

ANALYSIS OF EXCIMER MIGRATION OBSERVATIONS IN MOLECULAR CRYSTALS

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The applicability of the concepts of polaron motion to the analysis of experiments on excimer migration is examined with particular reference to pyrene.

Structured absorption accompanied by a broad structureless emission with characteristically long lifetimes and temperature variation is the hallmark of excimers. Although understood relatively better in solution, excimers present a number of intriguing features in crystals. The process of their formation and that of their migration are the main focus of recent research^{1,2}. The latter is often approached via polaron concepts, the basic assumption being that an excimer is well described as an electronic excitation dressed with the "excimer oscillation". While in solution formation is understood in a straightforward way as occurring as a result of the translational motion of the molecules and the consequent encounter of an excited and unexcited molecule, in crystals the situation is much less clear. The simplest way to address excimer migration is in terms of harmonic oscillator potentials and small polaron theory^{3,4}. However, at least in pyrene, activation energies associated with excimer migration have been found⁵⁻⁷ to be considerably lower than would be expected from the characteristics of the optical spectra. We have found that this discrepancy forces us to abandon simplistic polaron concepts based on harmonic oscillators and to consider, as others have suggested^{8,9}, more realistic potentials. We carry out explicit calculations based on such potentials. For crystals such as pyrene, which have preformed dimers, we use Morse potentials typified by the expression $\exp[-c(x-a)] - c \exp[-(x-a)]$ and shown in fig. 1, x being the intermolecular separation, a the relative displacement of the potential in the electronic ground and excited state, and c a suitable constant.

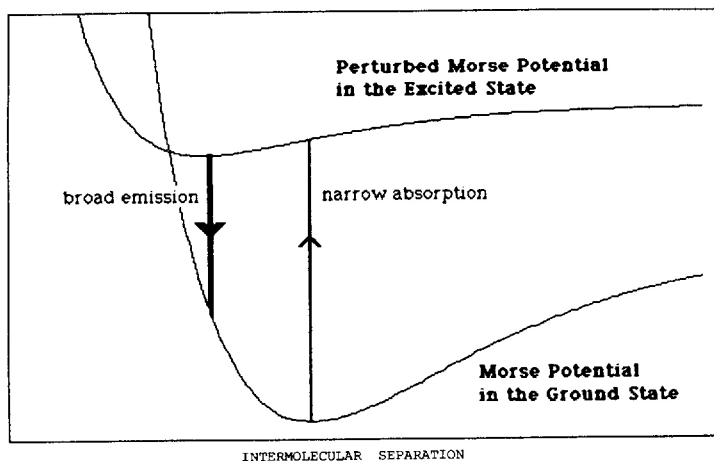


figure 1

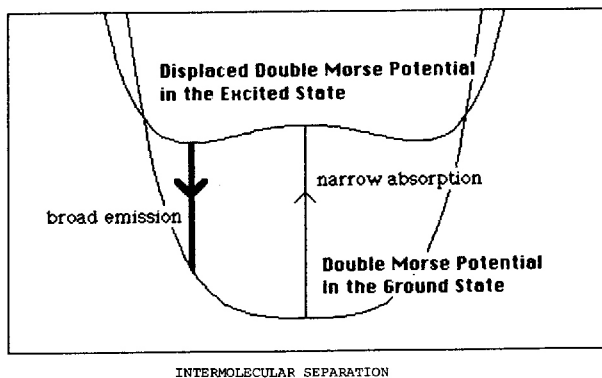


figure 2

For stack crystals such as dichloroanthracene¹ we use Morse-based potentials such as $\{\exp[-(c-1)a]\}\cosh(cx) - c \cosh(x)$ (fig. 2). We calculate wave functions, overlap integrals, optical spectra, and migration quantities including activation energies. Preliminary results resolve the discrepancies mentioned above concerning pyrene and show that the basic behavior of excimers appears to be explained naturally in this scheme.

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