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Stepwise Solvation of the Intramolecular-Charge-Transfer Molecule p-(Dimethylamino)benzonitrile

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This paper presents a systematic study of gas-phase p-(N,N-dimethylamino)benzonitrile (DMABN) both in a supersonic jet expansion and in a thermalized vapor. From the jet studies, the excited- and ground-state vibrational spectra of the isolated molecule are resolved, and the spectroscopy of the stoichiometric complex with water, methanol, ammonia, and acetonitrile in the beam is reported. It is concluded that 1:1 complexes are not sufficient for the local perturbation to cause charge separation. At higher temperatures in the jet, we observe emission that we attribute to DMABN self-complexes. Under high pressure and temperature vapor conditions (>30 mTorr, 60 °C), red-shifted fluorescence from DMABN is observed. This is attributed to the charge-transfer state of DMABN in self-complexes.

Introduction

Many recent investigations have focused on the role of the solvent in the charge-transfer process for molecules in solution.[1-20] Both intramolecular[8-14] and intermolecular[15-17] charge separations have been studied. The solute–solvent interactions can be passive, as observed in the cage effect where the primary role of the solvent is to trap the solute particles within a volume enabling them to collide and react with each other.[18-20] The solute can also be actively coupled to the medium, as in the case of charge-transfer reactions where the energies of initial, intermediate, and final states, the reaction pathways leading to different products, and the kinetics of the transitions can be dramatically affected by the solvent. Static[1,3,10] and dynamic[4,6,14] polarity effects, as well as local solute–solvent interactions[21] such as hydrogen bonding are important in these latter processes.

An example of a molecule that interacts strongly with polar solvents is p-(dimethylamino)benzonitrile (DMABN). In polar solvents, an excited DMABN molecule undergoes a rotation of the dimethylamino group about the amino–phenyl bond to achieve a perpendicular geometry with respect to the plane of the benzene ring.[22] This motion results in charge separation, as evidenced by the measured increase in the excited-state dipole moment from 6 to 16 D.[23] In polar solvents, the twisted, charge-separated form is stabilized, and a dual fluorescence appears. It consists of a UV component plus a new red-shifted emission that does not appear in nonpolar solvents. Rapid equilibration between the twisted and planar forms in polar media yields the dual fluorescence. This twisted internal-charge-transfer model (TICT), was first proposed by Grabowski and co-workers.[22] Picosecond spectroscopic studies[11,24] have confirmed that (i) the planar state is the precursor of the twisted state and (ii) equilibrium between the two states is established during the excited-state lifetime. Further, the dominant solvent effect on the dynamics of the charge separation in this case has recently been attributed to static polarity effects.[10] The proposal of a barrier whose height changes with the polarity of the medium gives a simple explanation for the appearance of dual fluorescence in polar solvents and a single UV fluorescence in alkanes: a certain polarity is required before the TICT barrier is low enough to allow the forward TICT process to proceed within the lifetime of the initially excited state.

The recent work by Robinson et al.[25] and others[26] attempts to deduce the number of water molecules that must be present in order to induce effects such as the one described above for DMABN. The idea is that a critical number of solvent molecules

exists for a given charge-transfer or proton-transfer process. It is conceivable in the case of DMABN that a 1:1 DMABN/solvent complex could provide sufficient stabilization by charge-transfer or dipolar interactions to permit the photoisomerization of DMABN to its twisted charge-transfer state.[27-30]

(1) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(2) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

(3) Balzani, V.; Scandola, F. In *Energy Resources through Photochemistry and Catalysis*; Gratzel, T. J., Ed.; Academic: New York, 1983; 1.

(4) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387; *J. Chem. Phys.* **1983**, *78*, 470.

(5) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 1601.

(6) Van der Zwan, G.; Hynes, J. T. *Chem. Phys. Lett.* **1983**, *101*, 367; *J. Phys. Chem.* **1985**, *89*, 4181.

(7) Zusman, L. D. *Chem. Phys.* **1980**, *49*, 295.

(8) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

(9) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.

(10) (a) Hicks, J. M.; Vandersall, M.; Babarogic, Z.; Eisenthal, K. B. *Chem. Phys. Lett.* **1985**, *116*, 18. (b) Hicks, J. M.; Vandersall, M.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1987**, *135*, 413.

(11) Huppert, D.; Rand, S. D.; Rentzepis, P. M.; Barbara. P. F.; Struve, W. S.; Grabowski, Z. R. *J. Chem. Phys.* **1981**, *75*, 5714.

(12) Wang, Y.; Eisenthal, K. B. *J. Chem. Phys.* **1982**, *77*, 6076.

(13) Rotkiewicz, K.; Rubaszewska, W. *J. Lumin.* **1982**, *27*, 221.

(14) Kosower, E. M. *J. Am. Chem. Soc.* **1985**, *107*, 1114. Giniger, R.; Huppert, D.; Kosower, E. M. *Chem. Phys. Lett.* **1985**, *118*, 240.

(15) Miller, J. R. *Springer Ser. Chem. Phys.* **1985**, *42*, 234.

(16) McGuire, M.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 2549.

(17) Harrer, W.; Grampp, G.; Jaenicke, W. *Chem. Phys. Lett.* **1984**, *112*, 263.

(18) Frank, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30*, 120.

(19) Abul-Haj, N. A.; Kelley, D. F. *J. Chem. Phys.*, in press.

(20) Berg, M.; Harris, A. L.; Harris, C. B. *Phys. Rev. Lett.* **1985**, *54*, 951.

(21) Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1983**, *778*, 5266; *Chem. Phys. Lett.* **1983**, *94*, 448, 454.

(22) Grabowski, Z. R.; Rotkiewicz, K.; Rubaszewska, W.; Kirkor-Kaminska, E. *Acta Phys. Pol., A* **1978**, *A54*, 767.

(23) Baumann, W., personal communication.

(24) Wang, Y.; McAuliffe, M.; Novak, F.; Eisenthal, K. B. *J. Phys. Chem.* **1981**, *85*, 3736.

(25) Lee, J.; Robinson, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6153; *J. Chem. Phys.* **1984**, *81*, 1203.

(26) Hierl, P. M.; Ahrens, A. F.; Henchman, M. J.; Viggiano, A. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 3140, 3142.

(27) Visser, R. J.; Weisenborn, P. C. M.; Konijnenberg, J.; Huizer, B. H.; Varma, C. A. G. O. *J. Photochem.* **1986**, *32*, 217. Visser, R. J.; Weisenborn, P. C. M.; Varma, C. A. G. O.; de Haas, M. P.; Warman, J. M. *Chem. Phys. Lett.* **1984**, *104*, 38. Visser, R. J.; Varma, C. A. G. O.; Konijnenberg, J.; Bergwerf, P. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 347.

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‡Contribution No. 7562.

In order to investigate some of these ideas about the role of the solvent, we have undertaken studies of DMABN in a supersonic beam and in a thermalized vapor as a complement to liquid-state studies. The beam studies are similar to earlier work on solvation in the isoquinoline/water[21] system and on charge transfer in the anthracene/dimethylaniline[31,32] system. In the gas phase, some derivatives of DMABN have been studied.[13,30] Another compound thought to undergo TICT, 9,9'-bianthryl, has been studied in a supersonic jet,[34] where it was found that charge transfer occurs on the addition of one acetone molecule to the solute.[35] However, in this case, no evidence was given for the 1:1 stoichiometry, and it is not ruled out that higher complexes were responsible for the observed charge-transfer fluorescence.

The idea of the beam work is to generate 1:n solute to solvent complexes (water, methanol, ammonia, and acetonitrile were the solvents in these studies) and to determine thereby the relation between the solute–solvent interactions and the TICT process. Among the issues concerning the twisted internal charge transfer of DMABN are the critical number of solvent molecules, the relative contributions of the local and the long-range stabilizing forces (the latter force can be important in liquids), and the details of the solute–solvent interaction, e.g., steric effects, hydrogen bonding, and dipolar interactions. The high pressure vapor work sought to determine if, in a gas-phase dimer or small cluster, DMABN itself could act as a stabilizing solvent molecule to a photoexcited member of the cluster. Earlier work on very concentrated DMABN/alkane solutions showed that a ground-state molecule could form a loose complex with an excited DMABN[29] and thus provide the stabilization required for the photoisomerization to occur.

In this paper, we present a systematic study of solvated DMABN in a supersonic jet expansion. We resolve the excited- and ground-state spectra of the isolated molecule, and we report on the spectroscopy of the stoichiometric complex with solvent in the beam. It is concluded that 1:1 complexes are not sufficient to allow charge separation. In the thermalized vapor experiments, we observe both the UV monomer emission and the visible emission due to the charge separation made possible by the stabilization of DMABN self-complexes. Under appropriate conditions in the beam, and in the absence of solvent, we also observed visible emission that we attribute to DMABN in self-complexes.

Experimental Section

The two sets of supersonic beam apparatus used for this study have been described previously in detail.[36,37] The expansion condition is noted in each figure. Most excitation spectra and dispersed fluorescence for DMABN/H_2O complexes were recorded with a continuous-jet system.[36] The remaining spectra for the DMABN/H_2O complexes, spectra for the other DMABN/ solvent complexes, and spectra for the DMABN self-complexes were recorded with a pulsed-jet system.[37] In general, p-(dimethylamino)benzonitrile (DMABN) (Aldrich; 98%) and p-(diethylamino)benzonitrile (DEABN) (Pfaltz and Bauer; 97%) were seeded in different carrier gases: He, Ne, Ar, or N_2. The use of purified DMABN (99.5%) gave the same results as shown
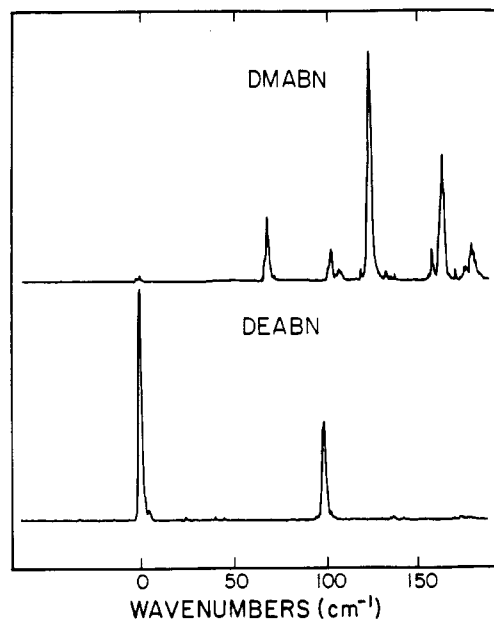
Figure 1. (Top) Portion of the fluorescence excitation spectrum of jet-cooled DMABN. Intensity is not corrected for the laser system response. Nozzle temperature was 160 °C, and laser-to-nozzle distance was 3 mm. He backing pressure was 40 psi. The resolution is limited by the laser bandwidth ($\sim$1.5 cm^{-1}). (Bottom) Portion of the fluorescence excitation spectrum of jet-cooled DEABN. Nozzle conditions are similar to those used for DMABN. Note that the two spectra are lined up with each other, using the first observed line as a marker. The actual assignment of the 0,0 band cannot be made without careful Franck–Condon analysis (see text).

here for the less pure preparation.

Different carrier gases were used at different stagnant pressures in order to determine the optimum cooling condition while minimizing the formation of van der Waals complexes. In the continuous jet, He at 40 psi backing pressure was used. For the pulsed jet, 50 psi He for DMABN self-complexes was used, while 70 psi He was used for complexes with other solvents. The nozzle diameter for the continuous and pulsed jets were 100 and 500 μm, respectively. To form solvent/solute complexes, a careful control of the solvent concentration was necessary. By controlling the temperature (from −70 to 25 °C) of the wet-line reservoir and by using water solutions with different concentrations of calcium chloride (0–6 M), we were able to change the partial pressure of solvent in the nozzle expansion.

For the continuous-jet apparatus, excitation spectra were obtained by using the frequency-doubled output of a nitrogen pumped dye laser with an amplifier stage. Lifetime measurements and dispersed fluorescence studies in the beam were obtained by using the frequency-doubled output of a synchronously pumped, cavity dumped dye laser.[36]

Excitation spectra using the pulsed system were obtained by using the frequency-doubled output of a YAG pumped dye laser (5-ns pulses) operated at 10 Hz. The signal was normalized with respect to laser intensity. Unlike the 0.4–3.2-Å resolution for the continuous apparatus we used for recording the sharp features of the fluorescence, wider slits (resolution of 24 Å) were used for recording emission at high temperatures.

The study of DMABN vapor at higher pressures and temperatures was carried out by heating doubly sublimed crystals in an open cell and irradiating the vapor above it. This procedure was found to be better than using a sealed evacuated cell containing crystals, since the presence of fluorescent adsorbed DMABN species on the quartz walls contaminated the signal from the free vapor species. Using an MKS Baritron gauge, we measured the vapor pressure of DMABN at 22 °C to be 30 mTorr (uncorrected). The temperature of the vapor was measured by placing a Cu–constantan thermocouple at the top of the cell and reading from a calibrated Omega digital meter. Picosecond kinetics were measured by the method of single-photon counting

(28) Chandross, E. A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic: New York, 1975; p 187.

(29) Nakashima, N.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3016.

(30) Wang, Y. *Chem. Phys. Lett.* **1985**, *116*, 286.

(31) Felker, P. M.; Syage, J. A.; Lambert, W. R.; Zewail, A. H. *Chem. Phys. Lett.* **1982**, *92*, 1.

(32) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 2233.

(33) Bischof, H.; Baumann, W.; Detzer, N.; Rotkiewicz, K. *Chem. Phys. Lett.* **1985**, *116*, 180.

(34) Khundkar, L. R.; Zewail, A. H. *J. Chem. Phys.* **1986**, *84*, 1302.

(35) Kajimoto, O.; Yamasaki, K.; Arita, K.; Hara, K. *Chem. Phys. Lett.* **1986**, *125*, 184.

(36) Lambert, W. R.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 2217. Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 2975.

(37) Keelan, B. W.; Syage, J. A.; Shepanski, J. F.; Zewail, A. H. *Proceedings of the International Conference on Lasers 1983*, San Francisco, CA; Society for Optical and Quantum Electronics, STS Press: McLean, VA, 1985; p 718.

using a synchronously pumped, cavity dumped dye laser.

Results

A. Isolated DMABN. The excitation spectra of jet-cooled DMABN and DEABN are rich and show spectroscopic manifestations similar to other alkylanilines.[38] The symmetry of the transition is effectively unchanged, and one expects the aniline-type modes to be active. In our excitation spectra, these modes (12 and 6a) can be assigned to observed bands with minor frequency shifts compared to aniline and *p*-alkylanilines.

Figure 1 displays a portion of the excitation spectra of the two molecules. The 0,0 region of DMABN shows a structure of low-frequency bands similar to that found in alkylanthracene,[32,39] bianthryl,[34] and many alkyl aromatics.[40] This structure could be due to low-frequency torsional modes that display the properties of a double-well potential[34,40] and hence the unique Franck–Condon pattern. Also, it is possible that some of the bands, especially the weak ones, are due to different conformers that freeze in during the expansion or to aggregates. The actual assignment of the DMABN origin cannot be made without a detailed analysis of the torsional structure similar to that done for bianthryl[34] and the systems described by Ito.[40] Thus we tentatively take the "origin" to be the strongest peak in the origin region.

For DEABN, the 0,0 region of the excitation spectrum appears to be less rich than that of DMABN. This observation may support the idea of the double-well potential, since here the "locking" of the amino group by the ethyl chains could result in a higher torsional barrier. Finally, the "origin" of DEABN is red-shifted from that of DMABN by 452 cm^{-1}. DMABN is red-shifted by 1644 cm^{-1} from aniline and by 701 cm^{-1} from *p*-methylaniline.

The dispersed fluorescence spectra of DMABN and DEABN are shown in Figure 2 for different excitation wavelengths. The first point to be noted is that, in all spectra, the dispersed fluorescence tails off after 6000 cm^{-1}. No further fluorescence was observed (with our sensitivity) upon inspection of the region to the red of that shown in Figure 2, where charge-transfer fluorescence is expected to appear (red-shifted by 6300 cm^{-1}). This feature was found to be insensitive to the excitation wavelength in the region studied. For DMABN, this is true up to 280 nm. The 308.7-nm excitation of DMABN and the 314.3-nm excitation of DEABN are very similar and are consistent with characteristics of the excitation spectra. Excitation of the weak band of DMABN at 309.9 nm (Figure 2, top) was recorded with lower resolution (because of weak intensity) and is shown here to emphasize that the major structures of its fluorescence spectrum are similar, although distorted somewhat due to the poorer resolution. From excitation and dispersed fluorescence, it is concluded that the isolated DMABN molecule cannot by itself undergo charge transfer (up to given excitation energies).

B. Complexes of Solvent/DMABN. In order to establish the formation of complexes between solvent and DMABN in the supersonic expansion, the fluorescence excitation spectra were recorded while the partial pressure of solvent was varied. In Figure 3, the spectral region about the strongest (308.7-nm) vibrational band is shown as a function of increasing water pressure (P_{H_2O}). A new band appears, which is blue shifted by 18 cm^{-1} from the main peak, and increases at first approximately linearly with P_{H_2O} independent of the carrier gas used. Similar new bands appeared on other vibrational transitions; e.g., a new peak on the 309.1-nm band appeared blue-shifted by 15 cm^{-1}. We assign these new bands to the 1:1 DMABN/water complex. The same behavior was found with the solvents CH$_3$OH, CH$_3$CN, and NH$_3$ over the temperature range of 70 to −15 °C. Attempts were made to form complexes with acetic acid and acetone. However, in spite of the
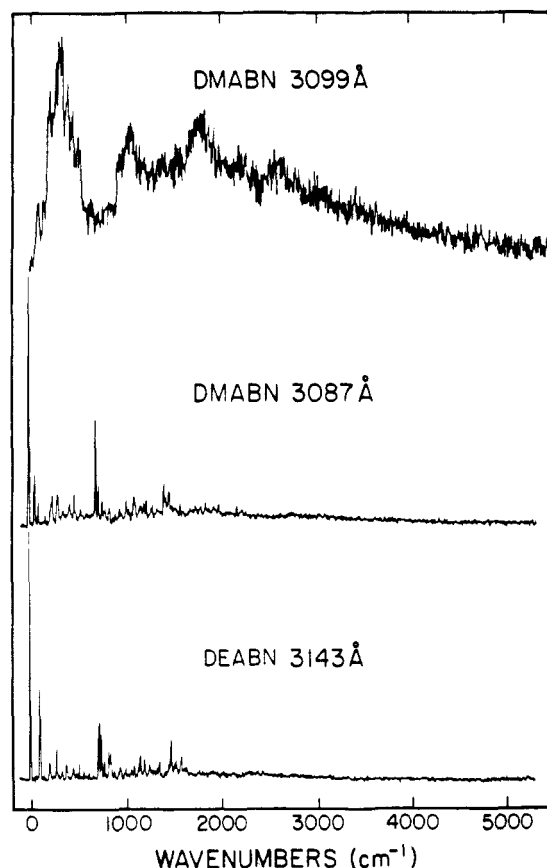
Figure 2. (Top) Dispersed fluorescence resulting from excitation of jet-cooled DMABN to the first band at 3099 Å. Resolution is low in this spectrum (3.2 Å) due to the low intensity of this band. Nozzle temperature was 160 °C, and laser-to-nozzle distance was 3 mm. He backing pressure was 40 psi. (Middle) Dispersed fluorescence resulting from excitation of jet-cooled DMABN to the 3087-Å band. Resolution was 0.8 Å, and nozzle conditions were similar to those mentioned above. (Bottom) Dispersed fluorescence resulting from excitation of jet-cooled DEABN to the 3143-Å band. Resolution was 0.8 Å, and nozzle conditions were similar to those mentioned above. (Note that the spectra are plotted relative to the excitation energy.)

fact that the DMABN signal drops significantly, we were unable to observe any new bands under similar beam conditions. Figure 4 shows the fluorescence excitation spectra (about the origin) of DMABN complexed 1:1 with NH$_3$, CH$_3$OH, and H$_2$O. (Note that the scale and wavelength scan direction are different from Figure 3.) The spectral shift relative to the strongest band of DMABN (308.7 nm) is 21, 15, and 18 cm^{-1}, respectively, to the blue (when CH$_3$CN is used there is a very weak band blue-shifted by 254 cm^{-1}). We assign these blue-shifted peaks as the 1:1 DMABN/solvent complex. The shifts for the three solvents are similar, but it is difficult to know from the shift the exact site for complexation.

A search for the long-wavelength emission that is characteristic of the CT band was made by exciting the complexes. In Figure 5, we have aligned the fluorescence spectra obtained by exciting the isolated and water-complexed DMABN, at 308.7 and 308.5 nm, respectively. These spectra are seen to be almost identical except for a constant shift due the binding of the water. More important perhaps is the noted absence of a new red-shifted emission for the complex, indicating that charge transfer does not occur.

Further support for the conclusion that charge transfer in the excited state does not occur for the complex comes from lifetime measurements. The isolated DMABN molecule under beam conditions has a lifetime of 5.3 ns (measured at 308.7 nm). The band at 308.5 nm of the complex has a lifetime of 5.3 ns. Since the fluorescence lifetime does not change, we conclude that the planar excited DMABN is the emitting state; i.e., the twisted charge-transfer state has not been formed. This is consistent with

(38) Powers, D. E.; Hopkins, J. B.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5721. Baskin, J. S.; Dantus, M.; Zewail, A. H. *Chem. Phys. Lett.* **1986**, *130*, 473.

(39) Syage, J. A.; Felker, P. M.; Semmes, D. H.; Al Adel, F.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 2896.
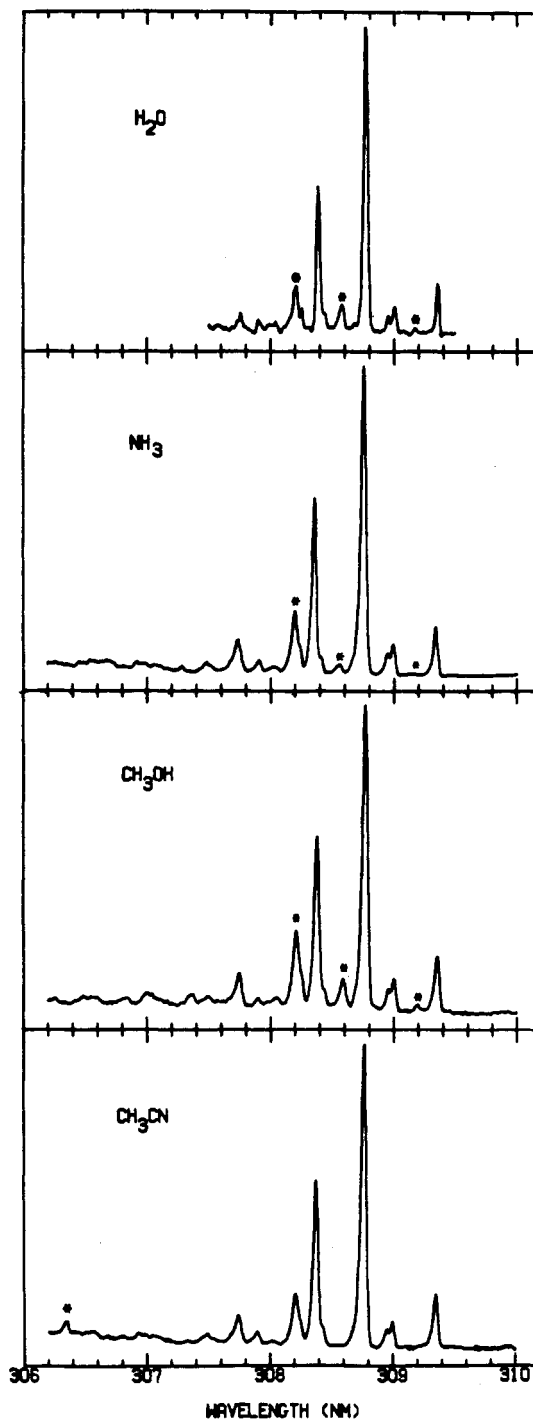
(40) Ito, M. *J. Phys. Chem.* **1987**, *91*, 517.
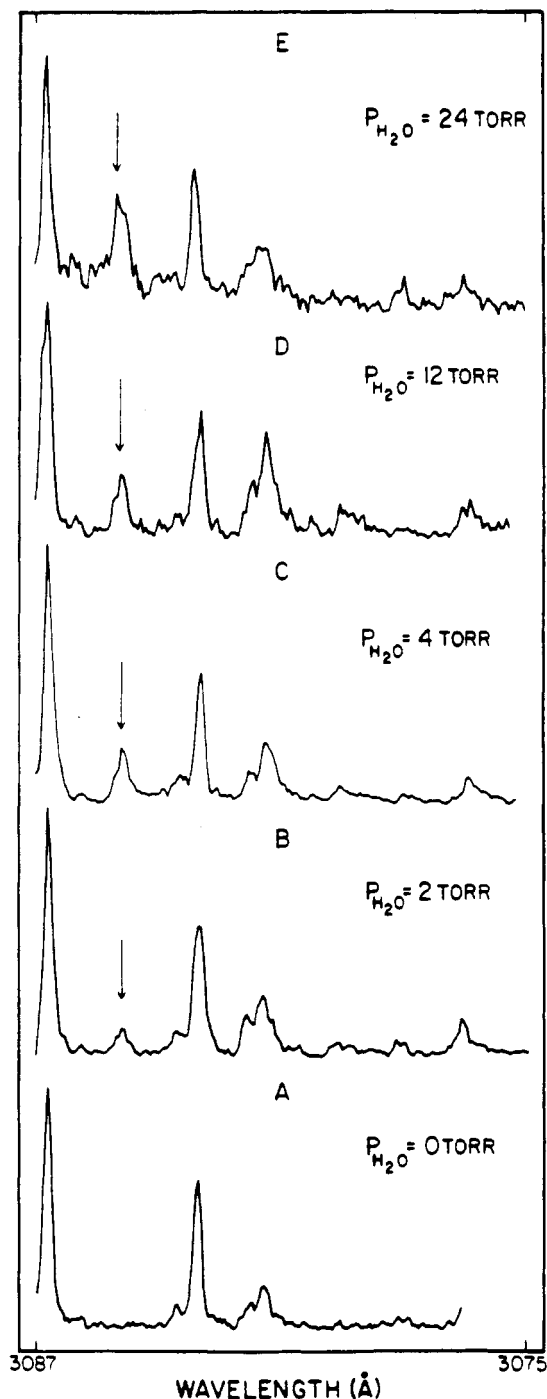
Figure 3. Portion of the fluorescence excitation spectrum of jet-cooled DMABN, showing the effect of increasing water partial pressure on the formation of the 1:1 complex (noted with an arrow). In each case the water partial pressure was varied. For case (A) 0, (B) 2, (C) 4, (D) 12, and (E) 24 Torr. Nozzle conditions were kept the same for all cases: temperature 160 °C, laser-to-nozzle distance 3 mm, and He backing pressure 40 psi. Laser bandwidth was 2–3 cm^{-1}.

other studies where it was found that excitation below the barrier for dissociation gives similar lifetimes for the complex as for the parent molecule.[41]

It is possible that if enough internal energy is given to the 1:1 complex, charge separation will occur similar to the situation found in anthracene/DMA systems.[31,32] In view of this, dispersed fluorescence spectra were recorded, under conditions for complex formation, for excitation at the same wavelengths as that of the isolated molecule. Spectra were also taken for excitation wavelengths corresponding to peaks attributed to the 1:1 complex. The
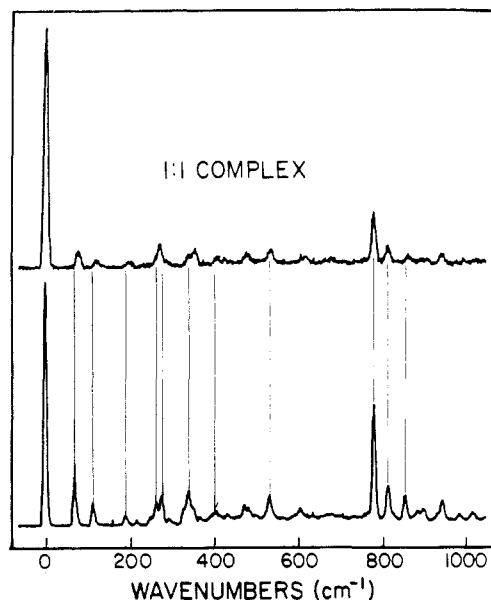
(41) Knee, J. L.; Khundkar, L. R.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 4715; *J. Chem. Phys.* **1987**, *87*, 115.

Figure 4. Fluorescence excitation spectra of jet-cooled complexes containing DMABN. The peaks of the complexes are indicated by an *. The peak at 308.2 nm contains contributions from both the bare molecule and the complex. The nozzle temperature was 150 °C, the laser-to-nozzle distance was 10 mm, and the helium backing pressure was 70 psi. Note that the scale and wavelength scan direction are different from Figure 3.

dispersed fluorescence gave no CT red-shifted emission. We have attempted to measure the lifetime of the water complex and the parent molecules at higher excess vibrational energies, similar to the isoquinoline study;[21] however, due to spectral congestion, we could not measure the signals for the complex. For the isolated DMABN molecule, lifetimes of 4.89 and 4.69 ns were measured for excess energies of 624 and 948 cm^{-1}, respectively. We plan to pursue this study by using picosecond mass spectrometry, as was done in the case of phenol/benzene complexes.[41]

Our beam results indicate that one solvent molecule (CH$_3$CN, H$_2$O, CH$_3$OH, NH$_3$) is not sufficient to stabilize the charge-transfer form of DMABN. Studies on the solvated electron by

Figure 5. (Top) Dispersed fluorescence resulting from excitation of the 3085-Å band of jet-cooled water/DMABN, 1:1 complex. Resolution was 0.8 Å. Nozzle temperature was 160 °C, water partial pressure 24 Torr, He backing pressure 40 psi, and laser-to-nozzle distance 3 mm. Laser bandwidth was 2–3 cm^{-1}. (Bottom) Dispersed fluorescence resulting from excitation of the 3087-Å band of jet-cooled DMABN. Resolution was 0.5 Å. Nozzle conditions were similar to above. Both spectra are shifted to coincide in order to allow for inspection of the effect of complexation.

Kenney-Wallace,[42] Kevan,[43] and others indicate that several alcohol molecules are required to stabilize the bare electron. In recent work by Robinson and co-workers,[25] it was pointed out that, for electrons and protons, a water cluster of 4 ± 1 members is the effective charge acceptor. With this in mind we have attempted to increase the density of solvation around DMABN in the beam to observe a threshold for the formation of the charge-transfer state.

In the attempt to make 1:n complexes of DMABN/solvent, a decrease in the parent molecule signal was observed. In addition, at high solvent vapor pressures, the background signal increases. This problem is similar to the one found by Even and Jortner[44] in their studies of fluorene complexes with water. We are attempting a new design in the beam to enhance the formation of large clusters.

C. Self-Complexes of DMABN. When the temperature of the nozzle of the jet containing DMABN was raised, a broad emission centered at 385 nm was observed. This band, which spans 48 nm, was especially apparent at high backing pressure. Therefore we assign this fluorescence to aggregates of DMABN itself.

Figure 6 shows the pressure dependence of the emission band at 385 nm when exciting at 309.9 nm. Variation in temperature affects the intensity of the band. At high backing pressure (50 psi) the broad 385-nm emission is observed, while at low backing pressure (10 psi) emission typical of the planar "monomer" (under 24-Å resolution) was observed centered at 330 nm. Intermediate pressures gave spectra with peaks at 330 and 385 nm. This general behavior with pressure and temperature was observed over the range of the aggregate emission (280–320 nm). Under conditions that gave optimum aggregate formation, dispersed fluorescence spectra were taken for excitation of the aggregate at the same wavelengths used for the bare molecule and when solvents were used. All spectra gave an emission composed of the monomer plus a contribution from the aggregate. The aggregate contribution was checked by taking spectra at low backing pressure and
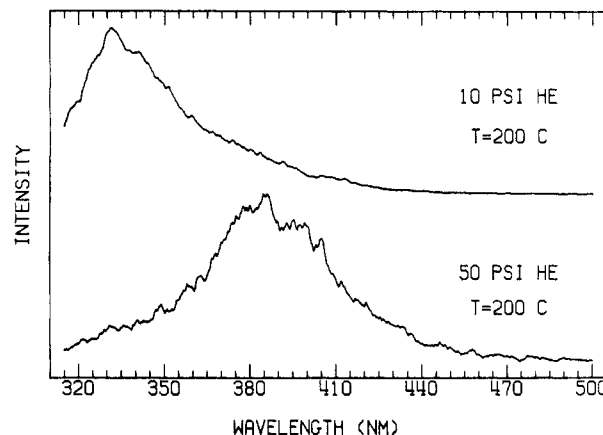
Figure 6. Dependence of the DMABN aggregate on He backing pressure while exciting at 309.9 nm. At high pressure, the "monomer" signal is nearly gone. At low pressure, the signal is that of the monomer under low resolution (24 Å). The monomer intensity is 3× that of the aggregate. The laser-to-nozzle distance was 10 mm.
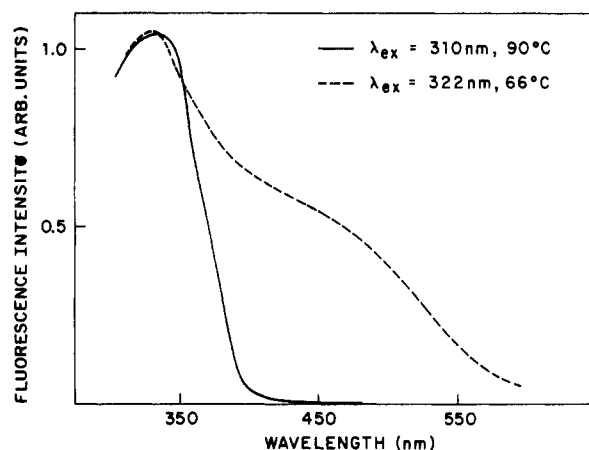
Figure 7. Fluorescence spectra of DMABN vapor in open cell at (—) λ_{ex} = 310 nm, 90 °C; (---) λ_{ex} = 322 nm, 66 °C.

verifying that only monomer-type emission remained. We observed no red-shifted emission that could be attributed to charge transfer.

The excitation spectrum of DMABN under optimum conditions for aggregate formation was taken over the range of 320–280 nm. Spectra were recorded under two detection conditions: total fluorescence and by scanning the laser with the monochromator set at 400 nm (2.4-nm resolution). The setting of the monochromator at 400 nm allowed maximum detection of the aggregate fluorescence, while trying to minimize contributions from the monomer. The excitation spectrum using total fluorescence shows the monomer bands on top of a broad background. With the monochromator set at 400 nm, smaller monomer band intensity on a structureless background is observed. The background signal was observed to begin at 320 nm and slowly rise as the excitation wavelength was scanned down to 280 nm.

These aggregates were also studied in the vapor above an open cell containing crystalline DMABN. By varying the temperature of the vapor and the excitation wavelength, we observed various bands that we attribute to the planar monomer, the planar dimer (or n-mer), and the twisted dimer (or n-mer). At 90 °C and excitation wavelength ≤310 nm, an emission centered at 330 nm is observed (Figure 7), which we attribute to the planar monomer. The band rises instantaneously within our resolution, and decays with a lifetime of 400 ± 100 ps, independent of the wavelength observed.[45] No visible emission is seen under these conditions.

(42) Kenney-Wallace, G. W.; Jonah, C. D. *Chem. Phys. Lett.* **1977**, *47*, 362.

(43) Kevan, L. *Acc. Chem. Res.* **1981**, *14*, 138.

(44) Even, U.; Jortner, J. *J. Chem. Phys.* **1983**, *78*, 3445.

(45) In the evacuated cell containing DMABN crystals at 90 °C, we observe UV emission due to the monomer with a lifetime of 3.0 ns. When this cell is opened to the air, the lifetime is reduced to 0.4 ns, as observed in the open vapor system.
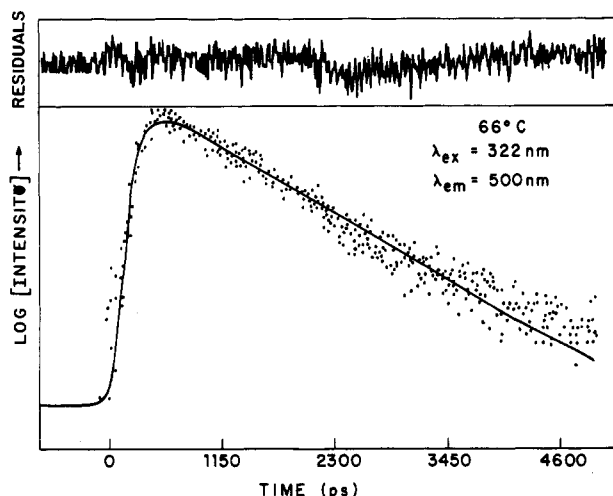
Figure 8. Formation and decay kinetics of fluorescence of DMABN vapor in open cell at 66 °C. The solid line represents the best fit of a rise time of 60 ps and decay of 1000 ps.

SCHEME I: Photophysical Processes in DMABN Vapor at 60 °C in an Open Cell
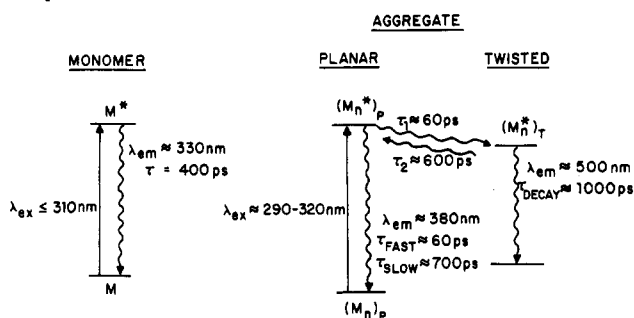
At $\sim$66 °C, and for excitation wavelengths of 290–320 nm, two red-shifted emitting species can be distinguished. (See Scheme I.) A band at $\sim$380 nm appears instantaneously and decays with two lifetimes: 90% of the intensity decays in 60 $\pm$ 30 ps and the remaining 10% decays in 700 $\pm$ 200 ps. A broad visible emission, centered at 500 nm, is observed to have a rise time of 60 $\pm$ 30 ps and a decay time of 1000 $\pm$ 200 ps (Figure 8).[46] The visible emission therefore originates from the 380-nm band. The two excited species appear to be equilibrated, as evidenced by the fact that they have approximately the same long lifetime. We attribute these two bands to the planar $[(M_n{}^*)_P]$ and charge-separated $[(M_n{}^*)_T]$ forms of a DMABN aggregate. From the different lifetimes of the 330- and 380-nm fluorescence bands, it is apparent that there is no equilibrium established between the monomer and aggregate forms in the excited state. This is not surprising, since the collision time between DMABN species at the very low vapor pressures of this experiment is longer than the typical lifetimes of the excited states.

The 380-nm species observed in the vapor above an open cell corresponds to the 385-nm emission observed in the beam experiment (reported herein) and to that observed in the concentrated hexane solution at 228 K.[29] However, in these latter two cases, no charge-transfer fluorescence accompanied the UV band. At the lower temperatures of these two experiments, there is apparently not enough energy to cross the excited-state barrier. This is in spite of the fact that, for the beam work, excitation of the aggregate was carried up to 3300-cm^{-1} corresponding monomer

excess energy. In contrast, we do observe charge transfer from a DMABN vapor at higher temperatures ($\sim$66 °C), presumably where the thermal population and/or aggregate size is such that barrier crossing can be achieved. At still higher temperature ($\sim$90 °C) the aggregates dissociate, and hence we see only monomer emission.

The absorption spectrum of DMABN in the gas phase contained in a cell at 30 mTorr and room temperature yields a broad band centered at 280 nm. For a change in temperature from 12 to 90 °C, the band shifts from 290 to 272 nm. These two bands are thought to represent absorption by the DMABN aggregate (dimer or n-mer) and monomer, respectively. This is a reasonable assignment based on the absorption bands for DMABN in hexane, at 282 nm, and as a polycrystalline powder, at 307 nm. The fluorescence spectrum shows a transition from visible to UV emission upon raising the temperature, and is coincident with the temperature-dependent changes in the absorption spectrum that we attribute to an increasing monomer/dimer (n-mer) ratio at higher temperatures.

Conclusions

We conclude from these studies in a thermalized vapor that self-complexes of DMABN (dimer or n-mer) can undergo a twisted internal-charge-transfer excited-state isomerization, on the basis of the observed visible emission characteristic of this polar state. Self-complexes were also formed in the beam, but charge transfer was not observed. Presumably, this reflects the differences in the internal temperature and/or size of the aggregates formed in the jet versus those formed in the vapor. In contrast, the beam studies reveal that the isolated molecule and the 1:1 complex with water, methanol, acetonitrile, or ammonia do not undergo a charge-transfer isomerization. These results can be understood in terms of the argument that a sufficiently polar solvent molecule or molecules are required before excited-state charge transfer and structural twist can occur. One solvent molecule is not enough to stabilize the charge-separated form. Although in the beam the solvent is frozen out, the evidence from liquid-state studies[10a] indicates that solvent dielectric relaxation (i.e., solvent motion) does not control the dynamics of TICT. Also of importance is the possible role of specific interactions between the solute and solvent. In protic solutions, hydrogen bonding is thought to oppose the charge transfer in DMABN by withdrawing electron density from the amino nitrogen.[10b] Since the geometry of the DMABN/solvent complex is not known yet, it is difficult to make any conclusions about the effects of hydrogen bonding on the dynamics of CT formation. Finally, while this work was in the writing stage, we learned of a jet study for the complexes with H_2O and CF_3H. The shift observed[47] for water is the same as ours (18 cm^{-1} to the blue). Further work is in progress.

Note Added in Proof. A very recent study[48] of DMABN complexes has reported similar findings about the spectroscopic shifts. The fluorescence lifetimes of the base and methanol complex are in agreement with our results.

(46) The lifetime of the red-shifted band was also studied in an evacuated cell containing DMABN crystals, and it was found to be the same as in the open system. See ref 24 for discussion of the kinetic equations used to extract the rate constants for the various relaxation processes.

(47) Kobayashi, T.; Futakami, M.; Kajimoto, O. *Chem. Phys. Lett.* **1986**, *130*, 63.

(48) Gibson, E. M.; Jones, A. C.; Phillips, D. *Chem. Phys. Lett.* **1987**, *136*, 454.