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Coherence in singlet-exciton motion in anthracene crystals

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We investigate the question of the transport coherence of singlet excitons by carrying out a theoretical analysis of some recently reported transient-grating experiments in pure crystals of anthracene. We calculate the coherence time and the mean free path of the exciton at 20, 10, and 1.8 K from the reported observations, and conclude that the latter indicate exciton motion in anthracene to be quite coherent at low temperatures. The mean free path is found to be of the order of 100 intersite distances at 20 K and more than 1500 intersite distances at 1.8 K. We suggest further experiments, give explicit predicted signals for specific values of the fringe spacing of the grating, and show that, on the basis of the reported values of the diffusion constant, one may expect a clearly nonexponential time dependence—with oscillations—in the signal at 1.8 K for fringe spacings as large as 1 μm. Signals without oscillations but with clearly discernible nonexponential character are shown to be expected for 1 μm fringe spacings at 10 K. We also present estimates of the mean free path of triplet excitons in several crystals including anthracene based on diffusion constants measured through Ronchi ruling experiments. They show coherence to be lost within distances of the order of a lattice constant for the temperatures studied, which are all above 100 K.

I. INTRODUCTION

Coherence in the transport of Frenkel excitons in molecular crystals has been a much debated topic for a number of years. Several of the major theoretical questions have been answered and reviewed in the recent literature.[1–3] However, a clear experimental demonstration of transport coherence, especially for *singlet* excitons, is, as yet, unavailable. Since triplet excitons can be studied through the use of techniques involving magnetic fields which probe their spin, some results concerning their coherence have been reported on the basis of optically detected magnetic resonance[4] and spin-echo methods.[5] However, even for triplets, coherence questions have not been answered conclusively.[6] For singlets, the situation is entirely unclear. It has been sometimes argued[7–9] that the temperature dependence of the energy-transfer rate observed in sensitized-luminescence experiments is an indication that exciton motion is coherent. However, that those experiments do not contain such information is clear for two reasons: First, recent work[10] has shown that it is quite possible, and indeed highly probable, that sensitized-luminescence observations in molecular crystals are capture controlled (rather than motion controlled), and that therefore the observed temperature dependence is indicative of the actual process of capture of the exciton by the dopants and not of the motion in the host crystal. Second, even if the observations were motion controlled and the observed energy-transfer rate were proportional to the exciton diffusion constant, a decrease of the diffusion constant with an increase in the temperature would show merely that motion is hindered by phonons or intramolecular vibrations in the crystal rather than assisted by them, as would be the case in an activated situation. Coherence has to do with the magnitude of the mean free path relative to the lattice constant and not with whether motion is assisted or hindered by phonons.

In a recent paper, Rose *et al.*[11] have reported an investigation of exciton transport in anthracene crystals at low temperatures using the method[12] of picosecond transient gratings. In this method a picosecond laser pulse is split into two parts and the two parts are caused to arrive simultaneously at a variable angle in the crystal. Optical absorption creates an exciton population which varies sinusoidally in space as a result of interference of the two pulses. The subsequent time evolution of the (transient) exciton grating thus produced is monitored through diffraction of a third laser pulse which is delayed appropriately. The evolution is affected by exciton motion and can be studied to extract transport parameters such as the diffusion constant, provided the relevant characteristic length, e.g., the "diffusion length," is comparable to the fringe spacing of the grating. This experimental technique, which was pioneered by Fayer[12] in the context of singlets in molecular crystals, is conceptually similar to the Ronchi ruling experiments developed earlier for triplets by Ern *et al.*,[13] and has also been recently used actively by Powell and others in the inorganic realm.[14,15]

The experiments of Rose *et al.*[11] constitute, to our knowledge, the first direct measurement of the diffusion constant for *singlets* in a pure molecular crystal. The diffusion constant they have reported varies from (10±2) cm^2/s at 1.8 K, through (1.3±0.4) cm^2/s at 10 K, to (0.8±0.2) cm^2/s at 20 K. They have touched on the coherence issue by suggesting that a quasicoherent transport might account for the increase of the diffusion constant at lower temperatures. The argument is similar to the one[7–9] that was applied to the early energy-transfer rates and which we have mentioned above to be not valid since it is certainly possible to have diffusion constants that decrease with increasing temperature even when the mean free path of the moving particle is of the order of the lattice constant.[16–18] However, we shall show below that the conclusion of partial coherence is very probably correct, although for quite different reasons. We use the theory of transient gratings developed by Kenkre *et al.*[19–22] and address the following issues:

(i) Does the *magnitude* of the reported diffusion constants contain sufficient information to answer the coherence question?

(ii) Should the large values of the reported diffusion constant D give cause for concern? To be noted here is the fact that a "hopping rate" F calculated from the expression $D=Fa^2$ from the values given in Ref. 11 (a is the nearest-neighbor distance) is of the order of 3×10^{14} s^{-1} (about 40 times larger than the Davydov splitting), even at 20 K.

(iii) If exciton motion is partially coherent at the temperatures studied, why are the signals not indicative of the oscillations or shape characteristics predicted by theory, as in Refs. 19—22?

We obtain an affirmative reply to the first question above, conclude that the large values of D/a^2 relative to the Davydov splitting involve no inconsistency and, indeed, are an indicator of coherence, and show under what experimental conditions explicit manifestation of coherence may be expected in the shape of the time dependence of the grating signal.

II. COHERENCE PARAMETERS FOR SINGLETS IN ANTHRACENE

The theory for transient gratings[19–22] shows that, if the observed transient-grating signal exhibits no discernible nonexponential character, i.e., can be described by $\exp(-Kt)$, the decay constant K is given by

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

Here, α is the reciprocal of the scattering time, $b=4V\sin(\eta/2)\approx4V\pi a/d$, η is the dimensionless wave vector of the transient grating, d is the fringe spacing, a is the intermolecular distance, τ is the exciton lifetime, and V is the matrix element of the intersite-transfer interaction, assumed to be effectively nearest neighbor for computational convenience. We take this opportunity to correct an error in the expression for K that has been given earlier[2,20] and also used[14] in the analysis of experiment. The erroneous expression is

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

It is identical to the correct expression (1) in the limit of complete incoherence, or in the absence of exciton decay, or generally when $\alpha\tau\gg1$, and may be converted to (1) by the simple replacement of α by $\alpha+1/\tau$. The difference, which is negligible in many practical cases, arises from a subtlety (see Appendix) in the connection between partially coherent exciton dynamics in the presence and absence of exciton decay. The correct expression (1) has also been given earlier in Refs. 21 and 22.

Since the grating signals in Ref. 11 have been reported to be exponential in time, we apply Eq. (1) to their data and construct Table I below. We take the intersite-transfer matrix element V to be 50 cm^{-1}, i.e., equal to roughly $\frac{1}{8}$ of the observed exciton bandwidth. This assumption involves an approximation which will be commented upon in detail below. Given a value of V, the only unknown in Eq. (1), viz., the scattering rate α (and therefore the mean free path of the exciton and the degree of its coherence), can be extracted from the experiments of Ref. 11 simply from the magnitudes of K. Neither the temperature dependence nor a nonexponential character of the signal is necessary for the purpose.

The first four columns of Table I contain experimental information from Ref. 11, d and K being, as stated above, the fringe spacing and the signal decay rate, respectively. The last three columns contain our deductions concerning the coherence parameters of the system. These are α, the reciprocal of the time between scattering events; Λ/a, the number of nearest-neighbor distances over which the exciton moves coherently, i.e., without being scattered; and Λ, the mean free path. We calculate the latter as the product of the average group velocity $Va\sqrt{2}$ and the time between scattering events $1/\alpha$, and take the nearest-neighbor distance a to be 0.524 nm. It is calculated as $a=\frac{1}{2}(a_0^2+b_0^2)^{1/2}$ where a_0 and b_0 are the anthracene lattice constants in the **a**-**b** plane.

TABLE I. Scattering rates α and mean free paths Λ for singlet excitons in anthracene as obtained from the transient-grating experiments of Ref. 11.

T (K)	τ (ns)	d (μm)	K (10^8 s^{-1})	α (10^9 s^{-1})	Λ/a	Λ (nm)
20	10	3.2	7.6	17	125	63
		4.6	4.2	21	101	53
10	10	4.1	10	7.4	286	150
		9.6	3.1	8.7	243	128
1.8				≤1.2	≥1770	≥930

The first two rows of Table I show the results of a detailed direct application of Eq. (1). In particular, the values for d and K given in the second row ($T=10$ K) were taken from the examples for the transient-grating signals presented in Fig. 2 of Ref. 11, while those in the first row ($T=20$ K) were obtained from the diagram presented in their Fig. 4(b). For $T=1.8$ K, signal details are unavailable, but the value of D has been reported directly[11] as being 10 cm^2/s. We cannot, therefore, use Eq. (1) to extract α, but it may be estimated from the reported D through the well-known relation $D=2V^2a^2/\alpha$. Because the diffusive-motion assumption made in Ref. 11 to extract D from K is not necessarily accurate, the resulting numbers are not as reliable as the others. This simplified procedure of obtaining α and Λ from the D's reported in Ref. 11 rather than from Eq. (1) involves an *a priori* assumption of transport incoherence (on the length scale of the fringe spacing) and yields, for the other temperatures studied, $\alpha(20\text{ K})=1.6\times10^{10}\text{ s}^{-1}$ and $\alpha(10\text{ K})=1\times10^{10}\text{ s}^{-1}$. The latter values are not very different from the results in Table I obtained from the exact prescription of Eq. (1). This fact should not be used to lend support to the validity of applying the simplified procedure at 1.8 K. The procedure is obviously expected to be less reliable than the use of Eq. (1) when exciton motion is substantially coherent, as is expected to be the case at $T=1.8$ K. Nevertheless, we show that the simplified procedure yields a reliable upper bound on the values of α. The experimental observable in a grating experiment is K. When values of D are reported directly in such an experiment under the diffusive-motion assumption, the observed K is interpreted through the incoherent limit of Eq. (1),

$$K=2[(b^2/2\alpha_i')+1/\tau]\ , \tag{2}$$

the quantity $b^2/2\alpha_i'$ being identical to $4\pi^2D/d^2$ with the correspondence $D=2V^2a^2/\alpha$. Equation (2) is obtained from Eq. (1) through a simple binomial expansion[2,19,20] in powers of b/α_i', and the subscript i refers to the incoherent limit being involved. By α_i' we mean α_i+1/τ. Since the correct interpretation of the observed K should be carried out by equating K to the right-hand side of Eq. (1), the relation between the correct α and the α_i obtained from the simplified procedure used above for $T=1.8$ K is obtained simply by equating the right-hand sides of Eqs. (1) and (2). The result is

$$\alpha'/\alpha_i'=2(\alpha'/b)^2\{[1+(b/\alpha')^2]^{1/2}-1\}\ . \tag{3}$$

It is easy to see that the right-hand side of Eq. (3) lies between 0 and 1 for all values of α' and b. This shows explicitly that α cannot exceed α_i. Inverting (3) gives the prescription

$$\alpha'=\alpha_i'[1-(b/2\alpha_i')^2]\ , \tag{4}$$

which allows one to obtain α from α_i if the fringe spacing required to obtain b from V and a is known. From Eqs. (3) and (4) it thus follows that the use of the simplified procedure, which has been used to obtain the coherence parameters for $T=1.8$ K, cannot overestimate the mean free path, i.e., the degree of coherence, and that the more incoherent the motion the smaller the error involved in using that procedure.

Two further comments concerning Table I need to be made. The lifetime of the exciton at 10 K given in the second column of Table I was obtained by extrapolating the diagrams in Figs. 3(a), 3(b), and 4(a) of Ref. 11 to $d=\infty$. Equation (1) shows that, for this limiting case, K should assume the value $2/\tau$, yielding $\tau(10\text{ K})=10$ ns. For $T=20$ K, their Fig. 4(b) yields $\tau(20\text{ K})\approx30$ ns, if the same extrapolation procedure is applied. In this case, however, the extrapolation seems to be subject to rather large uncertainties. On the other hand, Braun *et al.*[23] have determined the exciton lifetime in pure anthracene crystals by using two-photon excitation to avoid the influence of surface traps and exciton-exciton annihilation and by correcting for reabsorption effects. Their results are that τ depends only weakly on the temperature between 10 and 20 K. This agrees with the findings of Logan *et al.*[24] We have therefore taken the same lifetime for 10 and 20 K ($\tau=10$ ns) in Table I. This uncertainty in τ does not affect the results for α significantly. Had we taken $\tau=30$ ns, the corresponding values of α would have been 1.4×10^{10} and $1.3\times10^{10}\text{ s}^{-1}$ instead of the respective entries 1.7×10^{10} and $2.1\times10^{10}\text{ s}^{-1}$ in Table I.

Our use of Eq. (1) involves the replacement of long-range dipole-dipole interactions responsible for singlet-exciton motion by *effective* nearest-neighbor ones. We do this because theoretical calculations of the signal are considerably more complex for the former, and because the long-range character has, at least qualitatively, the same kind of effect on both the motion and extent of the observed bandwidth [which we use to deduce the nearest-neighbor matrix element V in Eq. (1)]. Thus, the V in our analysis does not equal the nearest-neighbor dipole-dipole matrix element, but is larger than the latter. The value we have used in constructing Table I is 50 cm^{-1}, which corresponds to $1.5\times10^{12}\text{ s}^{-1}$. This is roughly $\frac{1}{8}$ of the exciton bandwidth.[25] While such a prescription for obtaining the interaction matrix element is known to be valid for triplet excitons, the presence of long-range interactions for singlets excitons complicates the situation. A clear statement of its precise range of validity is unavailable and must await an exact treatment of long-range interactions. Meanwhile, we use the prescription in the spirit of representing the long-range interactions by effective short-range ones in the same way as for motion. We would like to point out that considerable uncertainty exists[26–31] in an unambiguous effective V for long-range interactions. If the number of nearest neighbors involved in the transport interaction is taken to be four, as would be the case in a simple two-dimensional crystal, the value of 50 cm^{-1} we have used appears to be compatible with the experimental finding of Glockner and Wolf,[25] who reported that the sum of the squares of the interaction matrix elements was equal to 9600 $\text{cm}^{-2}\pm50\%$. If one replaces the value of V we have taken by one a factor of f larger, one obtains a value of α which is f^2 times larger and a mean free path Λ which is $1/f$ times smaller than the values reported in Table I.

III. NONEXPONENTIAL SIGNALS AND PREDICTIONS OF THEORY

The answers to questions (i) and (ii) posed in Sec. I should now be clear. If V is known independently, the magnitude of the observed K is indeed sufficient to obtain coherence information because the theory of transient gratings[2,19–22] gives α directly through Eq. (1). The quantity D/a^2, which equals $2V^2/\alpha$ in general, need not be restricted to be of the order of V. Since $V\sqrt{2/\alpha}=\Lambda/a$, it is only for completely incoherent motion, wherein $\Lambda \leq a$, that D/a^2 is bounded above by $V\sqrt{2}$. That D/a^2 obtained from the observations[11] exceeds this bound appreciably is an immediate indication that the mean free path is appreciably larger than the lattice constant, and, alternatively, that the motion is coherent over an appreciable distance.

Question (iii) may be addressed by using the theory of Kenkre *et al.*[19–22] to calculate the explicit time-dependent transient-grating signal. It is generally given as

$$S(t)=e^{-2t/\tau}\left[J_0(bt)e^{-\alpha t}+\int_0^t du\, e^{-\alpha(t-u)} \times J_0\left(b(t^2-u^2)^{1/2}\right)\right]^2, \quad (5)$$

where the symbols have the same meaning as in Eq. (1). In Fig. 1 we show the observed signal of Ref. 11 for $T=10$ K and a fringe spacing of 4.1 μm (curve C) along with the theoretical result (curve A) from Eq. (5), as well as the exponential approximation e^{-Kt} (curve B) with K reported in Ref. 11. As expected, the latter two coincide almost exactly and are in complete agreement with the data. The reason for no vestiges of coherence being present in the signal, despite the fact that the mean free path is of the order of 100 intersite distances, is that, while the inequality $V \gg \alpha$ holds here, $b \gg \alpha$ does not. As has been explained in detail elsewhere,[21] the quantity b, which is essentially V reduced by the ratio (a/d) of the intersite distance to the fringe spacing, plays the role of an effective V in the grating experiment. It appears that, for $T > 1.8$ K and the fringe spacings used in Ref. 11, the interesting relation $V \gg \alpha \gg b$ prevails for singlets in anthracene. The first part of the inequality corresponds to the fact that the exciton moves coherently over many lattice constants, and the second part corresponds to the fact that its motion is, nevertheless, incoherent on the length scale of the fringe spacing. The absence of nonexponential character in the signal, despite the large value of Λ/a, is thus understood completely.

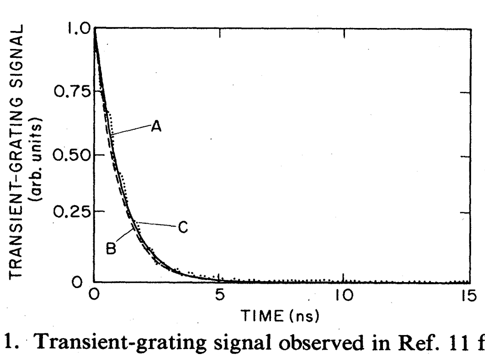

FIG. 1. Transient-grating signal observed in Ref. 11 for singlet motion in anthracene at 10 K (curve C, dotted) and comparison to the prediction of the exact theory of Refs. 19—22 (curve A), as well as to the exponential approximation (curve B, dashed). The experimental signal corresponds to a fringe spacing of 4.1 μm. Curve A is computed from Eq. (5). Curve B is an exponential with exponential given in Ref. 11, and, equivalently, by Eq. (1). Parameters used in the calculation are from Table I.

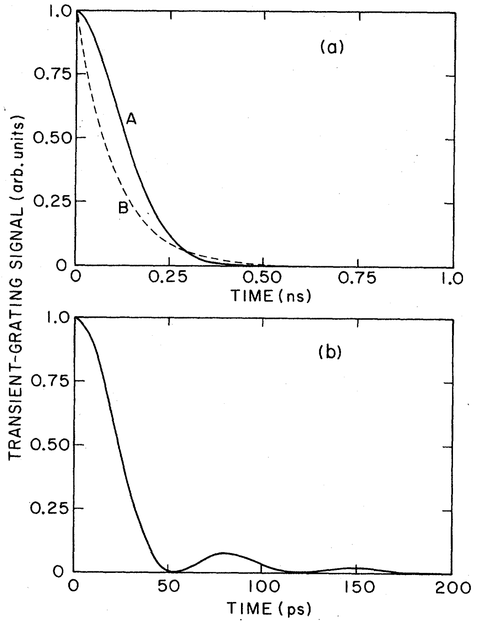

FIG. 2. Predicted transient-grating signals at 10 K with $\tau=1\times10^{-8}$ s, $\alpha=8\times10^{9}$ s^{-1}, and $V=1.5\times10^{12}$ s^{-1}. Fringe spacings of 1 and 0.2 μm are assumed, respectively, in (a) and (b). The exponential approximation (curve B) to the signal (curve A) is also plotted in (a). A slight departure from the exponential is seen in (a) and oscillations are clearly visible in (b).

We use the α's obtained in Table I to predict the explicit time dependence of the grating signal. For $T=10$ K, Fig. 2 shows the signal calculated from Eq. (5), a fringe spacing of 1 μm being used in Fig. 2(a) and one of 0.2 μm

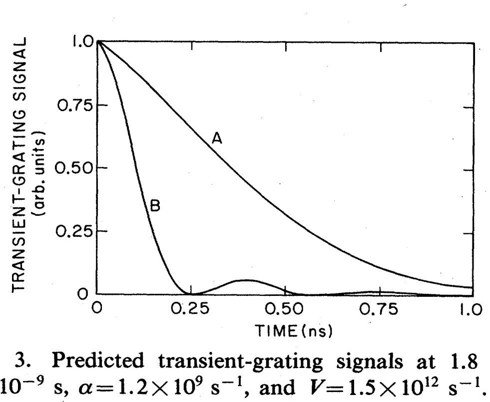

FIG. 3. Predicted transient-grating signals at 1.8 K with $\tau=2\times10^{-9}$ s, $\alpha=1.2\times10^{9}$ s^{-1}, and $V=1.5\times10^{12}$ s^{-1}. Fringe spacings of 4.1 μm and 1 μm are assumed, respectively, in curves A and B. It is to be noted that oscillations are discernible at this temperature for a fringe spacing as large as 1 μm, and that at 4.1 μm some nonexponential character in the shape appears.

in Fig. 2(b). In Fig. 2(a) we also display the corresponding exponential e^{-Kt}. The signal (curve A) departs from the exponential (curve B) already for a fringe spacing of 1 μm, and the characteristic curvature natural to coherent motion is visible. The fringe spacing of 0.2 μm brings out the expected oscillations in the signal explicitly. The high resolution and fine fringe spacings that are necessary to actualize Fig. 2(b), while possible in principle, may be difficult to achieve in the laboratory. However, for $T=1.8$ K, Fig. 3 shows that the case $d=4.1$ μm already begins to show some characteristics of coherence in the signal shape, and that oscillations are clearly visible even for $d=1$ μm. We stress that the latter value of the fringe spacing appears to be within the reach of present-day experimentation and that the former value was actually used in Ref. 11, at least for $T=10$ K.

IV. RELATED CONSIDERATIONS FOR TRIPLET-EXCITON MOTION

The Ronchi ruling experiment[13,32,33] plays the same role in investigations of triplet-exciton motion which the transient-grating technique[11] does in the singlet-exciton realm. Although it uses delayed fluorescence (rather than diffraction) as a probe of the evolution of the spatial inhomogeneity of the excitons, and involves an initial square-wave (rather than sinusoidal) exciton population, the kind of information that the Ronchi ruling technique provides, and the theoretical considerations it requires, are identical to those for transient-grating experiments. The necessary theory for coherence investigations has been given recently,[21,22] and it has been shown that coherence effects, if present, will be manifested measurably at low temperatures. Unfortunately, experiments using this technique have been carried out so far only at temperatures higher than 100 K. From the wealth of such data obtained by Ern and collaborators,[33] we select naphthalene and 1,4-dibromonaphthalene (1,4-DBN) at 300 K, and anthracene at four different temperatures, and extract the relevant coherence parameters for triplet-exciton motion by using considerations similar to those in Sec. II. The results are compiled in Table II.

For naphthalene and anthracene, the diffusion is effectively two-dimensional, whereas in 1,4-DBN it is one dimensional. The values quoted for D in Table II are, therefore, the average of D_{aa} and D_{bb} in the case of naphthalene and anthracene, but the principal value D_{cc} for 1,4-DBN. By the same token, V is taken as $\frac{1}{8}$ of the optically determined Davydov splitting for naphthalene and anthracene and $\frac{1}{4}$ of the exciton bandwidth for 1,4-DBN. For napththalene and anthracene, the nearest-neighbor distance a is given by $\frac{1}{2}(a_0^2+b_0^2)^{1/2}$ as in Table I. For 1,4-DBN, it is the lattice constant c_0. The respective experimental information is given in the first five columns of Table II along with the sources of information about a and V. The resultant values of the coherence parameters α and Λ/a appear in the last column. We obtain them from the respective expressions $\alpha=2V^2a^2/D$ and $\Lambda/a=\sqrt{2}V/\alpha$. Absence of detailed information concerning the specific ruling periods d used (which are analogous to the fringe spacings in the transient-grating experiment) forces us to use the simplified procedure of obtaining α, or what we have called α_i in Sec. II, directly from the reported D. However, the correction term given in Eq. (4), which distinguishes the correct α from the α_i, is completely negligible in the present case. Except for a proportionality constant of the order of 10, the quantity $b/2\alpha_i'$ appearing in Eq. (4) equals the product of V/α_i' and a/d. An estimate of the former is available from the last column of Table II, and we see that it is of the order of 1. Ruling periods are of the order of 10—50 μm, while a is smaller than 1 nm. Consequently, $(a/d)^2$ is smaller than 10^{-8}, and we see that α is indistinguishable from α_i'. We conclude that triplet motion in the systems studied is highly incoherent, the mean free path being smaller than, or at most of the order of, the nearest-neighbor distance. This conclusion is not surprising because the results presented in Table II were all obtained at relatively high temperatures. It is, no doubt, highly desirable to extend the Ronchi ruling experiment to low temperatures, particularly in view of recently reported observations[5] of highly coherent triplet-exciton motion at low temperatures, and of questions[6] regarding the interpretations of related experiments.

TABLE II. Coherence parameters for triplet excitons as obtained from the Ronchi ruling experiments of Ref.33.

Crystal	T (K)	D (10^{-4} cm^2/s)	a (nm)	V (10^{10} s^{-1})	α (10^{10} s^{-1})	Λ/a
Anthracene	371	1.6	0.524[a]	6.75[c]	16	0.6
	298	1.5			17	0.6
	160	2.5			10	1.0
	118	4.0			6.3	1.5
Naphthalene	300	0.3	0.510[a]	3.75[d]	24	0.2
1,4-dibromonaphthalene	300	3.5	0.409[b]	22.2[e]	47	0.7

[a] Reference 34.
[b] Reference 35.
[c] Reference 36.
[d] Reference 37.
[e] Reference 38.

V. DISCUSSION

In the light of the present application of existing transient-grating theory to experimental findings in anthracene, we believe that the observations reported by Rose *et al.*[11] strongly indicate the existence of coherent transport of singlet excitons at low temperatures. In arriving at this conclusion, we have not used arguments based on the temperature dependence of the observables, but have deduced the values of the exciton mean free path from the magnitude of the observed decay exponent of the grating signals and from known values of the exciton bandwidth. Our analysis is based on what appears to be an effectively one-dimensional transport equation, the assumption of an initially site-diagonal exciton density matrix, and nearest-neighbor transfer interactions. The first is not an approximation because the grating experiment is effectively one dimensional.[2,19] A detailed discussion of this point and application to anisotropic crystals has been given by Fort *et al.*[22] The changes that a different initial density matrix would involve have been discussed in Ref. 21. However, while certainly of theoretical interest, this issue seems to have little practical relevance at the present time, unless excitons can be created with definite phase relations in the experiment. The uncertainty[26–31] in the transfer interactions deduced from observed singlet-exciton bandwidths, on one hand, and our use of *effective* nearest-neighbor matrix elements, on the other, do introduce some numerical uncertainty into the deduced coherence parameters for singlets. Nevertheless, we expect the conclusions drawn to be basically valid. For triplets, the analysis is practically exact.

The explicit predictions for transient-grating signals given in Figs. 2 and 3 are specific to anthracene at the temperatures indicated, and are based on our application of the theory to the observations in Ref. 11. We emphasize that they show that oscillations and nonexponential character, which would be unequivocal signatures of coherence,[2] might be observed for $T=1.8$ K for fringe spacings as large as 1 μm. Such experiments, when carried out, would remove the uncertainties mentioned above in the deduced values of coherence parameters.

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APPENDIX

The generalized master equation

$$dP_m(t)/dt=\int_0^t dt'\sum_n [\mathscr{W}_{mn}(t-t')P_n(t') - \mathscr{W}_{nm}(t-t')P_m(t')] \qquad \text{(A1)}$$

governs the evolution of the probabilities P_m of a moving particle of arbitrary coherence, the $\mathscr{W}$'s being responsible for describing the coherence features.[2] If the moving particle can also decay during motion with a decay rate $1/\tau$, a term P_m/τ is appended to the left-hand side of the equation:

$$dP_m(t)/dt+P_m(t)/\tau=\int_0^t dt'\sum_n [\mathscr{W}_{mn}(t-t')P_n(t') - \mathscr{W}_{nm}(t-t')P_m(t')]\ . \qquad \text{(A2)}$$

It is natural to suppose that, the decay and motion processes being independent of each other, the $\mathscr{W}$'s in (A2) are the same as those in (A1). This supposition, which appears entirely reasonable, is actually incorrect and leads to the erroneous expression

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

reported in Refs. 2 and 20 for the exponent of the transient-grating signal in a simple linear chain. The subtlety lies in the fact that the physics of the situation demands that the solutions of (A2) for $P_m(t)$ equal those of (A1) multiplied by the factor $e^{-t/\tau}$. Differentiation of such a product and the use of (A1) show immediately that the $\mathscr{W}(t)$'s in (A2) must therefore equal the product of the $\mathscr{W}(t)$'s in (A1), and the same factor $e^{-t/\tau}$. When calculations of $\mathscr{W}(t)$'s are carried out from the microscopic evolution, this factor must be taken into account explicitly. It is clear that the multiplicative factor can make little contribution if the $\mathscr{W}(t)$'s decay very rapidly. Thus, for completely incoherent motion, for which the memory functions are δ functions,[2] no correction factors appear. This is reflected in the fact that, for the simple linear chain, the difference between the above-mentioned result and the correct expression given in Eq. (1) of the text disappears whenever $\alpha\tau \gg 1$. It is trivial to show this explicitly by expanding the expressions in powers of $1/\alpha\tau$.

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