance between traps and is varied by changing the trap concentration. As this length is a random quantity and controllable only in an average way, and as coherence is a delicate property affected strongly by random variations, a different experimental probe must be sought which would have a systematically varied measuring unit.

We have recently found[6] that Ronchi grating experiments[7] constitute an excellent candidate for such a coherence probe. Triplets are created in the crystal by illumination through a ruling, i.e., an alternating series of opaque and transparent strips. The evolution of the spatially periodic inhomogeneity thus created is measured by observing the total delayed fluorescence from the crystal. It follows[6] that the observed signal is sensitive to $\Sigma_k \Psi^k \Psi^{-k} g^k g^{-k}$ where k spans the relevant Fourier space, Ψ^k is the Fourier transform of the

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probability propagator, and g^k is the transform of the square wave corresponding to the mask placed over the crystal during illumination. The quantity ψ^k contains coherence and other motion information directly, and g^k provides the systematic probe varied by changing the spatial periodicity of the mask. By contrast, in trapping experiments, the observable is sensitive to $\Sigma_m \Psi_m p_m$ where Ψ_m is the propagator and p_m is the trap pair correlation function which is experimentally controllable only in an average way through the trap

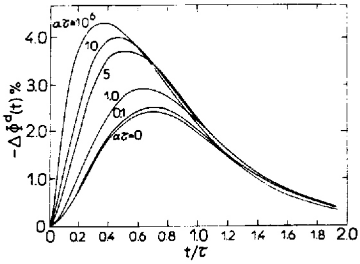

FIGURE 1
Intermediate coherence behavior as reflected in the time dependence of the delayed fluorescence decay signal.

concentration. As an example, we display above the normalized difference between the delayed fluorescence signals in the presence and absence of the ruling, plotted as a function of time in units of the lifetime τ. The bottom curve ($\alpha\tau = 0$) and the top curve ($\alpha\tau \geq 10^6$) signify the limits of perfectly coherent and completely incoherent motion respectively, and $1/\alpha$ is the scattering time. For all curves the ratio of the ruling period to the transport length (a generalization of the diffusion length to motion of arbitrary coherence) is 5. The characteristic curvature near the origin, the slower rise, and the displacement of the peak towards larger times are distinctive signatures of coherence. They arise directly from the pronounced differences in $\psi^k(t)$ for different degrees of coherence.

The primary advantage of the proposed experiment is that coherent and incoherent motion are expected to result in clear differences in the *time dependence* of the signal and not merely in slight changes in features such as temperature variation which could arise from a variety of alternate sources. It is important, therefore, to ensure that other phenomena such as vibrational relaxation do not mask the coherence effects. To this end we have carried out an analysis of relaxation effects on the Ronchi signal by using the theory[8] of the interplay of exciton motion with relaxation. We find that the time dependence of the signal will change if relaxation occurs on a time scale comparable to that of motion. Fortunately, the effect is opposite to that of coherence: finite relaxation rates result in a steeper rise and a displacement of the peak towards smaller times. No other curvature changes occur. It is therefore to be concluded that relaxation effects will not detract from the use of this probe for exciton coherence. We hope that the suggested experiment will be carried out in the near future for a definitive investigation of exciton coherence.

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