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COHERENCE INVESTIGATIONS AND INITIAL CONDITION EFFECTS IN TRANSIENT GRATINGS IN MOLECULAR CRYSTALS

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Abstract - We present the basic theory of transient grating and Ronchi ruling experiments with particular emphasis on coherence issues, the recent applications of the theory to experiments involving singlet and triplet excitons in molecular crystals, and an analysis of initial states relevant to the experiment.

I - INTRODUCTION AND RESULTS

Transient grating observations and Ronchi ruling experiments constitute a powerful experimental probe for the investigation of the motion of singlet and triplet excitons in molecular crystals/1-4/. Its advantage over other methods lies in its directness and its lack of need for external detectors for the measurement of exciton motion parameters. A detailed theory of these experiments, particularly directed at coherence investigations, has been constructed in the last several years/5-7/. Recently, that theory has been applied/8/ to singlet investigations/3/ carried out by Fayer and collaborators in pure anthracene at 20 K, 10 K, and 1.8 K, and to triplet investigations/1/ carried out by Ern and collaborators in various crystals including anthracene and dibromonaphtahlene. In the latter case the mean free path has been found to be of the order of an intersite distance but in the former case it has been found to be more than 1700 intersite distances at 1.8 K/8/. We believe this is the first clear demonstration of singlet exciton transport coherence in a molecular crystal. A detailed study of the effect of initial conditions involved in the creation of these gratings has also been carried out/9,10/. These initial conditions are yet inaccessible to experimental investigation and constitute an open question/9-11/ in the construction of the theory. A unified analysis of the initial condition effects and the relations that exist among various treatments in the literature is now available. Furthermore it can be shown that the effects are negligible in all except borderline cases, but that in them they might become observable in the future with improved experimentation.

II - THE IMPORTANCE OF GRATING OBSERVATIONS

There are two major reasons for the importance and timeliness of transient grating experiments. The first of these reasons is that work carried out recently in close collaboration of experiment and theory/12,13/ appears to lead inevitably to the conclusion that several of the traditional methods are unable to measure the extent of motion of excitons in pure molecular crystals. One is forced to conclude that what has been measured in the past through techniques such as sensitized luminescence is not exciton motion at all but parameters related to the final capture event in which the exciton passes to the guest molecule or trap. Required is thus a series of new experiments based on a new kind of observation which does not employ detector molecules. For triplet excitons, the grating technique (the Ronchi ruling method) is one of the very few such direct methods whereas for singlet excitons it is perhaps the only method which is experimentally practical at the moment.

The second reason is that the transient grating technique has been shown /14/ to be highly suited to the investigation of transport coherence. The characteristic length in grating experiments, viz. the fringe spacing, is a systematic quantity and under close control of the experimentalist. This is in contrast to the characteristic length in other experiments. Thus, even if sensitized luminescence were motion controled, it would not be able to measure the degree of exciton coherence decisively because the relevant characteristic length, viz. the average distance between traps, is highly random. Being a delicate quantity, coherence is not amenable to clear investigation through such a random probe.

III- BASICS OF THE THEORY AND APPLICATION TO EXPERIMENT

All the essential coherence characteristics of the grating observations can be understood easily through an analysis of excitons moving via nearest neighbor interactions on an infinite chain /5-8/. The transient grating signal, i.e. the square of the spatial inhomogeneity, equals $\exp(-2t/\tau)$ times $S(t)$, where τ is the exciton lifetime, and where the function $S(t)$ equals $[J_0(bt)]^2$ in the coherent limit, $\exp(-Kt)$ in the incoherent limit, and is given in the intermediate region by

$$S(t) = \{ J_0\,(bt) + \int_0^t du\, \alpha\ e^{\alpha u}\ J_0 [\ b(t^2-u^2)^{1/2}\ ]\ \}^2 \cdot e^{-2\alpha t}$$

Here α is the scattering rate, and b, which equals $V(a/d)(4\pi)$, is essentially the exciton bandwidth or intersite transfer interaction reduced by the ratio of the intersite distance a to the grating fringe spacing d, and J denotes the ordinary Bessel function.

It is important to notice that while the key ratio which measures the intrinsic coherence of the exciton is that of the mean free path to the lattice constant, i.e. V/α, the key ratio responsible for the presence or absence of oscillations is that of the mean free path to the fringe spacing of the grating, that is b/α. Situations can, and do, occur in which $b \ll \alpha$ but $V \gg \alpha$. In such cases the exciton is intrinsically quite coherent but no oscillations are observed in the grating signal. The degree of coherence can be extracted in such systems from K, the exponent of the grating signal. It is related to the underlying quantities through

$$K/2 = \{ [\ \alpha + (1/\tau)\ ]^2 + b^2 \}^{1/2} - \alpha$$

Aplication of the theory to various experiments has been carried out and values of the diffusion constant and the mean free path extracted from experiment /8/.

An important consequence of the theory is its prediction /8/ that oscillations, which would be an extremely clear manifestation of coherence, might be observed in pure anthracene crystals at 1.8 K with fringe spacings of 1 µm, provided the initial conditions are appropriate/10/. Such small fringe spacings, while not yet produced in these experiments, appear to be within the reach of experiment.

IV - INITIAL STATE ANALYSIS

Although the grating theory described above is well understood, there remains in it an open question. It concerns the nature of the initial conditions involved in the experiment. The assumption made in the standard theory/5-8/, viz. that the exciton density matrix is initially random, i.e., diagonal in the site representation, may or may not be valid in a given situation. It appears plausible that the actual physical manner of illumination might result in such a random initial density matrix, since, at least for the singlet transient grating experiment, the excitation occurs well above the exciton band and is followed by numerous transitions which are well expected to destroy any phase relations present in the original state/2,4/. It is, however, important to investigate the effects of non-random initial density matrices, because the nature of the processes leading from the initially excited state to the exciton state is not known in detail, and also because profound modifications in the time evolution of the signal can occur as a result of non-random initial density matrices/9,11/. There has recently been renewed activity in this initial state problem. At least five rather different initial states of the excitons have been shown to be consistent with the initial spatial inhimogeneity or probability distribution and yet lead to drastically different grating signals. The first of these is the random initial state/5-7/ in which the exciton density matrix is site diagonal. The second is the pair state/9,11/ in which the exciton occupies Bloch states of equal and opposite wavevectors separated by the grating wavevector. The third is a superposition of such pair states centered around arbitrary locations in the Brillouin zone with a Gaussian weight function of varying width/10/. The fourth is such a superposition with a weight function that is pseudothermal in nature, i.e. one which weights the center of the pair state with a Boltzmann factor/10/. The fifth is a true thermal distribution in the exciton band as far as the diagonal elements of the density matrix in the Bloch representation are concerned/10/.

A thorough study has uncovered striking relationships among the various initial conditions. Thus, the first two initial conditions emerge as the extreme limits of the third for infinite or zero width of the wavepacket, and also as the extreme limits of infinite or zero temperature limits of the fourth and fifth initial states. A variety of effects such as that of temperature variations, are being analyzed in this manner. The precise nature of the initial state is, however, still not known and must await, for its elucidation, further work along the experimental front.

Perhaps the most important conclusion of the initial state analysis is, however, that initial state effects are negligible for almost all experiments presented so far in Ronchi ruling and transient grating observations. What this means is that in none of the systems studied so far conclusions drawn from the application of the standard theory to experiment needs to be modified, with the possible exception of singlets in pure anthracene at 1.8 K. Even in this case the maximum effect of non-random initial conditions would be to minimize the oscillatory nature of the signal. Indeed, the conclusion about high coherence/8/ would be reinforced in the presence of non-random conditions.

V - SUMMARY

From our analysis we draw the following conclusions:

1. The transient grating and Ronchi ruling experiments are important not only for coherence studies but even for simple diffusion constant determination.
2. Adequate theory exists and has been applied successfully.
3. These applications have resulted in exciton diffusion constants (magnitude of motion parameters) and mean free paths (coherence studies) explicitly.
4. The applications have demonstrated, for the first time, that singlet motion is highly coherent in pure crystals at low temperatures, specifically in anthracene at 1.8 K.
5. Initial state effects are understood within a unified framework but require further investigations, particularly along experimental directions.

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