CONSEQUENCES OF INITIAL CONDITION ANALYSIS
FOR THE INTERPRETATION OF
TRANSIENT GRATING OBSERVATIONS*

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ABSTRACT

With the help of a recently constructed theory of the effects of initial
conditions on transient grating (and Ronchi ruling) signals, we present a
detailed analysis of the consequences of the initial state on experimental
observations. Such an analysis is necessary because the relevant information
about the initial state is not available from existing experiments. We show
explicitly that the changes in the interpretation of data that different initial
conditions might require could be substantial in principle but are of no
practical importance in experiments reported so far. For instance, the
interpreted mean-free-path of Frenkel excitons in molecular crystals remains
entirely unaffected for all observations except one at 1.8 K in anthracene, for
which, the uncertainty factor is 2 under the worst of conditions. We also
present a revised table of coherence lengths and mean free paths updated
from our previous work.

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1. Introduction

Transient grating and (Ronchi ruling) techniques$^{1,2}$ have emerged as one of the most direct probes of Frenkel excitons in molecular solids$^3$. New information has been gathered recently$^{4,5}$ on systems of interest and detailed theoretical interpretation has been given$^6$ resulting in explicit values of the exciton mean free path and coherence time. However, an uncertainty appears to be present in this interpretation because the initial state produced in these experiments is not known with precision. A theory of the effects of initial conditions on the grating signal was therefore constructed recently$^7$. Preliminary calculations from that theory led to the qualitative conclusion$^7$ that, while substantial effects could arise in principle from variation in the initial state, they are probably negligible for experiments carried out so far in the molecular crystal domain. A detailed quantitative investigation of this matter is the content of this Letter. We use the theory of Kenkre and Tsironis$^7$ to study the exponent of the transient grating signal for two extreme initial conditions, viz. the random and the pair-state, and compare the similarities and differences specifically in the context of the experiments of Rose et. al.$^5$ (and also of Ern et. al.$^1$ on Ronchi rulings). The conclusions we draw reinforce the qualitative remarks made earlier$^7$ and show explicitly that no revision in previously interpreted values of mean free paths and scattering times of excitons is necessary.

From the initial condition analysis of ref. 7, we derive expressions for the transient grating signal exponent $k$ in the two extreme initial condition cases: the random and the pair-state. The derivation is in section 2 and the result is equations (13) and (14). We carry out a comparative examination if these two signals in section 3, graphically (in figs. 1 and 2) as well as
analytically. Figures 2a and 2b show, in particular, the maximum errors that uncertainties in initial conditions could introduce in the interpretation of data. We end the Letter with a revised table of scattering times and mean free paths obtained from our interpretation of experiments¹,⁵ on molecular crystals.

2. Extreme expressions for the Transient Grating Signal Exponent

The observed transient grating signal is proportional²,³ to the amplitude of the inhomogeneity in the exciton density (or probability) and has been denoted in earlier references²,⁷ as S(t). In the following we shall use s(t) to denote the square root of this signal since it is the inhomogeneity amplitude s(t) – or its Laplace transform ŝ(ε) – that is given directly by theory. Thus

\[ \tilde{s}(\varepsilon) = \int_0^\infty s(t)e^{-\varepsilon t}dt = \int_0^\infty \left[\frac{1}{\lambda^2}S(t)\right]^{1/2}e^{-\varepsilon t}. \] (1)

The random initial condition²,³,⁶ referred to above assumes that the initial density matrix \( \rho \) is diagonal in the representation of the site eigenstates (\( m, n, \) etc.):

\[ \rho_{mn}(0) = \frac{2}{N} \cos^2\left(\frac{m\eta}{2}\right)\delta_{mn}. \] (2)

Here \( N \) is the number of sites and \( \eta \) is the dimensionless wavevector of the grating given by
\[ \eta/2 = \left(2\pi a/\lambda \right) \sin \left(\theta/2\right) = \pi a/d, \quad (3) \]

where \( a \) is the intersite distance, \( \lambda \) the wavelength of excitation, \( \theta \) the angle of crossing of the exciting laser beams, and \( d \) the spacing of the interference fringes that form the grating.

The pair-state initial condition\(^7\)\(^-\)\(^9\), on the other hand, assumes that the initial exciton state is made up of two Bloch states whose (dimensionless) quasimomenta differ by the (dimensionless) grating wavevector \( \eta \):

\[ \rho_{mn}(0) = \left(2/N\right) \cos(m\eta/2) \cos(n\eta/2) \exp[\text{i}x(m-n)]. \quad (4) \]

The two quasimomenta are \( x + \eta/2 \) and \( x - \eta/2 \) respectively.

The two initial conditions (2) and (4) involve the same initial probability distribution, viz. \( \rho_{mm}(0) = \left(2/N\right) \cos^2(m\eta/2) \), but result in different forms of the evolution of the grating signal. The respective signals are\(^7\)

\[ \tilde{s}(\epsilon) = \left\{ \left(\epsilon^2 + \alpha^2 \right) + b^2 \right\}^{1/2} - \alpha \}^{-1} = \tilde{s}_{\text{rand}}(\epsilon) \quad (5) \]

for the random case and

\[ \tilde{s}(\epsilon) = [\tilde{s}_{\text{rand}}(\epsilon)][\tilde{f}_x(\epsilon)] \quad (6) \]

for the pair-state case, the factor \( \tilde{f}_x(\epsilon) \) being given by
\[ f_x(\epsilon) = (\epsilon' + \alpha) \left[ (\epsilon'^2 + \alpha^2) + b^2 \right]^{1/2} \left[ (\epsilon' + \alpha^2 + b^2 \sin^2 x \right]^{-1}. \quad (7) \]

As has been shown in ref. 7, the maximum deviation from the random condition occurs for the pair-state with \( x = 0 \). We will therefore only consider that extreme. Thus, we compare the two signals

\[ \tilde{s}_{\text{rand}}(\epsilon) = \left[ (\epsilon' + \alpha) + b^2 \right]^{1/2} \alpha^{-1} \quad (8) \]
\[ \tilde{s}_{\text{pair}}(\epsilon) = \left[ (\epsilon' + \alpha) + b^2 \right]^{1/2} (\epsilon' + \alpha)^{-1} \left[ (\epsilon' + \alpha) + b^2 \right]^{1/2} \alpha^{-1} \quad (9) \]

In the above equations (5)-(9), \( \epsilon' = \epsilon + 1/\tau \), \( \tau \) is the lifetime of the exciton, \( \alpha \) is the scattering rate for the exciton, and \( b = 4V \sin (\eta/2) \). In the following we will make the approximation \( b = 4V \eta a/d \), which involves the replacement of the sine by its argument and is always valid in all experiments of interest since the lattice constant is much smaller than the fringe spacing.

The complete time dependence of the transient grating signal may be obtained from (8) and (9) and has been discussed earlier. Our interest in this Letter lies in the interpretation of existing experiments all of which have displayed exponential signals. It is obvious that, whenever a quantity \( s(t) \) appears to be exponential, i.e., may be represented by \( \exp(-kt) \), the exponent \( k \) is given by

\[ k = \frac{\int_0^\infty dt \ s(t)}{s(\epsilon)} \quad (10) \]

Using this prescription to extract the apparent exponent of the signal for the two cases represented by (8) and (9), we have
\[ k_{\text{rand}} = \{[\alpha + (1/\tau)]^2 + b^2\}^{1/2} - \alpha \quad (11) \]

\[ k_{\text{pair}} = [\alpha + (1/\tau)][(\alpha + (1/\tau))^2 + b^2]^{-1/2} k_{\text{rand}}. \quad (12) \]

While it is certainly possible to carry out all of the following calculations retaining the term \(1/\tau\) in the expressions, the term is negligible with respect to \(\alpha\) for the experimental observations of interest in molecular crystals since the lifetime \(\tau\) is of the order of nanoseconds or longer while scattering times are at least about two orders of magnitude shorter. As in ref. 7 therefore, we shall drop \(1/\tau\) here and write

\[ k_{\text{rand}} = (\alpha^2 + b^2)^{1/2} - \alpha \quad (13) \]

\[ k_{\text{pair}} = [1 + (b/\alpha)^2]^{-1/2} [(\alpha^2 + b^2)^{1/2} - \alpha]. \quad (14) \]

Equations (13) and (14) – or their more complete forms (11) and (12) – form our point of departure for the discussion in section 3.

3. Effects of Initial Conditions

Equations (13) and (14) show the similarities and differences in the grating signal for the two initial conditions explicitly. We see that \(k_{\text{rand}}\) and \(k_{\text{pair}}\) are identical to each other for small enough \(b/\alpha\), i.e. for large enough incoherence. However, they can be sharply different for systems in which the transport is highly coherent on the length scale of the interference fringes.
Both $k$'s coincide with each other for large $\alpha$ but $k_{\text{rand}}$ increases monotonically to the value $b$ as $\alpha \to 0$ whereas $k_{\text{pair}}$ increases to a maximum and then decreases with decreasing $\alpha$, eventually vanishing at $\alpha = 0$. Fig. 1 shows the differences and similarities.

In the random case, the signal $s(t)$ is the Bessel function of zero order$^3$ for completely coherent transport ($\alpha = 0$). Its decay becomes slower as the scattering rate increases. This is connected simply to the fact that exciton motion, which is responsible for the destruction of the inhomogeneity, becomes slower – less efficient – as the scattering of the exciton increases. In the limit of infinite $\alpha$ the exciton does not move and the grating is permanent.

For the pair-state case, the situation is more complex. As in the random case, the grating tends to be permanent as the exciton motion becomes ineffective as a result of large scattering. However, the grating is also permanent in the limit of no scattering. This occurs, as explained elsewhere$^9$, because of the coherent construction of a perfect standing wave by the two Bloch states comprising the initial grating. As $\alpha$ increases, the scattering first causes the grating to evolve through a mixing of Bloch states. However, with enough scattering, the effect described above in the large $\alpha$ limit occurs and the grating again becomes permanent. In the pair-state case, therefore, the behaviour of $k$ is not monotonic. Fig. 1 shows this clearly. The non-monotonic behaviour is apparent also in ref. 7 and in the numerical work of Garrity and Skinner$^6$.

It is clear from fig. 1 that substantial differences could indeed occur in the actual $\alpha$ (if the actual initial condition were pair-state) and the $\alpha$ interpreted on the basis of the random initial condition result if $\alpha/b$ were sufficiently small. The experimental situation, however, corresponds to
values of \(\alpha/b\) so large that no appreciable difference exists. To show the
relation of the actual \(\alpha\) to the \(\alpha\) interpreted on the basis of the random initial
condition analysis, we will assume the former to be as different as possible
from the latter, i.e. to correspond to the pair-state initial condition despite
the fact that it is highly unlikely that it will be so in the experiments carried
out so far. Equations (13) and (14) then result in

\[
\alpha_R = (1/2) \left[ f - (1/f) \right] \quad (15)
\]

\[
f = (\alpha_p^2 + 1) + (1/\alpha_p) + \alpha_p \quad (16)
\]

Here \(\alpha_p\) and \(\alpha_R\) are the values of the ratio \(\alpha/b\); the former obtained with the
actual \(\alpha\) (the actual initial condition being assumed pair-state for maximum
deviation) and the latter obtained on the basis of the random initial condition
analysis. In fig. 2a we plot (15) to show the relation of the two \(\alpha\)'s in an
\(\alpha\)-range chosen to bring out the differences clearly. Fig. 2b shows a plot of
\(\Lambda_p\) versus \(\Lambda_R\). These are the corresponding values of \(\Lambda/d\), the ratio of the
mean free path to the fringe spacing in the experimentally relevant range.
Experimental points from Rose et. al.\(^5\) on singlet excitons in anthracene are
marked on the curve in fig. 2b. The values of \(\alpha/b\) in those experiments are
19, 35, 52, and 61 for all temperatures above 1.8 K. We mention in passing
that these values have been calculated by assuming \(V\) to be \(10^{13}\) s\(^{-1}\) rather than
\(1.5 \times 10^{12}\) s\(^{-1}\) which was the value used incorrectly in ref. 6.

It is seen that, with the exception of the 1.8 K point, no discernible effect
of the initial conditions exists. For 1.8 K, detailed information about fringe
 spacings is not available in the literature but under maximum deviation
conditions $\alpha_R$ can be calculated to be of the order of, but larger than, 2. This point has been indicated in fig. 2a. A solution from (15) and (16) shows that $\alpha_p = 1.68$. We see that, were the initial condition pair–state, the error in $\alpha$ at 1.8 K would involve an underestimation of the coherence or the mean free path by a factor of 1.2. Thus, in such a case, the conclusion we have drawn earlier, that singlet motion in anthracene is highly coherent, would be reinforced since the actual $\alpha$ would be smaller than the $\alpha$ interpreted on the basis of the random initial condition. For the experiments of Ern on triplet excitons at room temperature, the motion is so incoherent and the value of $\alpha/b$ therefore so huge, that no practical difference exists between the results for the different initial conditions.

4. Concluding Remarks and Revised Tables

We have thus shown explicitly that, while interesting in principle and certainly capable of making their presence felt in appropriate systems, initial condition effects are not discernible experimentally in transient grating observations reported so far in molecular crystals. No modification of the interpreted values of scattering times and coherence lengths of excitons deduced earlier is therefore necessary on this count. A table of these scattering times and coherence lengths (mean free paths) constructed in ref. 6, but now revised to correct for certain missing factors of $2\pi$ (which we have mentioned in an erratum elsewhere), is presented below. The symbols $T$, $\tau$, $d$, $K$, $\alpha$, $\Lambda$, $a$, $D$, $V$, represent, respectively, the temperature, the exciton lifetime, the fringe spacing, the grating signal exponent, the scattering rate,
the mean free path of the exciton (the coherence length), the intersite distance, the exciton diffusion constant, and the intersite matrix element. For a more detailed explanation of the table the reader should refer to ref. 6.

### TABLE 1: SCATTERING RATES \( \alpha \) AND MEAN FREE PATHS \( \Lambda \)
FOR SINGLET EXCITONS IN ANTHRACENE AS OBTAINED FROM
THE TRANSIENT GRATING EXPERIMENTS OF ROSE et al. 1984(ref.5)

<table>
<thead>
<tr>
<th>( T[K] )</th>
<th>( \tau[\text{ns}] )</th>
<th>( d[\mu\text{m}] )</th>
<th>( K[10^6\text{s}^{-1}] )</th>
<th>( \alpha[10^{11}\text{s}^{-1}] )</th>
<th>( \Lambda/a )</th>
<th>( \Lambda[\text{nm}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>10</td>
<td>3.2</td>
<td>7.6</td>
<td>6.7</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.6</td>
<td>4.2</td>
<td>8.3</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>4.1</td>
<td>10</td>
<td>2.9</td>
<td>46</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.6</td>
<td>3.1</td>
<td>3.4</td>
<td>39</td>
<td>20</td>
</tr>
<tr>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td>( \leq 0.47 )</td>
<td>( \geq 280 )</td>
<td>( \geq 150 )</td>
</tr>
</tbody>
</table>

### TABLE 2: COHERENCE PARAMETERS FOR TRIPLET EXCITONS AS OBTAINED
FROM THE RONCHI RULING EXPERIMENTS OF ERN et al.(ref.1)

<table>
<thead>
<tr>
<th>CRYSTAL</th>
<th>( T[K] )</th>
<th>( D[10^{-4}\text{cm}^2/\text{s}] )</th>
<th>( a[\text{nm}] )</th>
<th>( \eta[10^{11}\text{s}^{-1}] )</th>
<th>( \alpha[10^{11}\text{s}^{-1}] )</th>
<th>( \Lambda/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>371</td>
<td>1.6</td>
<td>0.524</td>
<td>4.24</td>
<td>63</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.5</td>
<td></td>
<td></td>
<td>67</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>2.5</td>
<td></td>
<td></td>
<td>40</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>118</td>
<td>4.0</td>
<td></td>
<td></td>
<td>25</td>
<td>0.24</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>300</td>
<td>0.3</td>
<td>0.510</td>
<td>2.36</td>
<td>95</td>
<td>0.03</td>
</tr>
<tr>
<td>1,4 DBN</td>
<td>300</td>
<td>3.5</td>
<td>0.409</td>
<td>13.8</td>
<td>186</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Acknowledgements

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FIGURE CAPTIONS

FIG. 1 The exponent $k$ of the grating signal plotted as a function of the scattering rate $\alpha$ (both quantities expressed in units of $b$) for the two initial conditions under study: the solid curve represents the random case and the dashed curve represents the pair-state case. The two cases are seen to differ significantly for large coherence but to coincide for large scattering.

FIG. 2a The maximum error that the assumption of a random initial condition could introduce into the interpretation of the grating signal shown through a plot of $\alpha_P$ versus $\alpha_R$. The former is the actual value (in units of $b$) of the scattering rate $\alpha$ that would correspond to the observed signal if the actual initial condition were pair-state. The latter is the value (in units of $b$) obtained under the assumption of a random initial condition as in ref. 6. The arrows correspond to the 1.8 K measurement of Rose et. al. (ref. 5) on singlets in anthracene and represent the maximum error that could be introduced by the random initial condition assumption in the interpretation of any of the grating or ruling experiments reported so far in molecular crystals.

FIG. 2b The maximum error that the assumption of a random initial condition could introduce into the interpretation of the grating signal as in fig. 2a, but shown here through a plot of $\Lambda_P$ versus $\Lambda_R$. These correspond to $\alpha_P$ and $\alpha_R$ of fig. 2a and denote the values of the ratio of the mean free path $\Lambda$ to the fringe spacing for the pair-state and random phase initial condition respectively. The points indicated by the arrows represent all the measurements on singlets in anthracene reported by Rose et. al. (ref. 5). It is clear that no discernible initial condition effect is involved in any of those observations except the one at 1.8 K measurement. For that measurement the mean free paths differ by at most a factor of 2.
FIG. 2b  Kenkre-Schmid
$k \text{ (in units of } b) \rightarrow$

$\alpha \text{ (in units of } b) \rightarrow$

$0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \quad 14 \quad 16 \quad 18 \quad 20$