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Comments on "Triplet-exciton annihilation and triplet spin relaxation in molecular crystals"

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A recent analysis of the magnetic-field dependence of delayed fluorescence from crystalline naphthalene is examined. An allegedly unusual high-field spectrum that has motivated the introduction of spin-relaxation anisotropy in the analysis is shown to be *currently* accountable only as data that are not high field. The claim that there exists for triplet excitons in naphthalene a relaxation mechanism other than the known one of hopping among inequivalent sites, based as it is on a discrepancy between theory and experiment for the EPR (electron paramagnetic resonance) linewidth, is shown to be unnecessary by demonstrating that the theory is valid provided the EPR data are properly corrected for orientational disorder. The use of nonsecular contributions to the EPR linewidth to obtain relaxation rates is discussed.

In a recent issue of this journal Altwegg and Zschokke-Gränacher[1] (AZ) published experimental data for the magnetic field dependence of delayed fluorescence from single-crystal naphthalene at room temperature and interpreted the results using Suna's theory[2] of the effect. The data, presenting angular dependence at 8 kG, are described as "high field" and taken by the authors as exhibiting an anomalous angular variation by contrast with comparable data for anthracene.[3] The unanticipated spectrum was accommodated by including in the theory the anisotropy of spin relaxation, again unlike anthracene for which the analysis produced a very good fit to experiment using only an isotropic rate.[2]

In the course of their analysis, which required an indirect determination of relaxation rates because no measured rates were available, AZ were led to seek such rates in the EPR linewidth spectrum of triplet excitons. The most important claim that emerges from their discussion in this regard is that "beside the hopping motion between inequivalent molecules, an additional process influences the spin relaxation rate."

We present evidence that an artificial problem has been created in the use of the data and that a second relaxation mechanism is unnecessary.

(1) AZ's basic evidence for assuming a second relaxation mechanism for triplet excitons in naphthalene is the apparent inability of inequivalent hopping in the theory formulated by Reineker[4] to account for a published EPR linewidth spectrum. A similar disagreement was found for the anthracene spectrum,[5] but in that case the discrepancy was shown to arise from an inhomogeneous contribution from orientational disorder.[6] The prescription given in Ref. 6 for correcting a spectrum broadened by such disorder is

$$\Delta H(\mathrm{corr}) = \Delta H(\mathrm{expt}) - k|\vec{\nabla}_{\hat{n}} H_R(\hat{n})| , \qquad (1)$$

where ΔH represents linewidth, $H_R(\hat{n})$ is the resonant magnetic field in the direction of the unit vector $\hat{n}$, and k is a parameter to be determined for a given crystal.

We have applied (1) to the data in question for the *ac* plane and show a sample fit in Fig. 1 for the parameters given in the caption; the figure also shows the corresponding spectrum for the perfect lattice ($k = 0°$), i.e., the homogeneous linewidth of the theory. Aside from the obvious quality of the fit to (1), the values of the fitting parameters (Γ_1 in the linewidth theory and k in the correction procedure) are justifiable. For the earlier analysis of the anthracene spectrum in the *ac* plane, the distortion parameter k was almost the same (0.17°). The linewidth parameter, Γ_1 in Reineker's theory, can be approximated[5] by

$$D_{aa} = \frac{a^2}{4}\,\Gamma_1 \qquad (2)$$

for the nearest-neighbor hopping, where D_{aa} is the principal component along the a axis of the triplet exciton diffusion tensor and a is the lattice constant. Using reported values[7] of $D_{aa} = 3.3 \times 10^{-5}$ cm^2 s^{-1} and $a = 8.24$ Å, (2) yields $\Gamma_1 = 787$ g. It is clear then that the existing EPR data for naphthalene can be understood by current theory and that no novel relaxation mechanism need by invoked.

(2) We consider next AZ's use of the experimental EPR linewidth spectrum for the *ac* plane to determine the relaxation rate required in Suna's theory. The EPR data were invoked directly for this purpose since, with the assumption of an unknown relaxation mechanism, it would be impossible to calculate the rate.[8] The strategy adopted by AZ is to identify the appropriate spin relaxation rate ζ with the nonsecular contribution to the linewidth [their Eq. (5.1)]:

$$\left(\frac{1}{T_2}\right)_{\mathrm{ns}} = \zeta(H). \qquad (3)$$

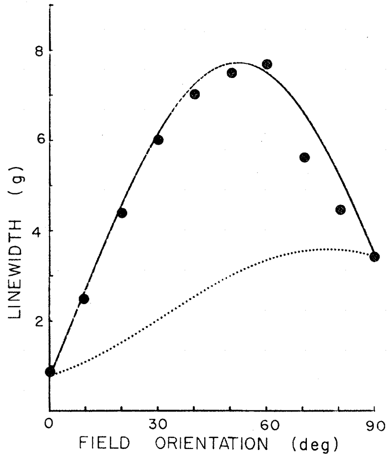

FIG. 1. Angular dependence of the EPR linewidth of triplet excitons for the ac plane of single-crystal naphthalene at room temperature. The width refers to the half-width at half maximum of a Lorentzian shape. The solid curve is calculated from (1) with an effective hopping rate $\Gamma_1 = 750$ G, $k = 0.18°$, and a microwave frequency of 35 GHz. The circles are the data of Ref. 12. The dotted curve shows the same calculation for $k = 0°$. The direction specified by 0° refers to the y^* axis.

The justification for (3) is the statement that the part of the linewidth, "which stems from transitions between magnetic sublevels, is the nonsecular part" of the linewidth. It is thus implied that these "transitions" occur at the appropriate rate.[9] The methodology implicit in (3) suffers from several defects.

First of all, EPR linewidth and spin relaxation (i.e., level equilibration) mechanisms need not have a common source and therefore there is no guarantee that the alleged second mechanism, presumably accounting for the linewidth discrepancy, will also contribute to ζ. It is of course true that hopping between inequivalent sites is a source of both linewidth and level relaxation in the molecular crystals under discussion.

Secondly, the justification for (3) quoted above is based on a questionable interpretation of the significance in a magnetic resonance linewidth formula of terms (the nonsecular) which contain only off-diagonal matrix elements. That is, by noting only the form of an accompanying matrix element, this interpretation construes a physical process and identifies an actual rate in an unknown linewidth mechanism. In fact, the linewidth terms in question cannot be assumed to express correctly the relaxation rate between the states represented even when there is a single mechanism underlying linewidth and level relaxation. The most appropriate example of the difference in this case is offered by the inequivalent hopping mechanism itself for which an explicit evaluation is possible. The comparison may be made from formulas in Ref. 2: Eq. (D6c) for linewidth and (D6d) for level relaxation rate.

Finally, it should be recognized that the technique adopted by AZ for dealing with an unknown relaxation mechansim faces a further problem. It is simply that, although secular terms vanish for the ac plane when the mechanism is inequivalent hopping, it is not correct to assume this if nothing is known about the mechanism.

(3) Since AZ's analytical program for explaining the field dependence of fluorescence in naphthalene will be affected by the issues raised above, is there anything that can be said about the data without appealing to such a calculation? It is, in fact, the character of these spectra that motivated the comparison with the high-field data of anthracene.[10] There is evidence that 8 kG is not a *comparable* regime for triplet excitons in naphthalene.

The excitonic spin Hamiltonian parameters for naphthalene are shown in Table I, which includes those for anthracene, tetracene, and pyrene for comparison. It has been found for anthracene[3] and tetracene[15] that at 4 kG the field dependence shows no change with increasing field while for pyrene[15] it is necessary to exceed 6 kG to observe the saturation. The relative magnitude of parameters in the table would suggest therefore that the high-field condition might not be adequately met for naphthalene at 8 kG. More compelling evidence comes from the naphthalene experiment itself since the angular spectrum for the ac plane exhibits an incipient low-field resonance structure.[3] This appears as two shallow, but distinct, minima bisecting the high-field resonances and 90° apart. (These are noted as being 65° and 155° relative to the c^* axis, but the figure seems to indicate a slight equal shift from these values for both.) For monoclinic symmetry these resonances[16] appear in the *ac* plane along the direction of

TABLE I. Triplet exciton spin Hamiltonian parameters (in G).

	Naphthalene[a]	Anthracene[a]	Pyrene[b]	Tetracene[c]
D^*	−30	∓62	420	−66
E^*	507	±353	−409	265

[a] Reference 12.
[b] Reference 13.
[c] Reference 14.

the x^* and y^* principal axes of the fine structure tensor. Their positions correspond, to within the definition of the published diagram, to those found by Haarer and Wolf[12] from the EPR spectrum, i.e., 22.4° from the crystallographic a axis for the x^* axis. In the light of these facts a special explanation for the character of the naphthalene field dependence is not yet required.

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[8] The linewidth theory is used to calculate this rate for the *ab* plane, however.

[9] Since the report does not present the details of the calculations performed, it is unclear how the rate in (3) is used. AZ present an equation from Suna's paper [their Eq. (4.3)] as a defining equation for ζ, but there is no demonstration that this is consistent with expression (3). The equation itself expresses the term in the full rate equation for the two-exciton density matrix that arises from spin relaxation and Suna deals with the problems created in this formulation by the fact that the excitons relax independently. Accepting Suna's method for incorporating monoexcitonic spin relaxation into the pair-annihilation rate constant, one must still attend to the particular form of the rate used. The parameter ζ used by Suna is an unweighted average over the three triplet sublevel depopulating rates: $\zeta = \frac{1}{3}\sum_n \zeta_n^{(1)} = \frac{1}{3}\sum_{n,\, m\neq n} \zeta_{nm}^{(1)}$. (In the second sum Suna inadvertently included the diagonal terms which have no physical interpretation.) The measured linewidth, on the other hand, is specific to a chosen pair of sublevels. On this basis alone the physical content of (3) is dubious.

[10] It is noteworthy that in an earlier study (Ref. 11) in which 8 kG is also the maximum applied field, AZ did recognize the low field resonances and, in fact, then remarked on the *similarity* to the anthracene spectrum. Their application of the theory, presumably then calculated for an arbitrary field, but with relaxation omitted (the formal equivalent in Suna's analysis to an isotropic rate), showed a reasonable fit to the data. Although offered as an example of the effects of exciton density, the spectrum is very similar in angular dependence to that in the current report. There is also in this paper additional evidence that 8 kG is not high field for naphthalene: In curves displaying the dependence of fluorescence on field magnitude for several orientations (Fig. 7), the fluorescence shows no saturation at this limit.

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[16] It is worth noting the data given by AZ for p-terphenyl because of the possibility that this system too is not in high field at 8 kG. Subsidiary minima in the ac plane (Fig. 3) appear to be approximately 90° apart and therefore may also mark the x^* and y^* principal axes for the p-terphenyl excitonic spin Hamiltonian.