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USEFULNESS OF SENSITIZED LUMINESCENCE AS A PROBE FOR EXCITON MOTION

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The result of a detailed application of theory to sensitized luminescence observations on a variety of molecular crystals is presented and the questions of their usefulness as a probe for exciton motion is analyzed.

Recent work carried out in close collaboration between theory and experiment leads us to believe that serious questions exist regarding the usefulness of sensitized luminescence as a probe to measure exciton motion in molecular crystals. These questions arise as a result not of inadequacies of the experimental technique but of ambiguities in the interpretation. For many years observations of quantum yields have been used to deduce the energy transfer rate k, and the exciton diffusion constant D has been extracted through the so-called Smoluchowski prescription $k = 4\pi RD$, the quantity R being a "trapping radius" often taken to be the lattice constant. Extensive information has been thus accumulated[1] and models have been proposed for the microscopic sources of the temperature dependence of the observations[2]. It is obvious, however, that *two distinct* quantities, the motion quantity D and a capture rate c, generally determine the single experimental observable k. Unless independent information about c is available, it is not possible to deduce more than lower bounds for D. While this fact has been recognized, the assumption of infinite c has always been made in the interpretation of experiment as well as in the development of theory. Two recent investigations suggest that the actual state of affairs might be exactly the opposite: that the observed k might be capture-limited and therefore microscopic theories which have always been motion-based might be completely off the mark. The first is a reinterpretation[3] of energy transfer and annihilation data[4]. It leads one to conclude that, if the usual assumption of short-range capture and annihilation is made, the energy transfer rate in anthracene is *capture-limited* at least at temperatures higher than 60 K; and that, in any case, it is by no means clear that the trapping process is motion-limited. The second is a transient grating experiment[5] in which the singlet diffusion constant in anthracene is observed to be so much larger than that deduced from the "Smoluchowski prescription" applied to the energy transfer data[4] that the latter must be associated *completely* with capture if one is to accept the grating result.

Since the problem arises from *two* unknowns contributing to *one* observed quantity, one could hope that time-resolved experiments would solve the problem as they provide a large number of values of the observable. At least for anthracene and naphthalene, however, they do not help. For singlet motion in the crystals studied it is found[4] that k displays no observable time dependence and that dependences reported earlier appear to have been an experimental artifact. Since trivial considerations show[6] that energy transfer generally does possess time dependence, one must understand when this time dependence is *indiscernible in experiment*. Very fast motion[6] or long-range capture would make motion details disappear from the trapping process. While these could explain that observed lack of time dependence of k, a much stronger statement can be made, valid for short-range capture and for slow motion as well. We have carried out an explicit comparison of an exponential with decay rate equal to the steady state k (capture limit) with the host luminescence intensity calculated for 2-d and 3-d motion with parameters chosen to give the greatest deviation from the exponential while maintaining the same average decay rate k (motion limit). We find that, under the conditions of the experiments, the two extreme limits and all intermediate cases differ very little from one another. A superposition of observed curves shows that the differences lie well within the normal scatter in the data. Thus, as long as the effective motion is 2-d or 3-d, (as is typical of singlet motion in molecular crystals) it is impossible to distinguish between capture-limited and motion-limited trapping from the observed time dependence. Therefore, sensitized luminescence, time-resolved or not, gives us *only lower bounds* on the motion, i.e. on the hopping rate F and the diffusion constant. Such bounds were given in ref. 3. A more extensive compilation follows.

HOST	GUEST	F	TYPE	Temp
anthracene	tetracene	$\geq 25\ ps^{-1}$	singlet	5–300 K
napthalene	anthracene	$\geq 3.7\ ps^{-1}$	singlet	4 K
napthalene	anthracene	$\geq 0.2 ps^{-1}$	singlet	300 K
p-terphenyl	tetracene	$\geq 11\ ps^{-1}$	singlet	250 K
tetracene	pentacene	$\geq 33\ ps^{-1}$	singlet	170 K
napthalene	β-methyl-napthalene	$\geq 7.6\ ns^{-1}$	triplet	16 K
napthalene	β-methyl-napthalene	$\geq 16\ ns^{-1}$	triplet	6 K

Distinguishable differences from the exponential are expected to occur for

1-d motion. We therefore studied triplet motion in TCB. Indeed we found that, if the motion were known to be incoherent, the data[7] would be compatible only with largely motion-limited trapping. However, spin echo experiments have been used[8] to conclude that triplet motion in TCB at low temperatures is coherent over very large distances. By fitting the results of 1-d motion with *arbitrary* degree of coherence to the phosphorescence data[7] we found the situation highly inconclusive. We refer the reader elsewhere for details[9] and point out that even in this 1-d system, sensitized luminescence, even time-resolved, does not lead to a unique picture of exciton motion. It is neither possible to distinguish between capture and motion as the limiting process nor between coherent and incoherent transport.

We conclude that, in spite of the experimental sophistication it has reached, this traditional probe is unable in its present form to draw unique conclusions about exciton motion, whether about its kind (coherence/incoherence) or about its extent (magnitude of D), and that motion-based microscopic interpretations must be viewed with great care. Unambiguous measurements of exciton motion require increased sensitivity in the tails, or complementing this potentially powerful technique with independent probes of just capture or motion.

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