LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area. (b) 50 words for each displayed equation: 1 ci 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1979 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Experimental test of the Anderson–Mott transition model for excitation transport

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Anderson localization and the resulting Anderson–Mott transition or "mobility edge" model have been applied to the excitation migration in ruby and other inorganic systems and more recently to mixed molecular crystals. The Lyo–Orbach theoretical adaptation of the Anderson model appeared to find its experimental verification in the spectral diffusion measurements on ruby and related systems. The energy migration experiments on the effects of donor (Cr3+) concentration were interpreted in the same manner. The Klafter–Jortner adaptation of the Anderson model to organic mixed crystals also predicts a critical donor concentration for the onset of exciton transport, and was applied to the donor concentration dependence experiments on isotopic mixed crystals of naphthalene, benzene, and phenazine in perdeuterophenazine, with further work claiming its complete adequacy for a series of experiments performed on phenazine in perdeuterophenazine systems. However, there has been continued controversy on this issue, both with respect to ruby and related systems as well as for organic crystals. The alternative viewpoint interprets the totality of observations on any given system as due to kinetics while the first approach allows kinetics to play a role only on one side of the Anderson mobility edge (i.e., above a critical donor concentration). In view of the plethora of arguments, experiments, simulations, and semantic problems, we felt the need for an experimental test that is unambiguous in its concept, interpretation and experimental validity. We claim to present such a test here.

The essence of the Anderson localization model is that "below" the transition there is an absence of transport or diffusion. In other words, there is no kinetics below the mobility edge. Accordingly, in the theoretical models time plays no role in determining the location of the transition (mobility edge). Consequently, the concentration of sensors (acceptors, "supertraps") should not affect the location of such a transition. In other words, the critical donor concentration should be independent of the acceptor concentration. This prediction is explicitly made by Klafter and Jortner. On the other hand, it is elementary that any kinetic model must include the acceptor concentration as an important parameter, irrespective of whether the kinetics is phrased in terms of a simply averaged donor population or takes into account donor clusterization. It is impossible to clearly separate donor concentration effects from acceptor concentration effects in binary systems like ruby or pheno­zine, where both donor and acceptor are made of the same chemical species (e.g., Cr ions or perprotonated phenazine). However, there is no such limitation in principle, for ternary systems. In the experiments described here we keep the relative acceptor-to-donor concentration constant over a large range of donor concentrations. This is repeated for different values of relative acceptor-to-donor concentrations.

Our system is a mixed crystal of (1) potassium fused, zone refined, C15D8 ("host"), (2) potassium fused, zone refined C15H8 ("donor"), and (3) zone refined betamethyl­naphthalene ("acceptor"). The details of preparation, purification, and analytical monitoring will be given elsewhere. The steady-state relative phosphorescence from the acceptor is monitored at 1.8 K as a function of donor mole fraction C and relative acceptor mole fraction S. The fraction I_S/I_tot is obviously a measure of the energy transport (without donor energy transport this fraction should be practically constant with C and roughly equal to S, that is, of the order of 10^-7–10^-6). The phenomenon of interest is the sudden rise ("onset") in I_S/I_tot at some critical value of C (= C_c). The problem under investigation here is whether C_c depends on S. The details of the spectroscopic measurements will be given elsewhere, and are similar to previous work. Figure 1 clearly reveals a strong dependence of C_c on S, irrespective of the exact definition of C_c. We see that a decrease by two orders of magnitude in S increases C_c by about a factor of 2. We note that such a factor of 2 corresponds in the Anderson model to an increase in the microscopic strain energy (W) by about one order of magnitude. It is hard to see how this would be caused by a decrease in the absolute acceptor concentration from about 10^-5 to 10^-5. On the other hand, our observations are at least qualitatively consistent with kinetic models.
Our conclusion strongly points against the current Anderson model\textsuperscript{5,12,13,14} regarding the onset of triplet energy transport in naphthalene (C\textsubscript{10}H\textsubscript{8}/C\textsubscript{10}D\textsubscript{8}). The same conclusion can be drawn from older experiments on the singlet naphthalene energy transport\textsuperscript{12,21} even though \(S\) was not as well controlled (relative \(S\) fluctuations there of up to an order of magnitude compared to well below a factor of 2 here). We suggest that this crucial test, or its equivalent, should be performed on all other systems listed as candidates for the revelation of an Anderson–Mott–like excitation mobility edge.

Note added in proof: The last three references of Footnote 7 (added in proof) calculate an Anderson transition "erosion" with increasing acceptor concentration which, however, is negligible for SC \(\leq 10^4\) (the experimental domain reported on here). We thank Dr. Jortner,

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Infrared spectrum and structure of the isolated HF\textsubscript{2}– ion in solid argon

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The bifluoride ion HF\textsubscript{2}– is of considerable interest as a strong hydrogen bond and the best documented example of a symmetrical hydrogen bond.\textsuperscript{1–5} Early spectroscopic studies of HF\textsubscript{2}– species were performed in condensed phases with considerable crystal or solvent interaction which produced broad absorptions.\textsuperscript{4} Recently the infrared spectrum of the ion pair CS\textsubscript{2}HF\textsubscript{2}– has been observed in solid argon.\textsuperscript{5} The HF\textsubscript{2}– anion has not yet been characterized in the gas phase, and the infrared spectrum of the isolated HF\textsubscript{2}– anion in solid argon is of interest. The controversy over the radical\textsuperscript{5} or anion\textsuperscript{1} identification of a centrosymmetric (Cl–H–Cl) species could be settled by the observation of a symmetrical (F–H–F) species under ionizing conditions since recent photolysis studies of Ar/HF/F\textsubscript{2} mixtures failed to produce any HF\textsubscript{2} radical species.\textsuperscript{5}

Matrix photoionization experiments were conducted on Ar/HF = 100/1 samples using the cryogenic vacuum apparatus\textsuperscript{6,10} and an 8 mm i.d. open discharge tube\textsuperscript{11} described previously for periods of 18–20 h. Infrared spectra were recorded on a Beckman IR-12 using re-