ULTRAFAST INFRARED AND VISIBLE SPECTROSCOPY OF INTERMOLECULAR ELECTRON TRANSFER FROM DIMETHYL ANILINE TO COUMARIN 337

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Ultrafast visible and infrared polarization spectroscopy has been used to reveal the orientation of donor and acceptor molecules in the intermolecular electron transfer between coumarin 337 and dimethylaniline.

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Recent efforts have focused on the role of non-equilibrium configurations of the solvent and the solute in electron transfer [1–2]. Intermolecular charge transfer reactions between a solute and a solvent may provide a direct probe of the first solvent-shell because of the rapid decay with distance of the electron tunneling probability. We have performed ultrafast pump experiments on the intermolecular electron transfer between coumarin 337 (C337) solute and dimethylaniline (DMA) solvent. The electron transfer process is illustrated in Figure 1.

We have performed 400 nm pump, 500 nm probe measurements, see Figure 2. The anisotropies taken at early (0.2 ps) and late (10 and 30 ps) times indicate that the C337 gain spectrum results from the same

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FIGURE 1 Following photoexcitation of C337, electron transfer from DMA to C337 occurs.

FIGURE 2 Transient absorption of C337 in DMA. 400 nm pump/500 nm probe.

transition as the optically pumped transition ($r = 0.4 \pm 0.05$), and a new, DMA radical cation absorption exhibits a transition moment nearly perpendicular to the pumped transition, $r = -0.2 \pm 0.05$.

FIGURE 3 C337 in Benzonitrile. Static and 5 ps delay after 400 nm pump spectra.

We have also performed visible pump IR probe experiments to reveal the S_0-S_1 transition moment *versus* the carbonyl and nitrile stretch absorption transition moments. (see Fig. 3.) These data indicate that the electronic transition moment direction of C337 is long axis polarized. The transition moment direction of the dimethylaniline radical cation absorption lies parallel to the DMA long axis. Therefore, the anisotropy indicates that the electron donor and acceptor molecules are aligned with their long axes roughly perpendicular. C337 and DMA have 10 D and 1.6 D ground state dipole moments, respectively, aligned roughly along their long axes. The observed anisotropy indicates that electron transfer is rate controlled by favorable overlap of the HOMO's of C337 and DMA, which is not necessarily optimized by the attractive and repulsive intermolecular interactions.

References

- [1] For recent reviews in this area see the centennial issue of *J. Phys. Chem.*, 1996 Vol. 100.
- [2] Nagasawa, Y. Yartsev, A. P. Tominaga, K. Bisht, P. B. Johnson, A. E. and Yoshihara, K. (1995). *J. Phys. Chem.*, **99**, 653.