

## 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; (c) 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<sup>a)</sup>

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Anderson localization<sup>1</sup> and the resulting Anderson-Mott transition or "mobility edge" model<sup>2,3</sup> have been applied<sup>4,5</sup> to the excitation migration in ruby and other inorganic systems<sup>6</sup> and more recently to mixed molecular crystals.<sup>7</sup> The Lyo-Orbach<sup>4,5</sup> theoretical adaptation of the Anderson model appeared to find its experimental verification in the spectral diffusion measurements on ruby<sup>8</sup> and related systems.<sup>9</sup> The energy migration experiments on the effects of donor (Cr<sup>3+</sup>) concentration<sup>10</sup> were interpreted in the same manner. The Klafter-Jortner adaptation<sup>7</sup> of the Anderson model to organic mixed crystals also predicts a critical donor concentration for the onset of exciton transport, and was applied<sup>7</sup> to the donor concentration dependence experiments on isotopic mixed crystals of naphthalene,<sup>11</sup> benzene,<sup>12</sup> and phenazine in perdeuterophenazine,<sup>13</sup> with further work claiming its complete adequacy for a series of experiments performed on phenazine in perdeuterophenazine systems.<sup>14</sup> However, there has been continued controversy on this issue, both with respect to ruby and related systems<sup>15</sup> as well as for organic crystals.<sup>16-18</sup> The alternative viewpoint<sup>15-18</sup> interprets the *totality* of observations on any given system as due to kinetics while the first approach<sup>1-5,7</sup> 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<sup>4,7</sup> *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.<sup>7</sup> 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 ("diffusion")<sup>19,20</sup> or takes into account donor clusterization ("percolation").<sup>11,16,17</sup> It is impossible to clearly separate donor concentration effects from acceptor concentration effects in binary systems like ruby<sup>8,10,15</sup> or phenazine<sup>13,14</sup> where both donor and acceptor are made of the same chemical species (e. g., Cr ions or protonated phenazine). However, there is no such limitation, in principle, for ternary systems.<sup>11,12</sup> 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, C<sub>10</sub>D<sub>8</sub> ("host"), (2) potassium fused, zone refined C<sub>10</sub>H<sub>8</sub> ("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 ("sensor")  $I_S/I_{tot}$  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  $10^{-3}$ - $10^{-4}$ ). 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.<sup>11,12,17,18</sup>

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<sup>7</sup> 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  $10^{-3}$  to  $10^{-5}$ . On the other hand, our observations are at least qualitatively consistent with kinetic models.<sup>11,19,20</sup>

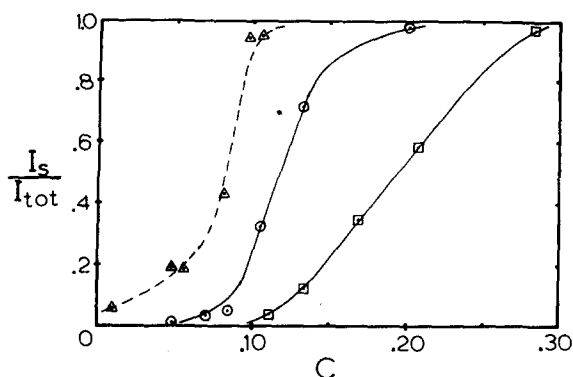


FIG. 1. Donor concentration ( $C$ ) dependence of the energy transport measure  $I_S/I_{tot} = I_S/(I_S + I_d)$ , where  $I_S$  is betamethylnaphthalene phosphorescence (0-0) and  $I_d$  is that of  $C_{10}H_8$ , all at 1.8 K. The parameter  $S$  is  $10^{-4}$  for the "square" data points and  $10^{-3}$  for the "circle" points. The "triangle" points are based on older data<sup>11</sup> and  $S \approx 10^{-2}$  at  $C = 0.1$ , but along this curve  $SC$  rather than  $S$  is approximately constant. The broken lines are merely visual aides.

Our conclusion strongly points against the current Anderson model<sup>4, 7, 13, 14</sup> regarding the onset of triplet energy transport in naphthalene ( $C_{10}H_8/C_{10}D_8$ ). The same conclusion can be drawn from older experiments on the singlet naphthalene energy transport<sup>17, 21</sup> 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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<sup>1</sup>P. W. Anderson, Phys. Rev. **109**, 1492 (1958); E. N. Economou and M. H. Cohen, Phys. Rev. B **5**, 2931 (1972).

<sup>2</sup>P. W. Anderson, Nobel Address, Rev. Mod. Phys. **50**, 191 (1978); N. F. Mott, *ibid.* **50**, 203.

<sup>3</sup>N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford University, New York, 1978), 2nd ed.

<sup>4</sup>S. K. Lyo, Phys. Rev. B **3**, 3331 (1971).

<sup>5</sup>R. Orbach, Phys. Lett. A **48**, 417 (1974).

<sup>6</sup>R. Flach, D. S. Hamilton, P. M. Selzer, and W. M. Yen, Phys. Rev. B **15**, 1248 (1977).

<sup>7</sup>J. Klafter and J. Jortner, Chem. Phys. Lett. **49**, 410 (1977); **60**, 5 (1978); J. Klafter, Ph.D. thesis, Tel-Aviv University, 1978; J. Jortner (private communication, January 1979).

<sup>8</sup>J. Koo, L. R. Walker, and S. Geschwind, Phys. Rev. Lett. **35**, 1669 (1975).

<sup>9</sup>C. Hsu and R. C. Powell, Phys. Rev. Lett. **35**, 734 (1975).

<sup>10</sup>G. F. Imbush, Phys. Rev. **153**, 326 (1967).

<sup>11</sup>R. Kopelman, E. M. Monberg, F. W. Ochs, and P. N. Prasad, J. Chem. Phys. **62**, 292 (1975); R. Kopelman, E. M. Monberg, and F. W. Ochs, Chem. Phys. **19**, 413 (1977).

<sup>12</sup>S. D. Colson, R. E. Turner, and V. Vaida, J. Chem. Phys. **66**, 2187 (1977).

<sup>13</sup>D. D. Smith, R. D. Mead, and A. H. Zewail, Chem. Phys. Lett. **50**, 358 (1977).

<sup>14</sup>D. M. Burland and A. H. Zewail, Adv. Chem. Phys. (in press); A. H. Zewail (private communication, December, 1978).

<sup>15</sup>P. M. Selzer, D. L. Huber, B. B. Barnett, and W. M. Yen, Phys. Rev. B **17**, 4979 (1978).

<sup>16</sup>S. D. Colson, S. M. George, T. Keyes, and V. Vaida, J. Chem. Phys. **67**, 4941 (1977).

<sup>17</sup>E. M. Monberg and R. Kopelman, Chem. Phys. Lett. **58**, 497 (1978); **58**, 492 (1978).

<sup>18</sup>R. Kopelman, E. M. Monberg, J. S. Newhouse, and F. W. Ochs, J. Lumin. (in press).

<sup>19</sup>A. Blumen and R. Silbey, J. Chem. Phys. (in press).

<sup>20</sup>J. Jortner (private communication, September 1978).

<sup>21</sup>R. Kopelman, E. M. Monberg, and F. W. Ochs, Chem. Phys. **21**, 373 (1977); P. Argyrakis and R. Kopelman, J. Chem. Phys. **66**, 3301 (1977).

## Infrared spectrum and structure of the isolated $HF_2^-$ ion in solid argon

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The bifluoride ion  $HF_2^-$  is of considerable interest as a strong hydrogen bond and the best documented example of a symmetrical hydrogen bond.<sup>1-3</sup> Early spectroscopic studies of  $HF_2^-$  species were performed in condensed phases with considerable crystal or solvent interaction which produced broad absorptions.<sup>4</sup> Recently the infrared spectrum of the ion pair  $Cs^+HF_2^-$  has been observed in solid argon.<sup>5</sup> The  $HF_2^-$  anion has not yet been characterized in the gas phase, and the infrared spectrum of the isolated  $HF_2^-$  anion in solid argon is of interest. The controversy over the radical<sup>6</sup> or anion<sup>7</sup>

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<sub>2</sub> mixtures failed to produce any  $HF_2^-$  radical species.<sup>8</sup>

Matrix photoionization experiments were conducted on Ar/HF = 100/1 samples using the cryogenic vacuum apparatus<sup>9, 10</sup> and an 8 mm i. d. open discharge tube<sup>11</sup> described previously for periods of 18-20 h. Infrared spectra were recorded on a Beckman IR-12 using re-