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Citation: The Journal of Chemical Physics **88**, 871 (1988); doi: 10.1063/1.454166
View online: http://dx.doi.org/10.1063/1.454166
View Table of Contents: http://aip.scitation.org/toc/jcp/88/2
Published by the American Institute of Physics

Chemical reactions in isolated clusters: Excited state electron transfer in 3- and 4-dimethylaminobenzonitrile[a)]

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(Received 21 August 1987; accepted 24 September 1987)

Two-color time-of-flight mass spectra of 3- and 4-dimethylaminobenzonitrile (3- and 4-DMABN) bare molecules and clusters with methane, water, acetone, dichloromethane, and acetonitrile are reported and discussed. The clusters and molecules are isolated and cooled in a supersonic expansion. Both 3- and 4-DMABN bare molecules display significant changes in geometry, associated with rotation–inversion coordinates of the dimethylamino group, upon excitation from the ground electronic state S_0 to the first excited singlet state S_1. Cluster spectra for the monosolvates [CH_4, H_2O, $(CH_3)_2CO$, CH_2Cl_2, CH_3CN] of 3- and 4-DMABN evidence two general types of behavior. (1) Cluster spectra have both red and blue shifts from their respective bare molecule origins which are relatively small (in general less than 200 cm^{-1}). These cluster spectra are nearly identical with the bare molecule spectra; the solvation process seems to have little effect on the DMABN molecule, especially the $-N(CH_3)_2$ moiety, for these clusters or cluster states. (2) Cluster spectra have shifts that are large (~500–1000 cm^{-1}) and to low energy of the bare molecule spectra. These cluster spectra are composed of both sharp and broad features which bear little resemblance to those observed in the respective bare DMABN molecule spectra. Results of calculations of cluster geometry suggest that thedifferent cluster spectra may be associated with clusters of different geometry. These data are interpreted in terms of solution behavior of 3- and 4-DMABN. The relationship between the twisted intramolecular charge transfer (TICT) state model proposed for 4-DMABN in dipolar aprotic solvents and these cluster results is explored.

I. INTRODUCTION

4-Dimethylaminobenzonitrile (4-DMABN) is a member of a class of molecules which exhibits dual fluorescence in polar solvents. The anomalous red shifted fluorescence (absent in nonpolar solvents) has been attributed[1] to a twisted intramolecular charge transfer (TICT) state resulting from an electron transfer in the excited state from the dimethylamino group to the cyano group and/or the aromatic ring and a concomitant 90° internal rotation of the amine with respect to the ring. The twisted geometry of the TICT state prevents back transfer of the electron because the n–π^* molecular orbital overlap vanishes in the twisted configuration; a full charge separation is thereby attained. The resulting excited state dipole (~16 D) is much larger than typical ground state dipole moments of polar molecules such as acetonitrile (3.92 D), sodium chloride (9.00 D), and water (1.85 D). Polar solvents are thus very effective in stabilization of the TICT state in 4-DMABN through a solute–solvent dipole–dipole interaction.

In addition to 4-DMABN, a large number of molecules with diverse structure have been shown to exhibit similar dual fluorescence behavior.[1] The common structural characteristic of these species is an electron donating subunit of the molecule which is connected, either directly or indirectly, to an electron acceptor group by a single bond, allowing the excited state charge transfer to occur with a concomitant internal twist of the groups.

An abundance of experimental and theoretical studies of these molecules has been performed[1] regarding dipolar stabilization of the TICT state and the temperature, solvent viscosity, and solvent polarity dependences for state crossing rates between the photoexcited S_1 state and the TICT state. Virtually nothing, however, is known regarding the potential surfaces associated with the twisting coordinates important for TICT state formation. In addition, the role of local solute–solvent interactions is unknown. These latter interactions will be strongly dependent upon the configuration of the solute in the solvent cage.

In the currently accepted TICT model, the geometry of 4-DMABN is twisted only in the TICT state. Microwave data on related molecules[2] would imply that, in the ground electronic state of the molecule, the amine nitrogen bonding is pyramidal with a pseudo-planar geometry: the carbon atoms of the methyl groups and the amino nitrogen atom form a plane which intersects the plane of the aromatic ring at a dihedral angle of about 27°. The S_1 state is similarly

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presumed to be pseudo-planar, although no direct experimental data are available concerning the excited state geometry until now. Data reported herein and analyzed in a future publication[3] indicate that both 3- and 4-DMABN are in fact twisted (or displaced) in their S_1 state equilibrium geometry. We note that the strong viscosity dependence for TICT state formation rates in solution, a major factor for originally invoking the model of a twisted geometry for the charge transfer state, has recently been shown[4,5] to be an experimental artifact: the viscosity dependence for TICT state formation from photoexcited S_1 is negligible. This is consistent with our discovery that the S_1 state is already in a displaced geometry in DMABN, at least to some extent. The degree to which the amine is actually "twisted" will be important in establishing the correctness of the TICT model and in interpreting the kinetic data.

Also important for the TICT state mechanism will be a determination of the geometry and potentials for amine torsion and inversion in DMABN clusters. By studying the potential surface changes resulting from clustering with protic and aprotic polar and nonpolar solvent molecules, one can hope to extrapolate cluster behavior to the behavior of the fully solvated molecule.

The results of a similar investigation of 3-DMABN and its clusters are also reported in this paper. To the best of our knowledge, the importance of charge transfer in the excited states of 3-DMABN or the appearance of a low lying TICT state in 3-DMABN has not been explored in any phase. In addition to laser jet spectra of 3-DMABN isolated and in clusters, we report room temperature solution static and picosecond time resolved fluorescence studies for this species. The impetus for the 3-DMABN studies is a better understanding of the nature of the electronic states involved in the dual fluorescence of 4-DMABN.

In addition to the spectroscopic data analyzed in this report, we also present the results of potential energy calculations for the various clusters. These data help in the determination of the cluster configurations, binding energies, and expected cluster spectroscopic shifts. We have found them quite helpful in the overall determination of the behavior of these clusters.

During the progress of this work three other laser jet studies of 4-DMABN have appeared: they deal with the spectra of the isolated molecule and certain clusters.[7–9] In all instances these works report fluorescence excitation and not mass detected spectra. The principal conclusion reached in these three studies is the same: monosolvated heterogeneous clusters of 4-DMABN do not exhibit dual fluorescence under isolated conditions. Thus, monosolvated clusters do not form the TICT state under these conditions. In this report, however, we present spectra obtained by two-color TOFMS which are not reported in these previous fluorescence studies. The importance of these new features is discussed with respect to the TICT state formation model.

II. EXPERIMENTAL PROCEDURES

The time-of-flight mass spectrometer (TOFMS) is as described elsewhere.[5] All experiments are performed with DMABN placed inside the operator module of an R. M. Jordon pulsed valve and heated to 65 °C. The carrier gas employed for the spectra displayed here is helium at 50 psig, although other pressures and other gases are also used to test for the presence of hot bands in the spectra. All cluster two-color TOFMS discussed in this report and depicted in the figures are obtained using the mass channel of the indicated cluster. Thus, the DMABN $(CH_3CN)_1$ spectra are obtained by monitoring the mass channel $(136 + 41) = 177$ amu, the DMABN $(CH_3COCH_3)_1$ spectra are obtained by monitoring mass channel $(136 + 58) = 194$ amu, etc.

In order to ensure that fragmentation of the parent cluster does not occur in these experiments, three precautions are taken: (1) the ionization beam intensity is kept as low as possible consistent with reasonable signal to noise ratios; (2) for each cluster studied, the energy of the ionization beam is lowered to its minimum value consistent with good signal to noise ratios–in the case of highly red shifted clusters, the energy is reduced $\sim 2000\ \text{cm}^{-1}$ from that used for isolated DMABN; and (3) higher mass channels, e.g., DMABN $(\text{solvent})_2$, are always monitored for intensity while recording the DMABN $(\text{solvent})_1$ cluster spectra.

4-DMABN (Aldrich, 98%) is used without further purification. 3-DMABN was synthesized and supplied by H. V. Secor.

Picosecond time resolved studies for solutions of 3-DMABN in CH_3CN are carried out by Professor David F. Kelley. These experiments employ 355 nm excitation, 10 nm resolution for dispersed emission, and streak camera detection. The time resolution for these experiments is ~20 ps.[10]

Lennard-Jones (6-12-1-10-12) potential energy calculations have been performed for clusters of 4-DMABN with all solvents employed in this study. The calculational methods have been thoroughly described in previous publications from our laboratory.[11] These present calculations are, however, more difficult and, in detail, less reliable than those previously published because (1) charges and charge distributions play a significant and decisive role in DMABN cluster systems and (2) potential parameters for the –CN moiety attached to aromatic rings have not been previously determined.

We have thus varied both charge distributions and potential parameters over a wide range of values. For example, atomic polarizabilities for the C and N atoms for the cyano group have been varied from those of aromatic C and N value to those of the C and O values found for carbonyl. Due to the large dipole moment of the solute and solvent molecules considered, the parameters affecting the binding energy and geometry of the clusters most significantly are the charges and their distribution over the molecular framework. We have mostly utilized the substituent charge distributions for 4-DMABN calculated by Lipinski *et al.*[12] together with those of Popkie and Kaufman[13] for benzonitrile to estimate the atomic charges for the ground state of 4-DMABN. Variation of these charges, while maintaining both overall solute neutrality and solute dipole moment, results in some changes in our calculated cluster geometries and binding energies but not in the number of potential energy minima found for each cluster.

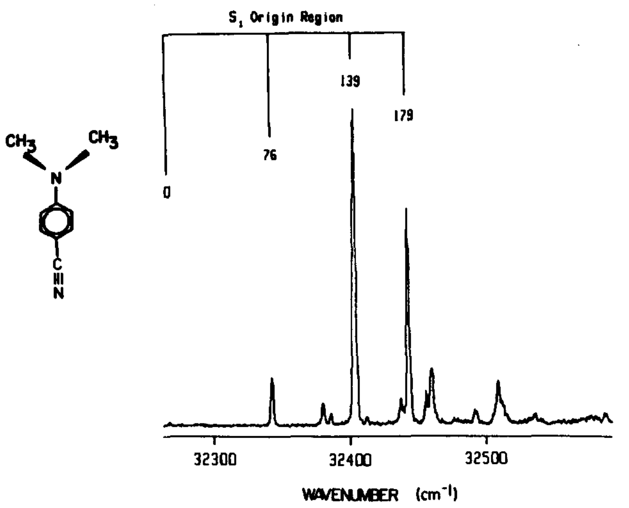


FIG. 1. Two-color TOFMS of 4-DMABN seeded in a supersonic expansion of helium at 50 psig. The weak feature at 32 264 cm^{-1} is tentatively assigned as the $S_1 \leftarrow S_0$ origin band. The low frequency features in this region are associated with the amine inversion and torsion motions which are strongly coupled. The origin region pattern is repeated at higher energy vibronic levels (e.g., $6a_0^1$ and 1_0^1).

3-Dimethylaminobenzonitrile(*3-DMABN*). A solution of 1.0 g (8.46 mmol) of 3-aminobenzonitrile in 50 mL of acetonitrile was treated with 4.35 mL (58 mmol) of 37% aqueous formaldehyde, cooled to 0 °C and treated with 531 mg (8.46 mmol) of sodium cyanoboride. The mixture was stirred for 1 h at 0° then allowed to warm to room temperature and stirred for 3 h. A trace of bromcresol green indicator was then added along with sifficient 5% hydrochloric acid to give a yellow color. An additional 600 mg of sodium cyanoborohydride was added as needed in 200 mg increment with alternate addition of 5% hydrochloric acid to finally give a persisting yellow color. The reaction was then stirred for an additional 12 h. The acetonitrile was removed using a rotary evaporator and the residual aqueous solution was treated with ether and an excess of 5% hydrochloric acid and the combined acid extracts basified in the cold with 50% KOH solution, extracted with ether and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure was followed by bulb-to-bulb distillation to give 1.15 g (92.9%) of colorless crystalline 3-DMABN which melted on warming to room temperature: bp 85 °C (oven) (0.05 mm Hg); ^1H NMR ($CDCl_3$) δ 2.97 (*s*,6H), 6.87–6.89 (*m*, 2H), 6.95 (*d*, 1H, $J = 7.5$ Hz), 7.27 (*m*, 1H); ^{13}C NMR ($CDCl_3$) 40.13, 112.71, 114.73, 116.21, 119.34, 119.81, 129.71, 150.20. Idoux, Gupton, and Colon [Synth. Commun. *12*, 907 (1982)] report obtaining a trace of this compound but do not specify any spectroscopic properties.

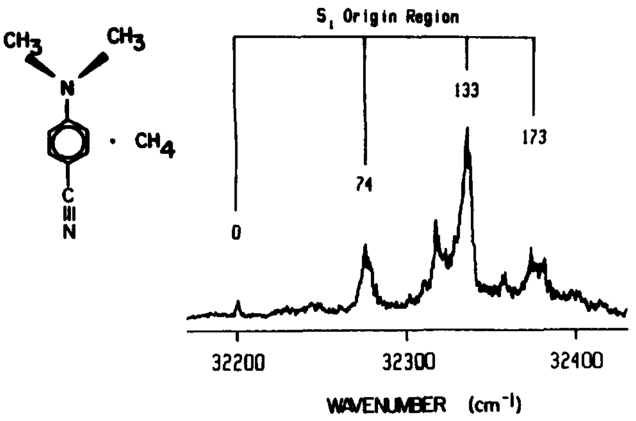


FIG. 2. Two-color TOFMS (cf. Fig. 2) of the 4-DMABN $(CH_4)_1$ cluster. The weak origin is red shifted 63 cm^{-1} from the bare 4-DMABN 0_0^0 transition. Note that the vibronic structure in the origin region is virtually identical to that of bare 4-DMABN molecule.

III. RESULTS AND DISCUSSION

The mass selected two-color TOFMS of 4-DMABN seeded in a supersonic expansion of helium is shown in Fig. 1. The weak feature which appears at 32 264 cm^{-1} is the lowest energy "cold" band in the spectrum and is tentatively assigned as the $S_1 \leftarrow S_0$ 0_0^0 transition of 4-DMABN. The other bands in the origin region are associated with the low frequency, large amplitude internal coordinates of the molecule. These coordinates include those for amine inversion, amine torsion, and methyl torsion. We are currently in the process of assigning the features in the spectrum in order to detail specifically the S_0 and S_1 equilibrium geometries of the molecule and the potential functions governing these motions.[3] The methyl group torsion does not appear to be important for the spectrum: large changes in both the amine inversion and amine torsion potential surfaces occur upon electronic excitation. These latter two motions appear to be strongly coupled.

The spectrum in Fig. 1 is virtually identical to recently reported[7–9] fluorescence excitation spectra of jet cooled 4-DMABN. The 0_0^0 region spectrum shown in Fig. 1 is repeated in the $6a_0^1$ (+ 501 cm^{-1}) and the 1_0^1 (+ 784 cm^{-1}) regions almost exactly.

Figure 2 shows the spectrum obtained, similar to that in Fig. 1, for the cluster 4-DMABN $(CH_4)_1$. The weak origin feature at 32 201 cm^{-1} is red shifted from the bare 4-DMABN origin by 63 cm^{-1}; this red shift is comparable to those observed for benzene/methane and aniline/methane clusters.[6] The observed low frequency band structure displayed in the spectrum is very similar to that shown for the bare 4-DMABN. Thus, methane is a minor perturbation to the 4-DMABN chromophore in both S_0 and S_1.

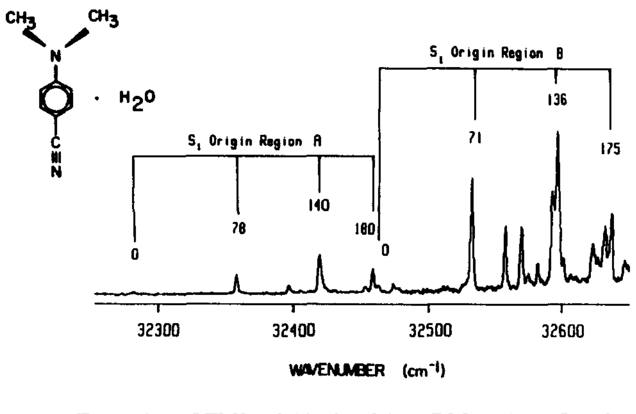


FIG. 3. Two-color TOFMS (cf. Fig. 2) of the 4-DMABN $(H_2O)_1$ cluster. Two distinct configurations (A and B) are observed with spectra blue shifted by 14 and 199 cm^{-1}, respectively. Again, the origin region pattern of bare 4-DMABN molecule is nearly duplicated for both configurations.

The spectrum of the 4-DMABN $(H_2O)_1$ cluster is shown in Fig. 3. The figure reveals two distinct "spectra," indicating the presence of two distinct cluster configurations (A and B). The spectra are shifted to the blue of the bare 4-DMABN origin by 14 and 199 cm^{-1}, respectively. The spectrum of configuration A shows low frequency band structure identical to that of bare 4-DMABN. Configuration B displays similar band structure, although several new features appear in its spectrum. Nonetheless, both water cluster configurations reveal little significant perturbation to the chromophore.

The recently reported fluorescence excitation spectra of jet cooled 4-DMABN/water clusters[7-9] do not reveal any indication of configuration B; in our TOFMS this configuration appears more prominent than configuration A. Since our expansion conditions are very similar to those of Refs. 7–9, and thus both configurations should be present in all three studies, configuration B (with the large blue shift) must be nonfluorescent.

The TOFMS of 4-DMABN $(H_2O)_2$ reveals only one clear configuration with an origin shifted 401 cm^{-1} to the blue of the bare 4-DMABN origin. Experimental studies of water clusters of other aromatic systems,[14] and the general trends for additive cluster[6,15] shifts, would suggest that the 200 cm^{-1} blue shifted 4-DMABN $(H_2O)_1$ cluster spectra arises from a cluster with H_2O coordinated over the aromatic ring and that the 401 cm^{-1} blue shifted 4-DMABN $(H_2O)_2$ cluster spectra arises from a cluster with H_2O coordinated similarly to both the top and bottom of the aromatic ring. The cause of the low fluorescence quantum yield of this cluster configuration is not clear; however, such a configuration would maximize charge transfer stabilization in the 4-DMABN chromophore and excitation of this cluster could lead to fast decay to a relatively "dark" charge transfer state. Other nonradiative paths ($S_1 \rightarrow S_0$, T_n) are, of course, possible causes for this decrease in fluorescence intensity.

Our cluster calculations using an atom–atom Lennard-Jones (6-12-1-10-12) potential function[11] yield three stable configurations for the ground state 4-DMABN $(H_2O)_1$ cluster: (1) H_2O situated over the benzene ring displaced from the ring center toward the $N(CH_3)_2$ moiety with much the same orientation as found for $C_6H_6(H_2O)_1$.[14] The binding energy for this cluster is ~1000 cm^{-1}; (2) H_2O situated over to the *ipso* carbon to which the CN moiety is attached with one hydrogen atom oriented over and coordinated to the ring and the other pointing toward the CN carbon atom and coordinated to it. The binding energy for this configuration is ~950 cm^{-1}; and (3) H_2O situated with its oxygen atom over the $N(CH_3)_2$ *ipso* carbon with one hydrogen atom over the center of the ring and the other away from the ring nearly above the oxygen atom. The binding energy for this configuration is again ~950 cm^{-1}.

We suggest that the ~200 cm^{-1} blue shifted 4-DMABN $(H_2O)_1$ cluster spectrum (configuration B) arises from the ring centered calculated H_2O configuration 1 described above. The 14 cm^{-1} blue shifted 4-DMABN $(H_2O)_1$ cluster (configuration A) most likely corresponds to the calculated H_2O configuration 2 cluster described above because the origin structure of the free 4-DMABN is so well preserved and the cluster shift (related to the solvent–π interactions)[15] is so small. As pointed out in the previous section, detailed pictures of these geometries are probably inappropriate because the exact cluster geometry is a function of the particular parameters chosen for the atom–atom potential parameters. The stability of the three calculated geometries, however, is independent of the parameters chosen over the described very wide range of available choices.

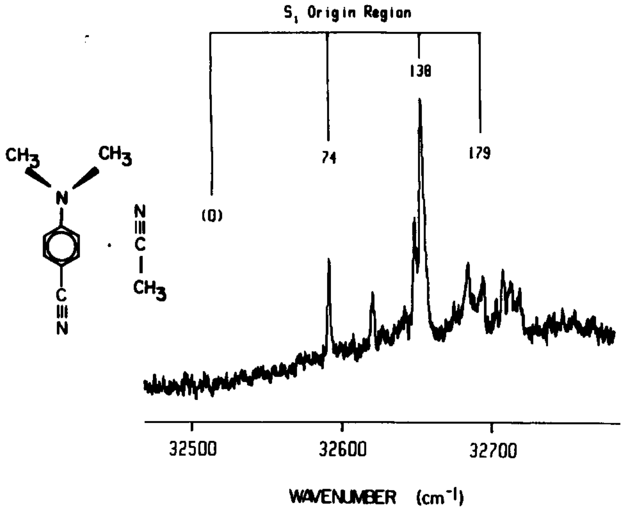


FIG. 4. High energy region of the TOFMS spectrum of the 4-DMABN $(CH_3CN)_1$ cluster. The spectrum is blue shifted by 252 cm^{-1} and exhibits a recognizable bare molecule origin region pattern. Note the presence of underlying background intensity across the spectrum.

The spectrum of the 4-DMABN $(CH_3CN)_1$ cluster evidences two origin regions (Figs. 4 and 5). The origin 252 cm^{-1} to the blue of the bare molecule origin is displayed in Fig. 4. This spectrum clearly reflects the 4-DMABN origin in structure. Figure 5 displays the second origin for the 4-DMABN CH_3CN cluster system ~900 cm^{-1} to the red of the bare molecule origin. Several important conclusions can be drawn from the observation of this lower energy spectrum. First, it appears with an enormous red shift (~900 cm^{-1}) with respect to the 4-DMABN $S_1 \leftarrow S_0$ origin. This is roughly an order of magnitude greater red shift than is typically seen for a heterogeneous cluster: a substantial cluster stabilization energy must be appropriate for the excited

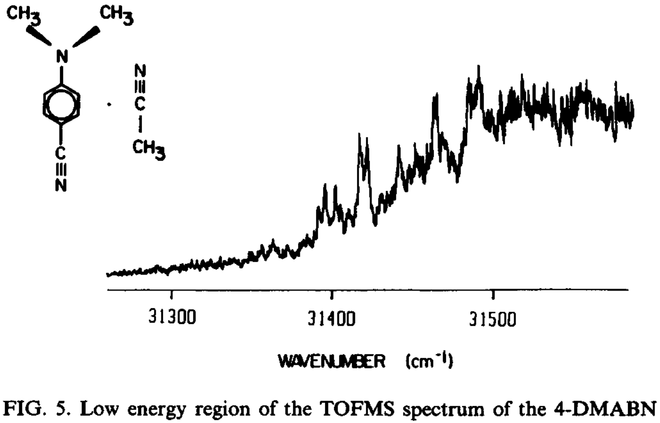


FIG. 5. Low energy region of the TOFMS spectrum of the 4-DMABN $(CH_3CN)_1$ cluster. The spectrum is enormously red shifted (~900 cm^{-1}) from the bare molecule $S_1 \leftarrow S_0$ spectrum. Note the unrecognizable pattern of vibronic structure.

state. The excited state binding energy is greater than the ground state binding energy by nearly 1000 cm^{-1}. Second, the low frequency structure in the region is unrecognizable in terms of the bare molecule spectrum. This indicates that the nonrigid character of the 4-DMABN moiety has been significantly changed by clustering with acetonitrile. Third, broad "humps" appear (not shown in Fig. 5) to higher energy in the spectrum built on this ~ 900 cm^{-1} red shifted origin which can be identified with the vibronic bands $6a_0^1$ and 1_0^1 of 4-DMABN. Thus, the excitation giving rise to the spectrum is primarily localized on the 4-DMABN chromophore.

Three sources for the deeply red shifted 4-DMABN $(CH_3CN)_1$ spectrum are plausible. First, two or more cluster configurations are present. In one of these, the solvent acetonitrile molecule is a minor perturbation to the chromophore: this cluster has a spectral blue shift relative to the bare 4-DMABN $S_1 \leftarrow S_0$ spectrum. In another cluster configuration, the solvent molecule is a major perturbation to the excited state chromophore. The S_1 state of the bare molecule has been stabilized considerably by the large dipole moment of the solvent. This stabilization is much greater for S_1 compared to S_0 due to the higher dipole moment for the excited state (9 D) relative to the ground state (6 D). Thus, a large spectral red shift is observed for the cluster. This shift can be expected to scale linearly with the dipole moment of the solvent molecule extrapolating to the bare molecule origin for zero solvent moment.

A second interpretation of the deeply red shifted 4-DMABN $(CH_3CN)_1$ spectrum requires no statement as to the number of cluster configurations contributing to the spectra. Instead one assumes that the blue and red shifted spectra are due to absorption to two different electronic states. In this interpretation, the blue shifted portion of the 4-DMABN $(CH_3CN)_1$ spectrum corresponds to the $S_1 \leftarrow S_0$ spectrum exhibiting minor chromophore perturbations by the solvent. The deeply red shifted portion of the cluster spectrum corresponds to an electronic state whose transition intensity has been induced by the presence of the solvent, probably as a result of significant dipole stabilization. One is tempted to assign this new electronic state to the TICT state of 4-DMABN. One problem associated with this assignment for the 4-DMABN $(CH_3CN)_1$ red shifted spectrum is that the oscillator strength for the TICT $\leftarrow S_0$ transition is thought to be vanishingly small for fully solvated 4-DMABN; however, the integrated intensity of the red shifted spectrum in Fig. 5 is roughly an order of magnitude greater than that of the blue shifted spectrum in Fig. 4. More likely, the newly observed excited state is a charge transfer (CT) state which is related to the TICT state, the latter having an adiabatic minimum located elsewhere on the accessible potential energy surface. The extended Franck–Condon envelope for the CT $\leftarrow S_0$ spectrum of 4-DMABN $(CH_3CN)_1$ could then be the result of a significant displacement of the CT equilibrium geometry along such coordinates as the twisting coordinate of the amine with respect to the aromatic ring, the inversion coordinate for the amine nitrogen rehybridization, or simply the relative motion of the solute and solvent molecule. These coordinates can be expected to be significant in maximizing charge transfer character in the chromophore. The broad lumps which appear in the region of $6a_0^1$ and 1_0^1 in the CT spectrum of the cluster may be the result either of a large density of spectrally active vibronic levels (i.e., spectral congestion) or of broadening by fast nonradiative decay, possibly to the TICT state.

A third interpretation of the red shifted acetonitrile cluster spectrum is similar to the previous one: again, either one or more cluster geometries may exist. The spectrum is assigned not to a new electronic state, but rather to a new potential minimum in the S_1 excited state potential surface. This new minimum derives from a higher energy charge transfer state of 4-DMABN which is stabilized by the acetonitrile solvent molecule and has a minimum separated along one or more coordinates from the S_1 minimum. An avoided crossing of the S_1 and CT surfaces takes place somewhere on the surface between the two minima. The only differences between this interpretation and the previous one are that this interpretation requires that (1) the S_1 and CT minima are connected adiabatically, and (2) these minima are separated along at least one normal coordinate of the cluster. This distinction may be important in understanding the dynamic interconvertability of the S_1 and CT states.

We have performed Lennard-Jones cluster calculations in an attempt to ascertain the number and type of ground state 4-DMABN $(CH_3CN)_1$ cluster configurations which may be observed. These calculations show that the most tightly bound configuration (~ 1700 cm^{-1} binding energy) is one with the acetonitrile situated above the solute aromatic ring with its dipole moment aligned roughly antiparallel to that of the solute. This is the most effective geometry for solute dipole stabilization. Another stable configuration has a perpendicular geometry with the acetonitrile's methyl group pointing down toward the ring and centered over the *ipso* ring carbon of the CN group. This is also a very stable configuration, with a binding energy of ~ 1100 cm^{-1} and is considerably less effective in dipolar stabilization. These two configurations are consistent with the first interpretation stated above. The deeply red shifted 4-DMABN $(CH_3CN)_1$ spectrum could be assigned to a cluster with antiparallel solute–solvent geometry while the blue shifted spectrum could be assigned to the perpendicular geometry. This latter assignment, which is consistent with a small spectral shift, is also consistent with the lack of significant perturbation to the fairly distant dimethylamine moiety of the solute, as indicated by the vibronic band structure in the origin region of the blue shifted spectrum.

These calculational results may seem to be fairly convincing evidence that the two 4-DMABN $(CH_3CN)_1$ cluster spectra observed correspond to the two cluster configurations calculated; however, an additional third configuration is calculated albeit with a much smaller binding energy (~ 500 cm^{-1}) and a fairly low barrier to conversion to the much more stable antiparallel configuration. This third configuration also has a mostly antiparallel geometry but the acetonitrile is centered over the dimethylamino group of 4-DMABN and would be expected to generate significant perturbations to the torsion and inversion potentials for the amine. No evidence for such a configuration has been seen in the 4-DMABN $(CH_3CN)_1$ spectrum.

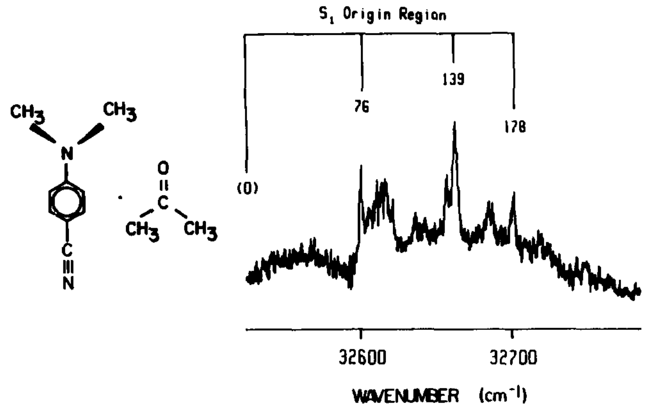


FIG. 6. High energy region of the TOFMS spectrum of the 4-DMABN $[(CH_3)_2CO)]_1$ cluster. The spectrum is blue shifted by 260 cm^{-1} and exhibits structure typical of $S_1 \leftarrow S_0$ bare molecule spectrum.

Note that the presence of several stable cluster configurations does not necessarily rule out the possibility that the observed blue and red shifted spectra are transitions to different electronic states or different minima on the same excited state surface of the same cluster configuration.

In an attempt to determine which of the above three possible interpretations of the 4-DMABN $(CH_3CN)_1$ spectrum is correct, four additional series of experiments are carried out: (1) a search for higher order clusters of 4-DMABN with CH_3CN; (2) a search for benzonitrile/CH_3CN clusters; (3) solvation of 4-DMABN with other aprotic polar solvent molecules; and (4) a study of 3-DMABN molecular, solution, and cluster spectra. Below we discuss the results of these four studies with respect to the 4-DMABN TICT behavior.

No clear origin is observed in the red shifted region of the 4-DMABN $(CH_3CN)_2$ cluster. Instead, a broad featureless background is observed which extends nearly 2000 cm^{-1} to the red of the $S_1 \leftarrow S_0$ orgin of 4-DMABN.

The TOFMS spectrum of the benzonitrile $(CH_3CN)_1$ cluster shows only a single sharp and intense origin shifted 94 cm^{-1} to the red of the $S_1 \leftarrow S_0$ origin of bare benzonitrile.

While both of these results are interesting, neither of them readily eliminates any of the above three possible interpretations of the 4-DMABN $(CH_3CN)_1$ cluster spectra. Spectra of other DMABN/polar solvent clusters are, however, quite interesting.

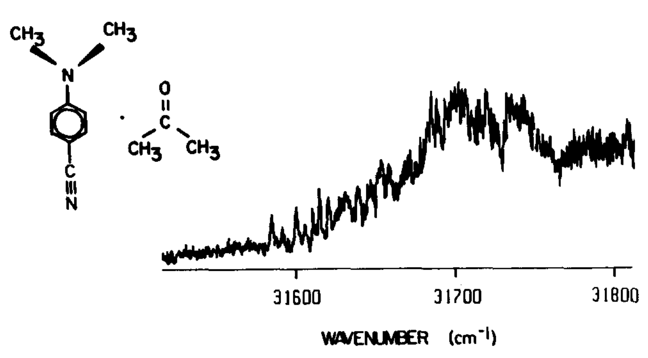


FIG. 7. Low energy region of the TOFMS spectrum of the 4-DMABN $[(CH_3)_2CO]_1$ cluster. The spectrum displays an enormous red shift (680 cm^{-1}) and unusual vibronic structure.

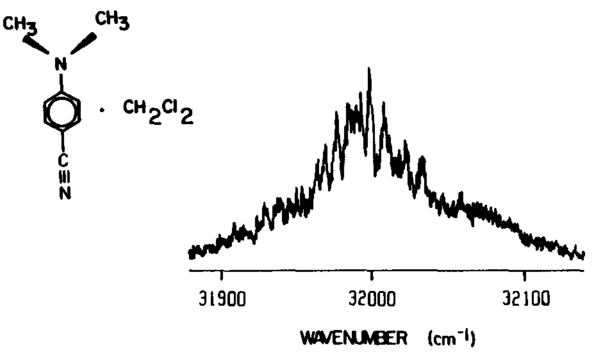


FIG. 8. TOFMS spectrum of the 4-DMABN $(CH_2Cl_2)_1$ cluster. Again, the spectrum shows a large red shift ($\sim$320 cm^{-1}) and unusual vibronic structure compare to 0_0^0 transition of the bare molecule.

In Figs. 6 and 7, TOFMS spectra obtained for the cluster 4-DMABN $[(CH_3)_2CO)]_1$ are shown. The blue shifted (260 cm^{-1}) spectrum, nearly identical to that of the bare solute, is shown in Fig. 6. Again, this spectrum reveals little if any perturbation to the low frequency modes of the chromophore. A deeply red shifted spectrum ($\sim$680 cm^{-1}), analogous to that observed for the acetonitrile cluster, is shown in Fig. 7. This spectrum similarly displays structure seemingly unrelated to that of the bare molecule $S_1 \leftarrow S_0$ spectrum. Thus, 4-DMABN clusters with both acetone and acetonitrile behave in a similar fashion.

A portion of the 4-DMABN $(CH_2Cl_2)_1$ cluster spectrum is shown in Fig. 8. The spectrum is red shifted by about 320 cm^{-1} and once again displays unusual (reproducible) vibronic structure.

The red shifted spectra of monosolvated 4-DMABN with dichloromethane, acetone, and acetonitrile appear with red shifts that scale roughly linearly with the static dipole moments of the solvent molecules (1.6, 2.9, and 3.9 D,respectively); the shift roughly extrapolates to the bare molecule origin for zero solvent dipole moment. This trend is certainly evidence in favor of the interpretation (1 above) that only one excited state minimum (S_1) is being probed for each of the different cluster configurations.

And finally, another series of potentially useful experiments involve the previously unstudied isomer 3-DMABN. Our room temperature solution experiments with this molecule in dilute (0.25 mM) solutions of *n*-hexane and acetonitrile indicate that excitation at 300 and at 350 nm reveal no dual fluorescence in either solvent. In acetonitrile, the fluorescence is shifted to the red 30 nm from that observed in *n*-hexane and is broader, but no obvious anomalous fluorescence is present. Picosecond time resolved studies of this emission indicate an instrument limited rise time ($\lesssim$30 ps) with a single long decay time ($\gtrsim$5 ns). No variation in rise or fall times is observed for detected emission wavelengths from 380 to 560 nm in acetonitrile. These results suggest that the proposed TICT state in 4-DMABN is either absent or not accessible in photoexcited 3-DMABN. The former conclusion suggests the importance of the zwitterion resonance state (1) to the emitting CT state in 4-DMABN since similar resonance structures for 3-DMABN are considerably more energetic.

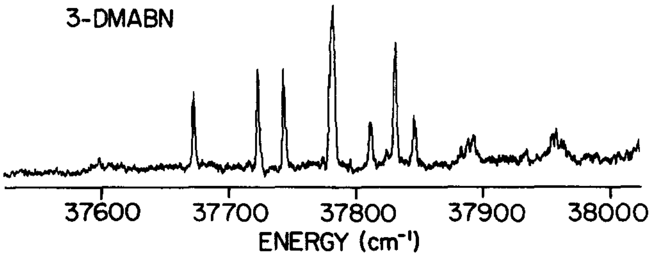
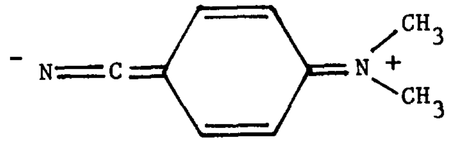


FIG. 9. TOFMS spectrum of 3-DMABN. The spectrum is red shifted from 4-DMABN by 2188 cm^{-1}.



(1)

The TOFMS spectrum obtained for 3-DMABN is shown in Fig. 9. The weak feature at 30 076 cm^{-1} is assigned to the $S_1 \leftarrow S_0$ origin. The other bands near the 0_0^0 region are associated with the low frequency amine motions in analogy to the assignments for 4-DMABN. The origin of 3-DMABN lies 2188 cm^{-1} to lower energy of the 4-DMABN origin. Note too the similarity in the low frequency modes of the two isomers: apparently the displacement of the dimethylamino moiety in the $S_1 \leftarrow S_0$ transition is not related to the TICT nature of the isolated 3- or 4-DMABN molecule or monosolvate cluster with various polar and nonpolar solvent molecules.

The TOFMS of 3-DMABN $(H_2O)_1$ is shown in Fig. 10. Unlike the water cluster spectra of 4-DMABN, the spectrum in Fig. 10 is red shifted with respect to the bare 3-DMABN origin by 446 cm^{-1}. Only one obvious configuration is present and some changes to the amine torsion and inversion potentials have occurred upon solvation.

The TOFMS of 3-DMABN $(CH_3CN)_1$ is shown in Fig. 11. As with 4-DMABN, a deeply red shifted spectrum (777 cm^{-1}) appears. No blue shifted spectrum has been observed for this cluster. The appearance of the red shifted spectrum of 3-DMABN $(CH_3CN)_1$ is clearly unlike both the bare molecule 3-DMABN spectrum and the red shifted 4-DMABN $(CH_3CN)_1$ spectrum. A progression in at least one ~42 cm^{-1} mode is evident in the 3-DMABN $(CH_3CN)_1$ cluster spectrum. Further, the spectral congestion (or broadening) that is so dominant and characteristic for the para isomer red shifted cluster spectrum is not present in the cluster spectrum of the meta isomer. These detailed spectroscopic differences could, however, be associated with small changes in dynamics, densities of states, potential surfaces, and/or internal hindering potentials.

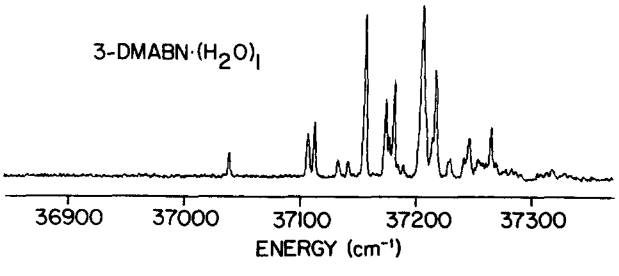


FIG. 10. Low energy region of the TOFMS spectrum of the 3-DMABN $(H_2O)_1$ cluster. A large red shift (446 cm^{-1}) from the bare 3-DMABN spectrum is observed.

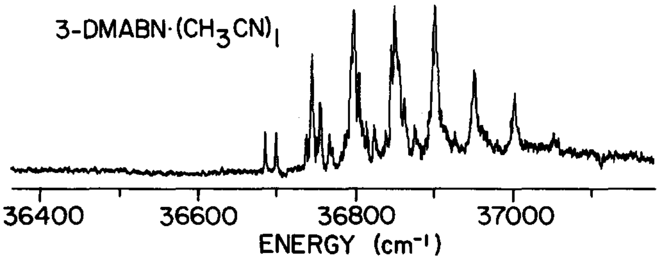


FIG. 11. Low energy region of the TOFMS spectrum of the 3-DMABN $(CH_3CN)_1$ cluster. A large red shift (777 cm^{-1}) from the bare molecule 0_0^0 spectrum and a ~42 cm^{-1} progression are apparent.

Similar behavior occurs in the monosolvated clusters of 3-DMABN with acetone and dichloromethane: large red shifts (665 and 390 cm^{-1}, respectively) are found but the spectra show considerably less spectral congestion compared to the 4-DMABN clusters. These data would tend to favor the assignment of the highly red shifted 4-DMABN cluster spectra to charge transfer or TICT state transitions.

IV. CONCLUSIONS

The two-color TOFMS of 3- and 4-DMABN bare molecules and clusters with CH_4, H_2O, CH_2Cl_2, $(CH_3)_2CO$, and CH_3CN have been presented and analyzed. A distorted or displaced S_1 excited state for DMABN is not necessarily associated with a charge transfer or TICT state formation: both 3- and 4-DMABN bare molecules and clusters evidence this behavior. Potential energy calculations suggest that independent of a wide range of parameter values chosen for the potential, multiple configurations are to be expected for the clusters of 3- and 4-DMABN with polar solvents. This suggests (but does not prove, of course) that the apparent multiple spectra for clusters of a single mass are associated with clusters of different configuration and not one cluster with "different electronic states" or different minima on a "single electronic potential surface."

The cluster spectra for 3-DMABN and 4-DMABN monosolvates are quite similar with regard to cluster shifts for all clusters studied. The highly red shifted cluster spectra for 3- and 4-DMABN are, however, quite different with respect to linewidth and apparent spectral congestion and/or lifetime. Nevertheless, the solvation static and dynamic behavior of 3- and 4-DMABN is quite different: 4-DMABN in strongly dipolar aprotic solvents evidences red shifted emission which appears with a solvent dependent lifetime[1,4,5] while we have shown that 3-DMABN evidences no such dynamics. How the highly red shifted cluster spectra for clusters with polar solvents relates to the proposed TICT state formation, is not at present clear. The highly red and blue shifted cluster spectra reported in this paper may not be related to the same excited electronic state whether the clusters are or are not of a single configuration.

The 3- and 4-DMABN $(H_2O)_1$ cluster spectra and spectral shifts reported herein are consistent with the recently reported observation[16] that DMABN does not undergo TICT state formation in water solutions.

Dispersed emission spectra for the highly red shifted cluster spectra would certainly help resolve questions regarding TICT or charge transfer state behavior in 3- and 4-DMABN monosolvate systems. In addition, studies of higher order clusters [(i.e., 3- and 4-DMABN $(CH_3CN)_{2,3,...}$] would also be quite interesting. Both of these experiments are currently underway in our laboratory.

ACKNOWLEDGMENTS

We wish to thank D. F. Kelley and H. V. Secor for their help with and discussions concerning this work. We also thank C. Lilly, A. Kassman, and B. LaRoy for their support and encouragement during this work.

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