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Mixing of the local $\pi\pi^*$ and charge-transfer states**

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Solvation effects on the electronic structure of 4-*N*,*N*-dimethylaminobenzonitrile: Mixing of the local $\pi\pi^*$ and charge-transfer states

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The effect of polar solvents acetonitrile and water on the electronic excited states of 4-*N*,*N*-dimethylaminobenzonitrile (DMABN) is studied through the optical spectroscopy of small clusters of DMABN/solvent. The clusters are created in a supersonic jet expansion. The results of mass resolved excitation spectroscopy (MRES), fluorescence excitation (FE), dispersed emission (DE), and photodepletion studies demonstrate that the solvent molecule can bind to DMABN at two distinct sites for the one-to-one cluster. Both DMABN (H_2O)₁ clusters generate small blue shifts for the $S_1 \leftarrow S_0$ cluster transition and evidence low-energy vibronic structure nearly identical to that found for the bare molecule. The DMABN (CH_3CN)₁ clusters behave quite differently. One cluster geometry induces a small blue shift of the $S_1 \leftarrow S_0$ electronic transition with little change in its vibronic structure and intensity pattern. We suggest this binding site involves the cyano end of the DMABN molecule. The second cluster geometry induces a large red shift ($\sim 1000\text{ cm}^{-1}$) and significant broadening ($> 10^3\text{ cm}^{-1}$) of the lowest-energy transition. This red shifted transition is associated with a charge-transfer transition within the DMABN molecule lowered in energy due to the acetonitrile coordination with the DMABN aromatic ring. The lowering of the charge-transfer state in DMABN (CH_3CN)_{*n*}, *n* = 1,...,5 clusters is supported by the following data: long wavelength emission from clusters with broad red shifted absorption; distinct lifetimes for emission at 350 nm (4.6 ns) and 400 nm (6.0 ns); broad red shifted absorption for one geometry of the DMABN (CH_3CN)₁ cluster. These results support the idea that the charge-transfer transition in DMABN is stabilized by short-range dipole-dipole interactions between DMABN and polar nonhydrogen bonding solvents.

I. INTRODUCTION

4-*N*,*N*-dimethylaminobenzonitrile (DMABN) fluoresces in two distinct regions:¹ one centered at 350 nm and referred to as a normal ($S_0 \leftarrow S_1$) emission; the other centered at 450 nm and referred to as anomalous emission. This unusual solution behavior is suggested to be due to the formation of a highly polar (charge-transfer) excited state which interacts with a local ($\pi\pi^*$) excited state under the influence of the solvent. The donor (*N,N*-dimethylamino)-acceptor (cyano) structure of DMABN and polar, nonhydrogen bonding solvents (e.g., acetonitrile, acetone, dichloromethane, etc.) ensures that the extended charge-transfer state is of low energy. The dipole moment of DMABN is reported to increase almost a factor of 3 upon excitation to the charge-transfer state (6–16 D). The large solvent shift for DMABN emission in polar solvents is indeed the indication of a charge-transfer state; the local excited ($\pi\pi^*$) state which appears in nonpolar solvent is nearly independent of solvent effects.

Appearance of the anomalous charge-transfer band has been correlated with dimethylamino group conformation for substituted DMABN. This observation leads to the proposal of a twisted intramolecular charge-transfer (TICT) model in which the charge-transfer excited state is stabilized and lowered in energy through a 90° twist of the dimethylamino group to a plane perpendicular to the aromatic ring.

The entire molecule is nearly planar in the ground state and in the first excited $\pi\pi^*$ state.² This twisting behavior has never been directly observed in the DMABN system; in fact, the dimethylamino group is twisted roughly 30° in the locally excited $\pi\pi^*$ state of the bare molecule.³

The effect of solvent on the charge-transfer state has been debated over the last 30 years. As originally proposed,¹ polar solvents reverse the ordering of the local $\pi\pi^*$ state and the extended charge-transfer state. Other proposals have been offered, however, to account for the dramatic spectroscopic changes found for DMABN solution behavior. These include excimer formation,⁴ complex formation with the solvent⁵ and twisting of the ground-state conformation under the influence of trace level impurities in solvation of hydrogen bonding.⁶ A more detailed investigation of DMABN solution phase spectroscopic behavior has led to the suggestion⁷ that solvent effects on the excited states of DMABN can be characterized as short range and long range: primary stabilization of the charge-transfer state is due to short-range specific interaction with polar solvents; secondary stabilization of the DMABN/solvent complex by long-range polarization interactions with more distant solvent molecules.

Apparently, microscopic solvation details are important for the formation and stabilization of the charge transfer state. These can best be probed through the investigation of solute/solvent clusters generated in the gas phase and accessed through the combined techniques of optical and mass

spectroscopy. Clusters can be employed to identify the local solvent binding sites for a solute molecule and also to distinguish between long-range and short-range solvent effects.

Such studies with other molecules (e.g., 9,9'-bianthyl⁸ and 4-dialkylamino-pyrimidines⁹) suggest that only one solvent molecule is required to lower the charge transfer state below the local excited state. This result, of course, demonstrates the importance of short-range interactions for the solvation stabilization of the charge-transfer state.

DMABN has been studied in the gas phase as an isolated molecule and under solvation conditions in clusters.^{9,10,11} The fluorescence excitation spectrum of the bare cold DMABN molecule shows well-resolved features.^{10(c)} Dispersed emission studies demonstrate that the first excited singlet states of the bare molecule is the $\pi\pi^*$ local excited state ($S_1 \leftarrow S_0$).^{10(a)} DMABN cluster studies show two types of clusters are formed: ones for which the spectra are sharp and not much displaced from the bare molecule spectrum [e.g., DMABN (CH_4)₁, (H_2O)_{1,2}]; and ones for which the spectra are greatly red shifted (600–1000 cm^{-1}), broad, and extend for more than 1500 cm^{-1} [e.g., DMABN (CH_3COCH_3)₁, (CH_2Cl_2)₁, and (CH_3CN)₁].¹¹ Mass detected excitation spectra have been obtained for DMABN and its clusters, but attempts to observe fluorescence spectra have not as yet been successful. The size of the red shift for the latter clusters correlates with the polarity of the solvent. Three possible models have been suggested for the observed DMABN/solvent spectra: (1) The two different cluster spectra are due to different cluster structures which affect the $S_1 \leftarrow S_0$ $\pi\pi^*$ spectra differently; (2) single-cluster geometries exist for these clusters but two transitions are observed CT $\leftarrow S_0$ (red shifted and broad) and $S_1 \leftarrow S_0$ (blue shifted and sharp); (3) the different spectra are caused by two different cluster solvation geometries and two different minima in the S_1 excited-state potential surface caused by interaction between the local and charge-transfer excited states. Emission arising from excitation of the broad red shifted cluster absorption has not been reported and would help identify the origin of these features.

In this paper we report significant extensions of these previous cluster studies of DMABN electronic state and structural properties. The focus of this current effort is the cluster spectrum of water and acetonitrile. Cluster geometries for a given cluster size (mass) are identified by a saturation pump-probe (hole-burning) technique and clusters with red shifted absorption are shown to generate red shifted emission. The red and blue emission from the clusters is found to have different lifetimes. These results suggest that a low-energy charge-transfer excited state is generated in one geometry of the DMABN/polar-solvent one-to-one clusters and that it mixes with the local excited ($\pi\pi^*$) state.

II. EXPERIMENTAL PROCEDURES

Both isolate DMABN and its clusters with various solvents are generated in a supersonic expansion. Tunable excitation sources are separate Nd/YAG pumped dye lasers (DCM and R 640). The dye laser output is doubled to attain the correct wavelengths. The mass resolved excitation, flu-

orescence excitation and dispersed emission techniques employed in this work are previously described.¹² The supersonic expansion is created by a pulsed nozzle heated to 110 °C to vaporize DMABN. The expansion gas is either helium or argon at a backing pressure of 50 psi. Acetonitrile vapor is premixed with the helium expansion gas for cluster formation. The DMABN sample is purchased from Aldrich.

Time-resolved fluorescence measures are made with a time correlated single photon counting apparatus previously described.¹³ A cw nozzle at 130 °C with a 100 μm pin hole is employed in this experiment. The concentration of acetonitrile in the expansion gas is maintained at 0.06% or less. The instrument response function for this system with a 1 m monochromator and a 2400 groove/mm grating used in first order is roughly 150 ps full width at half maximum.

III. RESULTS

A. Mass resolved excitation spectra of DMABN clusters

1. Acetonitrile solvent

The one-color MRES of DMABN (acetonitrile)_n, $n = 1, \dots, 5$, are displayed in Fig. 1. Spectra from larger clusters ($n \geq 6$) are too weak to record. The bare molecule origin is at 32 264 cm^{-1} . Only the spectrum of the $n = 1$ cluster has been previously reported.¹¹ The DMABN (CH_3CN)₁ cluster displays what appears to be two types of spectra. The first category contains features somewhat blue shifted with re-

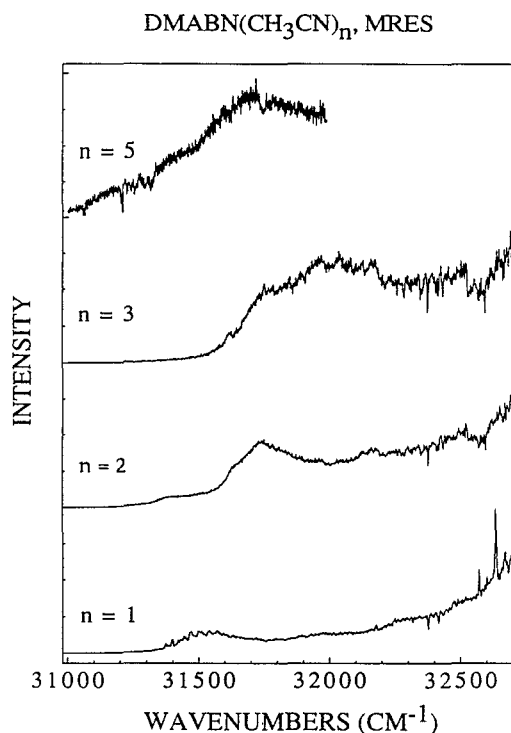


FIG. 1. MRES of DMABN clustered with acetonitrile. n represents number of acetonitrile molecules clustered with one DMABN molecule. The composition of the cluster is determined by the flight time calibrated with known mass molecules. The spectra have been calibrated by laser intensity.

spect to the sharp, bare molecule origin and the second category consists of the broad feature commencing at about 1000 cm^{-1} to the red of the bare molecule origin and increasing in intensity to quite high energy. This latter spectrum is, of course, quite intense. Reproducible, resolved features can be observed at the onset of this broad absorption around $31\,500\text{ cm}^{-1}$, separated by roughly 30 cm^{-1} . As will be demonstrated below, these two categories of spectra are associated with $\text{DMABN}(\text{CH}_3\text{CN})_1$ clusters of different geometries.

As shown in Fig. 1, large clusters of $\text{DMABN}(\text{CH}_3\text{CN})_n$ ($n > 1$) have red shifted spectra similar to that of $\text{DMABN}(\text{CH}_3\text{CN})_1$ but no sharp blue shifted features. The onset of the broad red shifted absorption for larger DMABN/acetone clusters varies slightly with cluster size and the resolved features near $31\,500\text{ cm}^{-1}$ are not observed for $n \geq 2$. The absorption for the largest clusters ($n \sim 5$) observed in this work is close to that of DMABN in an acetonitrile (or other polar solvent) solution.⁶

2. Water solvent

The one-color MRES of $\text{DMABN}(\text{H}_2\text{O})_{1,2,3}$ are readily observed and are displayed in Fig. 2. Relatively sharp spectra are observed for these clusters unlike those found for acetonitrile clusters. The first water cluster peak for $n = 1$ appears at 14 cm^{-1} to the blue of the bare DMABN origin. At $n = 2$ this shift is about 400 cm^{-1} . The $n = 1$ water cluster is composed of two distinct cluster structures, as will be provided later. The bare molecule $S_1 \leftarrow S_0$ structure is more or less preserved in both of these spectra, as it is in the $n = 2$ and 3 cluster spectra.

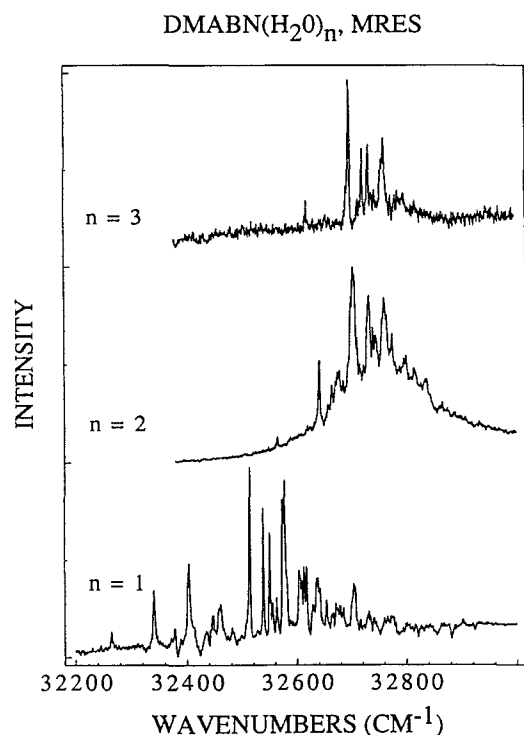


FIG. 2. MRES of DMABN clustered with water. n represents number of water molecules in the cluster of one DMABN .

3. Mixed acetonitrile–water solvent

$\text{DMABN}(\text{CH}_3\text{CN})_1(\text{H}_2\text{O})_n$ and $\text{DMABN}(\text{CH}_3\text{CN})_2(\text{H}_2\text{O})_n$ clusters readily appear in the expansion as the intensity of mixed clusters is larger than the intensity of the higher water clusters. As displayed in Figs. 3(a) and

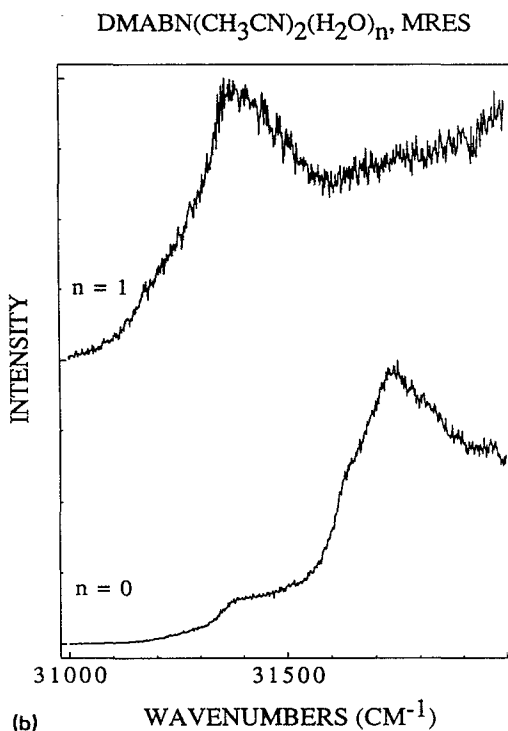
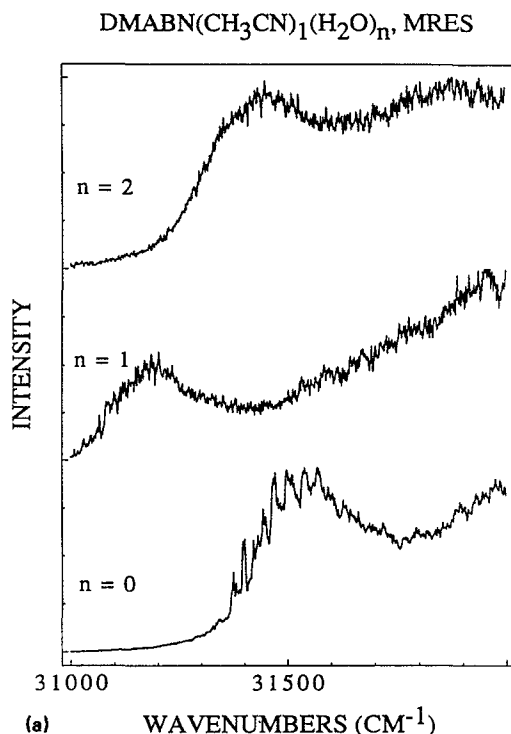


FIG. 3. MRES of DMABN clustered with both acetonitrile and water. (a) One acetonitrile and number of water, $n = 0, 1$, and 2. (b) Two acetonitrile molecules and number of water, $n = 0, 1$.

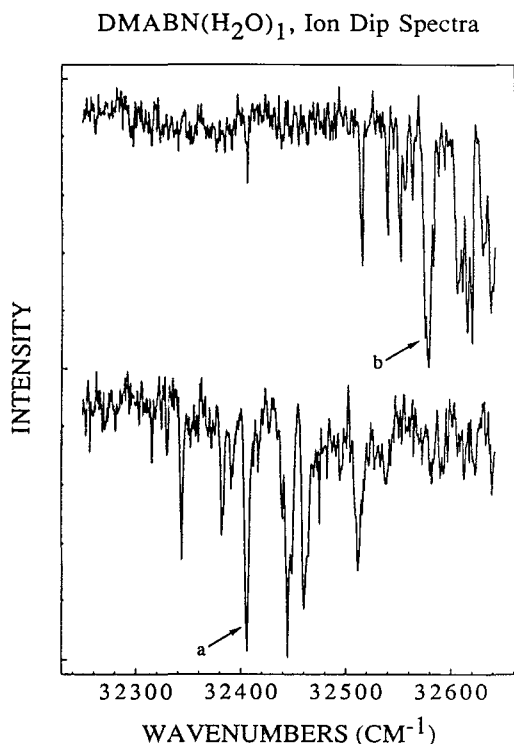


FIG. 4. Ion dip spectra of $\text{DMABN}(\text{H}_2\text{O})_1$. The top spectrum is obtained when the probe laser is tuned at peak *b* ($32\,488\text{ cm}^{-1}$) and the bottom spectrum at peak *a* ($32\,599\text{ cm}^{-1}$).

3(b), the spectra of mixed clusters ($\text{DMABN}/\text{CH}_3\text{CN}/\text{H}_2\text{O}$) are roughly 400 cm^{-1} red shifted from those of $\text{DMABN}(\text{CH}_3\text{CN})_{1,2}$, respectively. Note that the resolved features present in the red shifted $\text{DMABN}(\text{CH}_3\text{CN})_1$ cluster spectrum are still observable in the $\text{DMABN}(\text{CH}_3\text{CN})_1(\text{H}_2\text{O})_1$ spectrum, but the separation between the features is reduced from 30 to $\sim 20\text{ cm}^{-1}$. An additional water molecule ($\text{DMABN}(\text{CH}_3\text{CN})_1(\text{H}_2\text{O})_2$) blue shifts the absorption by roughly 200 cm^{-1} .

B. Population depletion: Assignment of cluster conformations

In order to interpret the spectrum of acetonitrile and water clusters with DMABN, one must first evaluate contributions of multiple cluster geometries for a given cluster composition. For example, we wish to determine if the sharp blue shifted features and the broad red shifted features of the $\text{DMABN}(\text{CH}_3\text{CN})_1$ spectrum arise from a single cluster geometry and two electronic states or can be associated with two distinct clusters of different conformation. In either case, these features are known to be associated with a $\text{DMABN}(\text{CH}_3\text{CN})_1$ cluster mass.

An experiment has been designed which can differentiate between clusters of different geometry with the same mass: the experiment is a cross between a hole burning and an ion dip experiment. The basic idea of the experiment is to excite the molecular beam of mixed species with an intense laser at a given resonance absorption and probe the resulting spectrum at a different energy with a laser of reduced intensi-

ty. The signal associated with the probe laser should decrease for transitions (species) with common ground states as the ground-state population will be depleted for the probe excitation. The presumption here is that the intense laser will drive both the $S_1 \leftarrow S_0$ and $I \leftarrow S_1$ transitions so that population is permanently lost to the ground state (0_0) of the pumped species. If this excitation sequence is carried out in the ionization/extraction region of the mass spectrometer, the microchannel plate detector overloads due to ions generated by the pump laser. Detector saturation can be avoided, however, if the pump excitation occurs outside the ion extraction region: the pump laser beam is thus shifted in space about 1.0 cm before the probe focus at the focal point of the time-of-flight mass spectrometer. The pump laser is then fired $5\text{ }\mu\text{s}$ before the probe laser is fired (the speed of the clusters is roughly $2 \times 10^5\text{ cm/s}$). In this way the ions created by the pump laser are not detected by or at least do not saturate the mass detector.

This experiment is demonstrated on the bare molecule. With the pump laser at the energy of a peak maximum more than 50% of the molecular population can be removed. The second (probe) laser can also be tuned to a peak absorption and the pump laser scanned to produce an "ion dip" spectrum of the bare molecule. This "ion dip spectrum" is a mirror image of the DMABN MRES. If the spectrum is monitored with the probe laser at a peak belonging to a particular conformation within a multiconformational distribution for a given mass cluster and the pump laser is scanned through the transition region, only a spectrum of the particular conformation accessed by the probe laser will be generated as the probe signal.

The ion dip spectrum of the DMABN bare molecule obtained in this fashion probed at $32\,403\text{ cm}^{-1}$, matches exactly the MRES of DMABN. This proves the earlier assignment of the origin spectrum of DMABN.¹¹ Only one conformer gives rise to the bare molecule absorption.

This method can also be applied to the spectrum of $\text{DMABN}(\text{H}_2\text{O})_1$ which has previously been suggested to arise from two different cluster geometries.¹¹ The ion dip spectra of this cluster are displayed in Fig. 4. Clearly, two totally different sets of features are detected by probing at $32\,418$ [Fig. 4(a)] and $32\,599$ [Fig. 4(b)] cm^{-1} . This confirms the assignment of the $\text{DMABN}(\text{H}_2\text{O})_1$ mass channel spectrum: the $\text{DMABN}(\text{H}_2\text{O})_1$ cluster exists in two different conformations. An ion dip spectrum is obtained for $\text{DMABN}(\text{CH}_3\text{CN})_1$ clusters which matches the blue shifted resolved MRES if the peak maximum at $32\,654\text{ cm}^{-1}$ is probed. This is displayed in Fig. 5. If the probe laser is moved off the blue shifted peak maximum to a background (broad) absorption position (associated with the red shifted spectrum of this cluster), no sharp ion dip features are observed [Fig. 5]. This demonstrates that the two spectra, sharp blue and broad red shifted, are associated with clusters of different conformations. Moreover, no resolved features are observed in the ion dip spectra if the resolved red shifted features are probed (pumped) while the rest of the spectrum is pumped (probed). Thus, both DMABN/water and acetonitrile one-to-one clusters have two different geometries in the supersonic jet expansion.

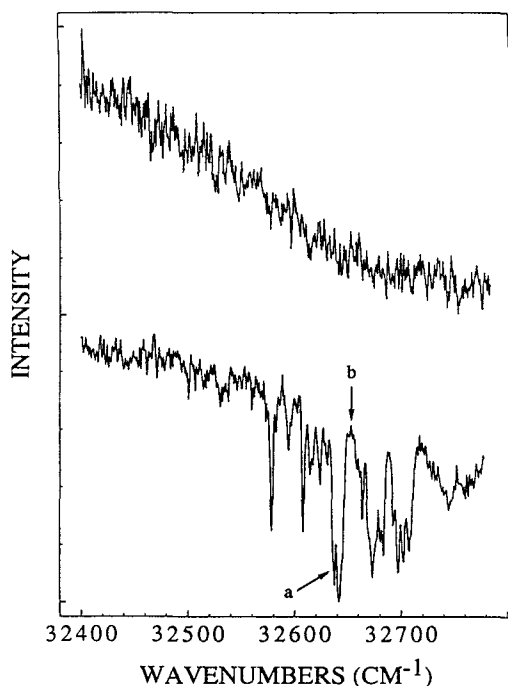
DMABN(CH₃CN)₁, Ion Dip Spectra

FIG. 5. Ion dip spectra of DMABN(CH₃CN)₁. The bottom spectrum is obtained when the probe laser is tuned at peak *a* (32 654 cm⁻¹) and the top spectrum at position *b* (32 665 cm⁻¹).

C. Fluorescence excitation spectra of DMABN/ acetonitrile

To enhance our understanding of the DMABN/acetonitrile cluster system and its excited electronic states further, we investigate the fluorescence emission from these clusters. The concentration of acetonitrile in these studies is kept below 0.015% at which level the MRES shows almost no higher order clusters of DMABN/acetonitrile. The fluorescence excitation spectra obtained by monitoring total and filtered fluorescence is displayed in Fig. 6. These spectra are, in general, similar to the MRES of DMABN(CH₃CN)₁. The intensity ratio of sharp to broad features is higher in the total emission spectrum than in the MRES. Additional proof that this emission can be associated with the DMABN(CH₃CN)₁ cluster comes from the observation of an ion dip mass resolved excitation signal generated by stimulated emission with the pump at 25 000 cm⁻¹ and the probe at 32 200 cm⁻¹. While the presence of (DMABN)₂ is confirmed by MRES under the conditions of these experiments, its emission is roughly a factor of 10 weaker than that present in Fig. 6, as can be seen in Fig. 7. A weak broad emission band can also be observed at about 32 000 cm⁻¹. This feature may well be due to impurities as it does not appear in the MRES.

Fluorescence excitation spectra are also observed with color filters placed before the photomultiplier tube. A U340 (Hoya Co.) will transmit most of the fluorescence with wavelengths *shorter* than 380 nm. A L40 (Hoya Co.) filter will transmit light at wavelengths *longer* than 400 nm. Fig-

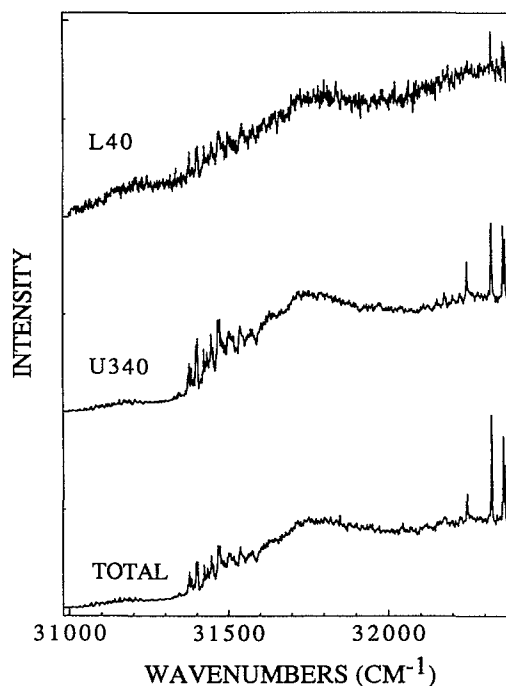
DMABN(CH₃CN)₁, FE

FIG. 6. Fluorescence excitation spectra of DMABN(CH₃CN)₁. Total: total emission without filter. U340: a U340 filter is inserted before photon-multiplier tube (transmits between 280–380 nm). L400: a L400 filter is inserted (transmits above 400 nm). The spectra have been calibrated over laser intensity. The concentration of acetonitrile is controlled in these experiments to 0.015%.

DMABN Dimer

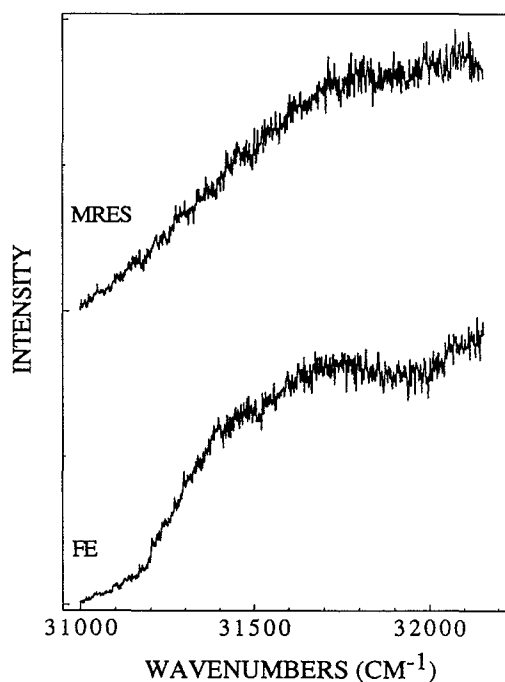


FIG. 7. Excitation spectra of DMABN dimer. FE: Signal is measured through emission. MRES: Signal is measured by mass resolved ion intensity. The spectra have been calibrated over laser intensity.

ure 6 also presents the fluorescence excitation spectrum of $\text{DMABN}(\text{CH}_3\text{CN})_1$ as viewed through these two filters. Four features of this cluster emission are immediately clear: first, the major portion of the fluorescence intensity is below 380 nm; second, nonetheless, a significant amount of fluorescence from this cluster is above 400 nm; third, the broad red shifted emission is more intense above 400 nm than are the resolved red shifted features; fourth, the sharp blue shifted $\text{DMABN}(\text{CH}_3\text{CN})_1$ features generate no emission above 400 nm.

D. Dispersed emission spectra of $\text{DMABN}(\text{CH}_3\text{CN})_1$

Employing the same nozzle and concentration conditions employed earlier for the fluorescence excitation spectra, we have also obtained dispersed emission spectra of $\text{DMABN}(\text{CH}_3\text{CN})_1$ at 1 nm resolution. These spectra are shown in Fig. 8. The spectra contained in Fig. 8 are obtained at excitation energies $31\,400$ and $31\,419\text{ cm}^{-1}$: both positions are near the onset of the red shifted absorption. The former energy is at a peak and the latter is at the broad background absorption. Note how similar the two dispersed emissions are. Additionally, the emission is red shifted from the excitation position and no resonance emission is observed, suggesting that either the Franck-Condon factor for emission and absorption are different (somewhat unlikely) or that some vibrational relaxation occurs prior to emission.

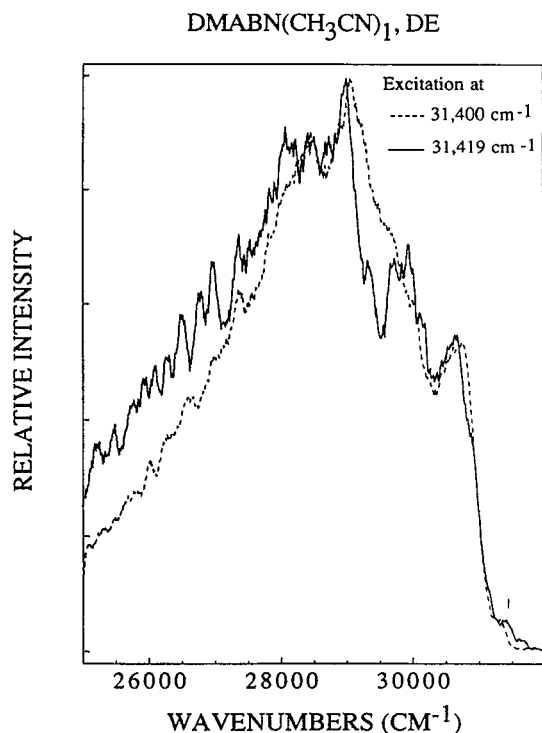


FIG. 8. Dispersed emission spectra of $\text{DMABN}(\text{CH}_3\text{CN})_1$. (---), excitation at $31\,400\text{ cm}^{-1}$ (sharp peak); (—), excitation at $31\,419\text{ cm}^{-1}$ (broad background close to the sharp peak).

E. Fluorescence lifetime for DMABN and $\text{DMABN}(\text{CH}_3\text{CN})_1$

A time-correlated single-photon counting technique¹³ (150 ps time resolution for dispersed emission) is employed to measure the emission lifetimes of the DMABN bare molecule and $\text{DMABN}(\text{CH}_3\text{CN})_1$ clusters. The bare molecule is excited at the maximum absorption peak ($32\,403\text{ cm}^{-1}$) and monitored at $350 \pm 0.5\text{ nm}$ and the cluster is excited at $32\,110\text{ cm}^{-1}$ and monitored at 350 ± 0.5 and $400 \pm 0.5\text{ nm}$. The three observed lifetimes are 5.6 ± 0.15 , 4.6 ± 0.15 , and $6.0 \pm 0.15\text{ ns}$, respectively. These data are presented in Figs. 9(a)–9(c). These times suggest that the two cluster emissions observed at 350 and 400 nm involve different excited states.

IV. DISCUSSION

The effect of a polar solvent on the $\text{DMABN } S_1 \leftarrow S_0$ spectrum depends on the solvent polarity and on the solvent hydrogen bonding capabilities. The general polar solvent effects can be distinguished in two groups: sharp blue shifted cluster spectra, exemplified by water; and both broad red shifted spectra and sharp blue shifted spectra, exemplified by CH_3CN , $(\text{CH}_3)_2\text{CO}$, CH_2Cl_2 , etc.¹¹ In both groups, the one-to-one polar solvent DMABN clusters can display two conformations. The results described earlier have focused on the $\text{DMABN}(\text{CH}_3\text{CN})_1$ cluster with the goal of determining its excited electronic state properties. These results demonstrate that the cluster has two distinct geometries. One geometry gives rise to sharp blue shifted spectra and the other gives rise to broad red shifted absorption with some resolved features near the onset of this absorption. The former cluster geometry has spectra very similar to both the bare molecule and the two $\text{DMABN}(\text{H}_2\text{O})_1$ cluster conformations. We will refer to this cluster conformation as geometry I and the other one as geometry II. In the following discussion, we will treat the nature of the solvent binding sites for the two $\text{DMABN}(\text{CH}_3\text{CN})_1$ cluster conformations and the effect these structures have on the cluster electronic states.

A. $\text{DMABN}(\text{CH}_3\text{CN})_1$ cluster geometry I

The spectrum associated with geometry I shows blue shifted sharp features nearly identical with those of DMABN and the $\text{DMABN}(\text{H}_2\text{O})_1$ clusters with regard to both peaks separation and intensity patterns. The most likely bonding site for acetonitrile under these conditions is away from the $(\text{CH}_3)_2\text{N}$ moiety. Additionally, if the acetonitrile were over the benzene ring one would expect a red shift for the cluster $S_1 \leftarrow S_0$ transition. The most likely structure for conformer I is thus with the CH_3CN coordinated to the $-\text{CN}$ moiety of DMABN . This geometry would not be expected to stabilize a charge-transfer excited state; indeed, no red shifted emission is found upon excitation of the sharp blue shifted features associated with conformer I. We conclude that the lowest excited state of this cluster is the local excited, $\pi\pi^*$ state found for the bare molecule, the water clusters of DMABN , and other typical aromatic/solvent clusters.

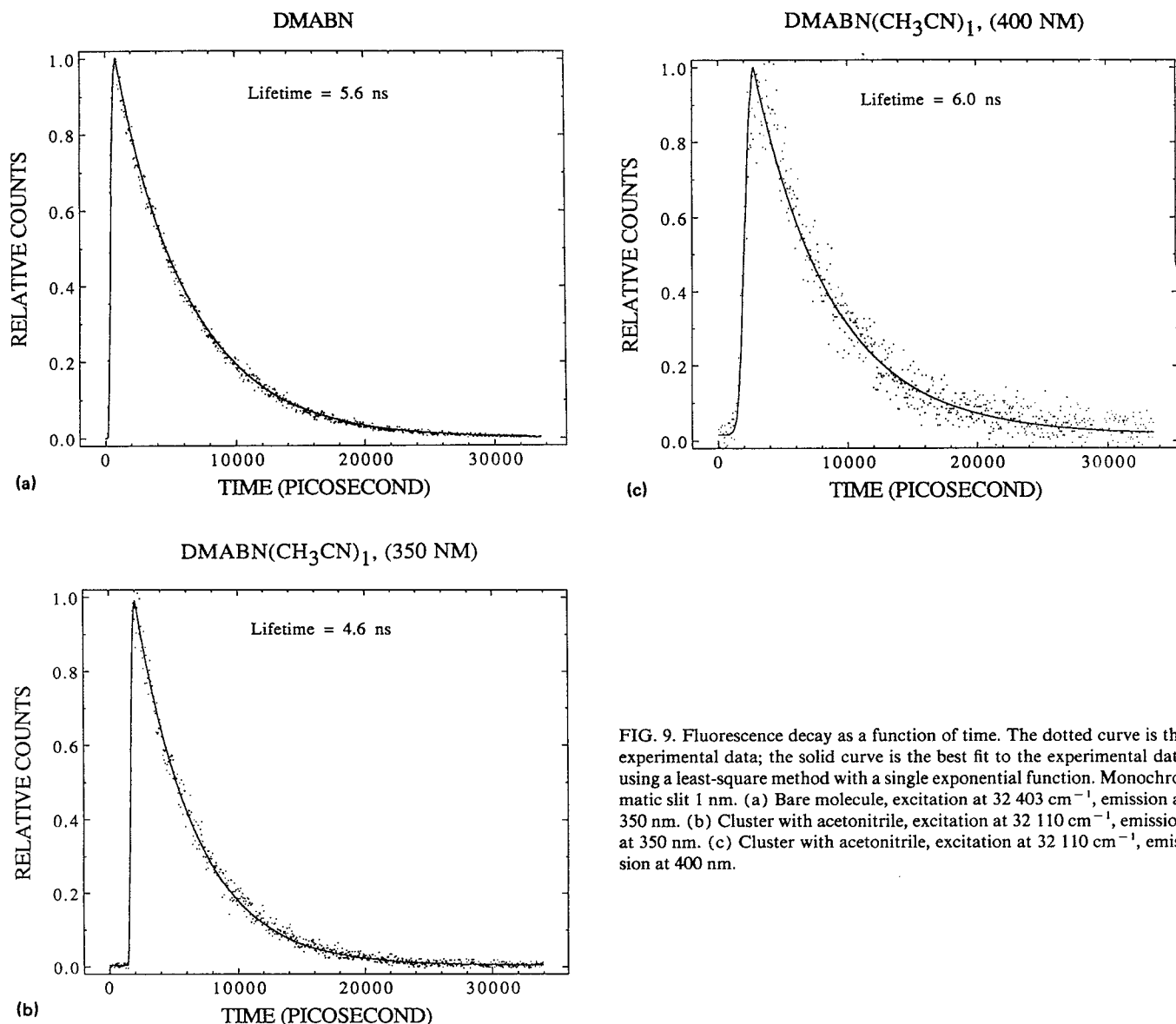


FIG. 9. Fluorescence decay as a function of time. The dotted curve is the experimental data; the solid curve is the best fit to the experimental data using a least-square method with a single exponential function. Monochromatic slit 1 nm. (a) Bare molecule, excitation at $32\,403\text{ cm}^{-1}$, emission at 350 nm. (b) Cluster with acetonitrile, excitation at $32\,110\text{ cm}^{-1}$, emission at 350 nm. (c) Cluster with acetonitrile, excitation at $32\,110\text{ cm}^{-1}$, emission at 400 nm.

The two observed DMABN (H₂O)₁ cluster conformers are of the same nature: the H₂O molecule could hydrogen bond to the C≡N moiety at the nitrogen and could also coordinate to the C≡N through a dipolar orientation. Additional H₂O molecules would hydrogen bond to the first one and thereby not perturb the overall blue shifted sharp features associated with this general conformation.

B. DMABN(CH₃CN)₁ cluster geometry II

The broad red shifted absorption observed for the DMABN(CH₃CN)₁ cluster is ascribed to another cluster conformer called geometry II. Its spectroscopic properties and, thus, by implication, its structure must be quite different from those of geometry I. The two possible (reasonable) binding sites for acetonitrile on DMABN are over the aro-

matic ring and at the nitrogen atom of the dimethylamino group. The large red shift of the absorption would tend to support a geometry with the acetonitrile over the aromatic ring with its dipole moment oriented antiparallel to that of DMABN (i.e., CN group to dimethylamino group and CH₃ group to the CN group of DMABN. This type of orientation could readily stabilize a charge-transfer excited state for the cluster.

C. Charge-transfer state formation and stabilization

For the bare molecule, water clusters and acetonitrile cluster geometry I, one can reasonably assert that any DMABN charge-transfer state, such that (CH₃)₂N⁺–C₆H₄–CN[–] is the zeroth-order description of the excited state, has not been lowered in energy with respect to the local

$\pi\pi^*$ first excited (benzene-like) electronic state. The first excited electronic state of the DMABN(CH₃CN)₁ cluster geometry II, characterized by a large red shift with respect to S_0 , a very large ($\Delta\nu > 2000\text{ cm}^{-1}$) bandwidth, and a few resolved features at its onset, is, however, not so clearly characterized. In this (geometry II) cluster conformation (and similarly for the DMABN/acetone and dichloromethane clusters) the DMABN first excited electronic state description must be very different from that of geometry I and the bare molecule.

The photodepletion/ion dip spectra for cluster geometry II suggest that the width of the system is not due to inhomogeneous broadening. These overall results are consistent with the proposal that a charge-transfer state has been stabilized in this geometry and that it interacts and strongly couples to the local excited $\pi\pi^*$ S_1 state of the bare molecule. This explains the broad absorption spectrum and its homogeneous behavior. The observed fluorescence measurements (fluorescence excitation and dispersed emission) further support this mechanism as will be discussed later.

The DMABN(CH₃CN)₁ emission spectrum generated by exciting the low-energy broad absorption of geometry II is also very broad and extends from $31\,200\text{ cm}^{-1}$ to less than $25\,000\text{ cm}^{-1}$, nearly independent of excitation energy. Some small changes in emission can be noted with excitation at the red shifted resolved features near $31\,420\text{ cm}^{-1}$ (see Figs. 6 and 8).

Importantly, the fluorescence lifetime differs depending on the wavelength of the observed emission: at 350 nm it is 4.6 ns and at 400 nm it is 6.0 ns. This difference in lifetime indicates that emission at 350 ($28\,570\text{ cm}^{-1}$) and 400 nm ($25\,000\text{ cm}^{-1}$) involves two different excited (vibronic or electronic) states. These two states may be the local and charge-transfer excited electronic states or two different cluster vibronic states belonging to the same electronic manifold. This latter possibility is less likely than the former because the high density of states of these clusters as reflected by the homogeneous width of the transition should lead to a much shortened nascent state lifetime for an initially excited vibronic state.

The overall understanding of the first excited electronic "state" of DMABN(CH₃CN)₁ is then as follows. Two excited zero-order electronic states exist in the region. One of them is the local $\pi\pi^*$ S_1 and the other is the charge-transfer state lowered in energy by the DMABN-CH₃CN (dipole-dipole) interaction in geometry II (CH₃CN over the aromatic ring). These states strongly couple with one another and the lower potential surface develops a barrier separating a mostly local excited state from a mostly charge transfer excited state. Absorption is to the mostly local $\pi\pi^*$ excited state, and the resolved features at the onset of the broad red shifted absorption band of geometry II probably are caused by local $\pi\pi^*$ -like vibronic states below the potential barrier between the two electronic states. Emission at 350 nm (short lifetime) is mostly due to the $S_0 \leftarrow S_1$ $\pi\pi^*$ transition and emission at 400 nm (long lifetime) is mostly associated with the $S_0 \leftarrow \text{CT}$ transition. The emission lifetime difference noted earlier is associated with the radiationless behavior of the two electronic states. Internal conversion and vibrational re-

laxation clearly play a role in controlling the observed lifetimes for the different emission characterized from cluster geometry II. This mechanism and model are presented in Fig. 10.

The above qualitative description of the energy levels and dynamics of DMABN(CH₃CN)₁ cluster geometry II is similar to that presented recently for indole clusters.¹⁵ In this instance the L_a and L_b states of indole have different sensitivities to interaction with polar solvents. The charge-transfer state of DMABN is even more polar than the L_a state of indole.

Larger clusters of DMABN/acetonitrile behave in a fashion that is consistent with the aforementioned discussion. For DMABN(CH₃CN)₂, the onset of the red shifted absorption is about 300 cm^{-1} to the blue of that for DMABN(CH₃CN)₁. One can suggest that the geometry I conformer solvation site is occupied in this cluster and that this reduces the charge-transfer state stabilization. Addi-

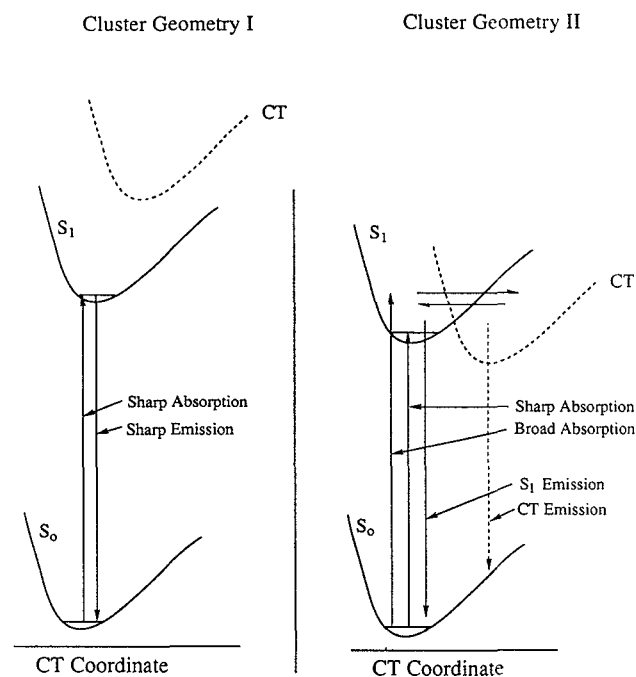


FIG. 10. A schematic diagram of the potential-energy surface of DMABN polar solvent cluster along the charge-transfer coordinate. Cluster geometry I yields sharp blue shifted absorption with respect to the bare molecule. In this case, both excitation and emission spectrum are well resolved, indicating little mixing of the CT state with the S_1 state: The CT state is not significantly stabilized with respect to the S_1 state. Cluster geometry II yields broad red shifted absorption with respect to the bare molecule. In this geometry the S_1 and CT clusters states are both stabilized (lowered in energy) with respect to the cluster S_0 state and are strongly mixed. Resolved features at the low-energy side of this red shifted absorption are observed due to the small barrier in the CT coordinate between the S_1 and CT states. When the excitation energy is above the barrier, rapid evolution to the charge-transfer state occurs leading to a broad absorption spectrum. As intramolecular vibrational redistribution from the DMABN modes to the van der Waals modes occurs the cluster will be trapped in either an S_1 -like or a CT-like excited state. Two emission lifetimes are thus expected for the cluster.

tional solvent molecules do not further alter the shift significantly. These results are consistent with those for dilute solutions of DMABN and a polar solvent in nonpolar solvents.⁷

The mixed acetonitrile/water cluster results are also interesting. DMABN(CH₃CN)_n (H₂O)₁ (*n* = 1,2) spectra are red shifted compared to the DMABN(CH₃CN)_n cluster spectra. Apparently, water in this cluster can further stabilize the charge transfer and/or the local $\pi\pi^*$ state, but it is not essential to induce the lowering of the charge-transfer state. Without a more detailed understanding of what the geometry of these clusters is one cannot be more specific about the nature of this effect.

The dimer of DMABN and the DMABN(CH₃CN)_m clusters have similar spectra but greatly different lifetimes.^{10(c)} While the two sets of species cannot thereby be mistaken for one another, the charge-transfer nature of their lowest excited electronic states probably arises by the same or similar mechanisms.

V. CONCLUSIONS

We have, in this work, further explored solvation effects on the excited states of DMABN. Photodepletion (ion dip) experiments demonstrate that DMABN(CH₃CN)₁ and (H₂O)₁ clusters have two distinct geometries. The two geometries of DMABN(CH₃CN)₁ clusters are reflected, in the MRES, fluorescence excitation and dispersed emission spectra. Both the cyano group and the aromatic ring are suggested as acetonitrile binding sites. Blue shifted sharp spectra are associated with the cyano group binding site (geometry I) and the ring binding (geometry II) is associated with the broad red shifted spectra of this cluster system. The geometry II is suggested to stabilize and lower in energy the DMABN charge-transfer state such that it couples strongly with the local excited (*S*₁) $\pi\pi^*$ state.

The charge-transfer state nature of the first excited state of DMABN(CH₃CN)₁ geometry II is further supported by the observation of red shifted emission from the geometry II cluster. These general results support the overall importance of short-range (dipole-dipole) interactions for the charge-transfer stabilization in the DMABN/polar nonhydrogen

bonding solvent clusters. Long-range interaction will surely further stabilize this state. The presented results offer no additional information concerning any accompanying motion of the various molecular moieties within the charge-transfer state.

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