

AN EXAMINATION OF RADIATIVE AND NONRADIATIVE EXCITATION TRANSPORT IN THIN ANTHRACENE CRYSTALS: TRANSIENT GRATING EXPERIMENTS

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Picosecond transient grating (TG) experiments have been performed on ultrathin anthracene sublimation flakes at room temperature. The laser excitation wavelength was tuned to the singlet exciton band and the diffracted signal was detected in the reflection geometry. An extension of the expression [1] for the contribution from optical reabsorption to the TG fringe spacing and time dependences is derived. It includes the effects of directional radiation from molecules and a critical angle for total internal reflection. The extension and the original treatment both show that reabsorption will only influence the grating for very large fringe spacings, and therefore does not inhibit the use of the TG for the study of exciton transport. The fringe spacing dependence for small fringes reveals no measurable exciton diffusion in either the *a*- or *b*-crystallographic directions. This sets an upper bound on the diffusion coefficient in anthracene at room temperature at $D \leq 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

1. INTRODUCTION

THE CONCEPTS of excitons and polaritons test our understanding of the basic interaction between light and matter. Molecular crystals provide systems that are simple enough to describe analytically, yet complex enough to demonstrate all the phenomena inherent in more complicated systems. For this reason, the dynamics of excitons, both singlets and triplets, have been studied extensively [2–5]. Experimentally, it is very difficult to elucidate transport properties of excitons. Many experiments have relied on exciton trapping [2]. These experiments are burdened by the fact that trapping dynamics are not well characterized and that the process of trapping affects the results.

The transient grating (TG) technique [4] provides a method for observing the spatial distribution of exciton populations without relying on the secondary trapping process. In the TG experiment, two picosecond laser pulses are overlapped spatially and temporally in a sample. The interference between the two pulses of wavelength λ creates a fringe pattern in the sample where the fringe spacing d is related to the angle between the beams, θ , by the relation:

$$d = 2\pi/\Delta = \lambda/2 \sin(\theta/2). \quad (1)$$

Light is absorbed in the grating peaks, creating excitons, while no excitons are formed in the grating nulls. The diffracted intensity of a probe pulse incident on

the grating at a later time will detect the difference between the number of excitons in the peaks and the number in the nulls.

In the absence of diffusion, population relaxation will cause the grating to decay with the excited state lifetimes. Diffusion of excitons will increase the grating decay by moving excitons from peaks to nulls; reducing the grating diffraction efficiency. In addition to exciton diffusion, there can also be transport because of optical reabsorption. Reabsorption is essentially photon transport. When an exciton fluoresces, the emitted photon can propagate in the crystal and be reabsorbed at another location. Thus, it appears as if the exciton has moved from one point in the crystal to another. Recently, Agranovich *et al.* have developed a theory for reabsorption at room temperature which predicted that the effective diffusion coefficient was very large, $\sim 1 \text{ cm}^2 \text{ s}^{-1}$ [1]. If this were indeed the case, it would be possible to observe radiative transport with the TG technique, but it would interfere with the measurement of exciton transport.

TG experiments on pure materials are complicated by processes which obscure the observation of electronic excitation transport. Foremost is the unwanted generation of acoustic waves and heat in the sample. This problem can only be overcome by a thorough understanding of the acoustic phenomena. For ultrathin crystals, this is a complex problem which is now understood [6]. It is also necessary to perform experi-

ments at intensities which are low enough to insure that there will be no exciton–exciton interaction. Because of the strong light-matter interaction, polariton effects can also complicate the experiment [1]. At room temperature, however, it is reasonable to assume that polariton effects are unimportant because thermal fluctuations rapidly damp the polaritons into excitons. The excitons will be localized excitations, and the oriented gas model of a molecular crystal will be valid.

TG experiments were performed on sublimation flakes of anthracene at a variety of fringe spacings ranging from $2.00\ \mu\text{m}$ to $0.45\ \mu\text{m}$. For these degenerate four-wave mixing (DFWM) experiments, the frequency of the laser was tuned directly into the singlet origin to search for exciton transport and radiative transport.

No fringe spacing dependence of the diffracted signal intensity is observed, demonstrating slow exciton transport and in apparent contradiction to the reabsorption theory. The approximations used to calculate the diffusion due to reabsorption in [1], however, are not applicable to the situation studied here. Slight modifications of the theory have been made, and the data is in agreement with the theory. The experimental results imply that the upper limit on the diffusion coefficient for either excitons or photons at room temperature is $5 \times 10^{-4}\ \text{cm}^2\ \text{s}^{-1}$. It is demonstrated that radiative transport will be significant only for extremely large fringe spacings.

2. EXPERIMENTAL PROCEDURES

The experimental set-up for performing the TG has been presented in the literature and will not be reproduced here [7]. Basically, a Q -switched, mode-locked, Nd:YAG is used to produce pulses of roughly $5\ \mu\text{J}$ and $30\ \text{ps}$, tunable from 365 – $415\ \text{nm}$. The samples were sublimation flakes of highly purified anthracene, ranging in thickness from 0.35 to $2.0\ \mu\text{m}$ s, which were optically contacted to fused quartz [6]. Since the samples are very thin, the Bragg diffraction condition is relaxed and the probe beam can be brought in perpendicular to the sample. This enables the probe beam to remain fixed while the fringe spacing is varied. The laser wavelength was tuned to the singlet origin at $\sim 3978\ \text{\AA}$ to minimize the heat deposited into the sample and thus the acoustic effect. Since the light is strongly absorbed at this wavelength, the diffracted signal was detected in the reflection geometry. This geometry reduces the contribution of acoustic phenomena [6] to a small constant offset in the signal caused by heating of the crystal.

3. THEORY OF RADIATIVE TRANSPORT

The influence of the excited state lifetime and diffusive exciton transport on the TG time and fringe spacing dependences have been discussed in the literature [4, 5] and are contained in the first two terms on the right hand side of equation (2), respectively. Radiative transport has been considered by Agranovich *et al.* [1]. Here we make two modifications of the radiative transport theory. Both change equation (18) of [1]. First, to correct for the fact that a dipole radiates power with a $\cos^2\ \Theta$ dependence, where Θ is the angle from the dipole axis, it is necessary to include this angular dependence in the integrand. Second, the previous theory did not allow any photons to escape from the crystal, making it effectively infinite. This overestimated the reabsorption effect. A reasonable correction is to include a critical angle, above which there is total internal reflection and below which the reflection coefficients are identically zero. This would underestimate the reabsorption effect if the actual critical angle is used. By adjusting the critical angle, the number of photons reflected back into the crystal can be matched to a real sample. The advantage of setting the reflection coefficient to zero is that the integral in equation (18) of [1] remains analytic.

When these corrections are made, the expression for the grating decay time τ is:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + D\Delta^2 - \frac{1}{\tau_0} \int a(\nu)K(\nu) \left\{ - \frac{((\Delta^2 + K(\nu)^2)n^2 - \Delta^2)^{1/2}}{2\Delta^2 n^2} + \frac{K(\nu)^2 + D^2}{2\Delta^3} \tan^{-1} \left[\frac{\Delta}{((\Delta^2 + K(\nu)^2)n^2 - \Delta^2)^{1/2}} \right] \right\} d\nu. \quad (2)$$

In this expression, τ_0 is the excited state lifetime, D is the exciton diffusion coefficient along the grating, Δ is the wavevector of the grating, $a(\nu)$ is the fluorescence lineshape multiplied by the fraction of absorption events at frequency ν that create excitons, $K(\nu)$ is the absorption lineshape, and $n = (\cos\ \Theta_c)^{-1}$, where Θ_c is the critical angle for total internal reflection. With this expression, it is possible to plot τ as a function of Δ . This is shown in Fig. 1 for five values of the exciton diffusion coefficient, ranging from 0 to $10^{-2}\ \text{cm}^2\ \text{s}^{-1}$. In evaluating equation (2), we used $\Theta_c = 38^\circ$, which corresponds to an index of refraction of 1.6 , and have used parameters from [1] and approximated $a(\nu)$ and $K(\nu)$ as Gaussians with 14% overlap.

As seen in the figure, the effect of reabsorption on the observed decay time is negligible, as indicated by the case when $D = 0\ \text{cm}^2\ \text{s}^{-1}$. It will only be manifested

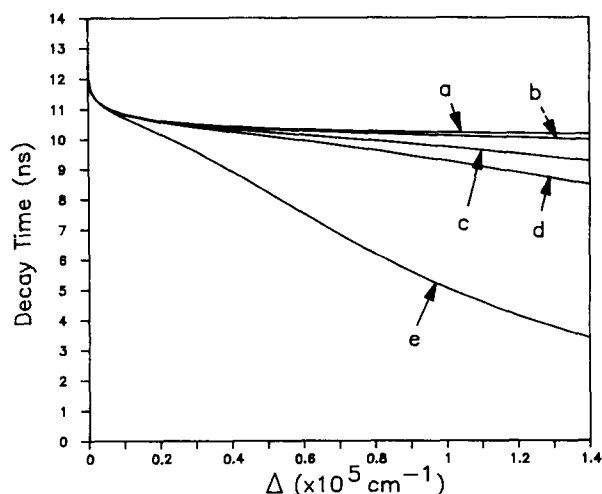


Fig. 1. Predicted grating decay times from equation (2) as a function of grating wavevector for five different values of the diffusion coefficient: (a) $D = 0$; (b) $D = 10^{-4}$; (c) $D = 5 \times 10^{-4}$; (d) $D = 10^{-3}$; (e) $D = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$. The critical angle of 38° corresponds to a refractive index of 1.6.

in experiments performed with a very large ($> 13 \mu\text{m}$) fringe spacings (very small Δ). In this region, the change in the observed decay time with respect to fringe spacing is large, corresponding to an effective diffusion coefficient for reabsorption of $\sim 1 \text{ cm}^2 \text{ s}^{-1}$, as predicted by Agranovich. These very large fringe spacings are difficult to achieve experimentally. However, since small fringe spacings are needed to detect small diffusion coefficients, TG experiments will be performed in the region of Fig. 1 where there is no significant contribution of reabsorption to the observed lifetime. So, in typical grating experiments, where $d \leq 10 \mu\text{m}$, reabsorption will not be apparent. Figure 1 also demonstrates that it would be very difficult to extract a diffusion coefficient if $D \leq 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ given the anthracene excited state lifetime, but should be readily observable for $D \geq 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$.

4. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the TG response of a $\sim 1 \mu\text{m}$ anthracene sublimation flake at two fringe spacings: $1.67 \mu\text{m}$ and $0.45 \mu\text{m}$. The two scans are identical. The scans can be fit to a biexponential decay. The shorter decay time is typically $\sim 1 \text{ ns}$ and the longer decay time is $\sim 10 \text{ ns}$. There is also a small offset in the data that is caused by the heating of the sample. Due to these complications, the 10 ns component of the lifetime can only be obtained to $\pm 0.5 \text{ ns}$. Neither of these

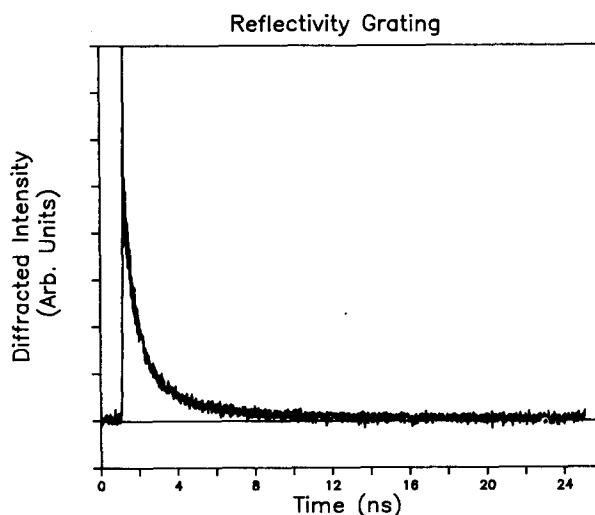


Fig. 2. Transient grating decay of $1 \mu\text{m}$ anthracene sublimation flake. The incident light was b -polarized with wavelength $\lambda = 3978.0 \text{ \AA}$, and the grating was directed along the b -axis of the crystal. The two scans in the figure were taken at fringe spacings of $1.67 \mu\text{m}$ and $0.45 \mu\text{m}$, and overlap quite well. This is evidence that no transport is observed at room temperature.

decay times shows any systematic variation with fringe spacing. Thus, within the limits of the experiment, a diffusion coefficient of $D = 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ would be perceptible. Therefore, the exciton diffusion coefficient must be less than this number. The same results were obtained with the grating directed along the a - or b -crystallographic axes.

The long time component of the exponential varies somewhat with the sample and is thickness dependent. It can be associated with the decay of polaritons through the bottleneck region as explained by previous researchers [9], or simply with the exciton state lifetime at room temperature. At room temperature, the difference is basically one of semantics.

The fast component is also independent of fringe spacing and has a decay time of $\sim 1.0 \text{ ns}$. This decay may be due to site surface excitons studied by a number of workers in this field [8], which are expected to have short lifetimes. Because the diffracted signal is detected in the reflection geometry, the experiment is more sensitive to the perturbation in the dielectric tensor caused by surface states. However, even under these conditions, where the penetration depth is ~ 50 molecular layers, one would not expect the site surface excitons to contribute so much to the signal. It is possible that molecules within a few tens of molecular layers from the surface are perturbed by their proximity to the surface and thus have a fast decay time.

Spatial redistribution of the excitons [10, 11] from

the front to the back surface may account for this fast decay, but the mechanism for this cannot be exciton diffusion. Considering the dispersion relations [12], diffusion in the *ab*-plane should be greater than diffusion along the *c*-axis. Since these experiments indicate that diffusion along the *b*-axis is $\leq 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, diffusion along the *c*-axis should be $\leq 10^{-4} \text{ cm}^2 \text{ s}^{-1}$. Nishimura *et al.* report a value of $D = 40\text{--}100 \text{ cm}^2 \text{ s}^{-1}$ along the *c*-axis [10]. This number is orders of magnitude too large to be exciton diffusion. Although photon diffusion cannot be ruled out, the calculations presented above for photon diffusion in the *ab* plane suggest that the large value reported for the *c* direction is inconsistent with radiative diffusion.

The magnitude of the diffusion coefficient at room temperature can be related to the exciton hopping time through the formula $D = l^2/2t$, where l is the lattice spacing and t is the hopping time. For transport along the *a*- or *b*-axis, a diffusion coefficient $< 5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ implies a hopping time of $> 10 \text{ ps}$, which is consistent with other studies [1].

Radiative transport is not important under these experimental conditions for several reasons. Given the small overlap of absorption and emission, only a fraction of the photons emitted get reabsorbed. The majority of excitons simply emit a photon which leaves the sample. The small overlap insures that a photon will not take more than 2 or 3 steps before being emitted from the crystal. At large fringe spacings, the effect of reabsorption is noticed because the reabsorbed photons are still located at or near the grating peaks. This makes the observed lifetime of the system longer than the excited state lifetime. When the fringe spacing is smaller the reabsorption integral

becomes independent of fringe spacing and is not noticed in the TG experiment.

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