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Comments on "Influence of spin relaxation on triplet-triplet exciton annihilation in organic crystals. Application to naphthalene"

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A recent extension of Merrifield's theory about the mutual annihilation of triplet excitons to the case of nonvanishing spin relaxation is discussed. Spin relaxation cannot be accounted for by solely increasing the dissociation rate of triplet pairs k_{-1} by the spin-relaxation rate ξ. Also it is explained why ξ had not been calculated correctly.

In a recent issue of this journal, Fave *et al.*[1] have published experimental data for the magnetic field dependence of the delayed fluorescence from single-crystal naphthalene. They have interpreted their results using a theory by Johnson and Merrifield[2] about "the effects of the magnetic field on mutual annihilation of triplet excitons." In addition, they have expanded this theory by explicitly taking into account an anisotropic spin relaxation of the triplet excitons. The spin-relaxation rates were taken from the theory by Suna[3] about "the kinematics of exciton-exciton annihilation." In principle, an expansion of the theory by Johnson and Merrifield by incorporating the triplet-spin relaxation is to be welcomed. However, while merging Suna's calculation of the anisotropic spin-relaxation rates with the simpler theory by Merrifield for triplet-annihilation rates, the authors of the presently discussed paper overlooked some important facts and assumptions of Suna's theory, as we would like to point out now. It also seems as if the spin-relaxation rates ξ_{nj} and the expressions "secular" and "nonsecular" have been misunderstood in the paper under discussion. We will try to clarify the meaning of the corresponding quantitites.

In Suna's theory the definition for $\xi_{nj}^{(1)}$ and $\xi_{nj}^{(2)}$, the spin-relaxation rates for the elements of the one-exciton density matrix, is given in Eq. (C1) of Ref. 3. The superscripts 1 and 2 denote the spin-relaxation matrices for the diagonal and the off-diagonal elements of the density matrix, respectively. As it is seen immediately from this Eq. (C1), the diagonal elements $\xi_{nn}^{(1)}$ and $\xi_{nn}^{(2)}$ cancel. It has been stated before[4,5] that these diagonal elements have no physical meaning. This means that Eq. (D10) in Suna's theory, the formula of an average spin-relaxation rate, should be written in full as

$$\xi_{\mathrm{av}}=\tfrac{1}{3}\sum_{j}\sum_{n}\xi_{nj}^{(1)}\ ,\quad n\neq j\ . \tag{1}$$

The expressions secular and nonsecular, which are used in the discussed paper for terms of the spin relaxation, are borrowed from ERS-line-shape theory, Notwithstanding that it has been shown[4] that the ESR-linewidth theory by Reineker[6] yields almost exactly the same values for the nonsecular part of the ERS linewidth as Suna's theory does for the spin-relaxation rate, the elements $\xi_{nn}^{(1)}$ cannot be related to the secular part of the ESR linewidth. It is not correct to use the expression *secular* in connection with the elements $\xi_{nn}^{(1)}$ and it is certainly wrong to include either the elements $\xi_{nn}^{(1)}$ or the secular part of the ESR linewidth in an average spin-relaxtion rate relevant for the triplet-triplet annihilation rate. These terms do not contribute to spin relaxation in the sense that they do not change the magnetic quantum number m.

In a rather extensive calculation, Suna[3] shows that inclusion of spin relaxation in his theory amounts to the replacement of the effective triplet lifetime β_{eff} by the sum $\beta_{\mathrm{eff}}+\xi_{\mathrm{av}}$, if the knowledge of an average spin-relaxation rate ξ_{av} is sufficient. In addition, the calculated triplet-annihilation rate has then to be multiplied by a function $c(\xi)<1$, which decreases the overall annihilation rate. $c(\xi)$ is almost equal to 1 in most cases[3].

The authors of the paper discussed here have tried to apply this result of Suna's theory to the simpler theory by Merrifield. However, the two theories differ in quite fundamental respects and the assumptions made in the two theories are by no means the same. Merrifield's theory deals exclusively with correlated triplet *pairs*, which are generated, dissociate, and annihilate with the rates k_1, k_{-1}, and k_2, respectively. Suna's theory, on the other hand, deals with *single* triplet excitons, which are always correlated to a greater or lesser extent depending on the hopping rates of the excitions and the dimensionality of the system. k_{-1} has therefore no meaning in Suna's theory[7] and there exists no direct correlation between k_{-1} and β_{eff}. Fave *et al.* have introduced spin relaxation into Merrifield's theory by solely replacing k_{-1} by $k_{-1}+\sum_j\xi_{nj}$. Yet, spin relaxation does not dissociate a triplet pair but, on the contrary, merely changes the spin state of a triplet pair. ξ_{nj} being a spin-relaxation rate of a *single* triplet exciton, the spin relaxation of a triplet pair state would have to be equal to $2\xi_{nj}$. Also, if k_{-1} has to be modified in the presence of spin relaxation, then k_1 must be affected, too, as the destruction of a pair in a given spin state by spin relaxation leads immediately to the generation of a pair in a different spin state.

As it is shown in Appendix C in Ref. 3, the calculation of the triplet-annihilation rate gets considerably more difficult if one deals with the complex matrices $\xi_{nj}^{(1)}$ and $\xi_{nj}^{(2)}$ instead of an average spin-relaxation rate ξ_{av} equal for all sublevels. One can no longer just replace β_{eff} by $\beta_{eff}+\sum_j \xi_{nj}$, n referring to the different sublevels; and it is not understandable why in the discussed paper k_{-1} was replaced by $k_{-1} + \sum_j \xi_{nj}$.

That the correspondence between the experiments by Fave *et al.* and their theory is reasonable, is quite accidental. The erroneous inclusion of the terms ξ_{nn} in the spin-relaxation rate and the oversimplified use of Suna's ansatz in their theory, $k_{-1}\rightarrow k_{-1}+\sum_j \xi_{nj}$ compensate each other. This can be seen from the numerical values for the two rates, $k_{-1}=3\times10^9\ \mathrm{s}^{-1}$,[1] $\beta_{eff}=1.6\times10^8\ \mathrm{s}^{-1}$.[4] Since spin relaxation adds to both rates and is of the same order of magnitude as β_{eff},[4] it has a greatly reduced effect on k_{-1} compared to the effect on β_{eff}. This compensates for the large spin-relaxation rates obtained by Fave *et al.*

As equivalent experimental data have been published before[8,9] and have been shown to be in good agreement with Suna's theory,[4,8] the usefulness of the results presented in the paper commented upon here is questionable. By now, it is generally accepted that the theory by Suna gives a more complete and fundamental description of the triplet-annihilation process than the theory by Merrifield. It is well known that Suna's theory yields correct resonance shapes, whereas Merrifield's theory is correct on resonance and far away from resonance only.[3] In the discussed paper, however, the authors claim that their theory produces the right resonance shape. Nevertheless, the agreement with their experiments is rather poor compared to the agreement obtained in Ref. 8 between Suna's theory (with the anisotropy of spin relaxation taken into account) and experimental data.[10] This is not only due to their misunderstanding of the theories by Suna and Merrifield but also to experimental problems like inhomogeneity of the magnetic field or poor crystal quality and misorientation of the crystal. The resonances in the crystallographic *a,c* plane [Fig. 4(a) in Ref. 1] should be of equal width and have a full width at half maximum of about 5° for a well-oriented crystal of good quality.[9]

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[10] In Ref. 1 experiment and theory differ by up to 7% in the crystallographic *ab* plane and by up to 5% in the *ac* plane. In Ref. 8, theory and experiments agree within 1.5% in both planes.