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Conformational changes upon $S_1 \leftarrow S_0$ excitation in 4-dimethylaminobenzonitrile and some of its chemical analogs

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One-color time-of-flight mass spectra (mass resolved excitation spectra) for jet-cooled 4-dimethylaminobenzonitrile (4-DMABN) and some of its chemical analogs, dimethylaniline (DMA), 3-dimethylaminobenzonitrile (3-DMABN), *N, N*-dimethyl-4-(trifluoromethyl)aniline (4-CF_3-DMA), and 4-(d_6-dimethylamino)benzonitrile (4-d_6-DMABN), are presented and analyzed. Near the origin of the $S_1 \leftarrow S_0$ transition the low frequency modes can be assigned to motions of the dimethylamino group for this series of molecules. The inversion motion of the dimethylamino group and the dimethylamino group torsion about the C_{ipso}–N bond (the twist coordinate) in S_1 give rise to the most prominent peaks in this spectrum. The potential parameters for the twist coordinate of 4-DMABN and DMA are quite similar in S_1: $B = 0.546$, $V_2 = 175$, and $V_4 = 525\ \text{cm}^{-1}$ for 4-DMABN and $B = 0.546$, $V_2 = 175$, and $V_4 = 515\ \text{cm}^{-1}$ for DMA. The V_2 and V_4 terms are slightly larger for 3-DMABN and 4-CF_3-DMA. The inversion motion is also similar for these molecules but is more anharmonic for the para-substituted dimethylanilines, 4-DMABN and 4-CF_3-DMA, than for the meta and unsubstituted molecules. A Franck–Condon intensity analysis for the dimethylamino twist in these molecules suggests that this group in 4-DMABN is displaced in the excited state by ~30° with respect to its planar orientation in the ground state. In both solutions and monosolvate clusters of 4-DMABN with polar aprotic solvents, a low lying charge transfer (CT) state is identified in addition to the usual $\pi\pi^*$ excited state of the bare molecule. The relation between the bare molecule 4-DMABN twisting displacement upon excitation and the low lying CT state is discussed.

INTRODUCTION

Intramolecular charge transfer (CT) reactions constitute an important class of unimolecular reactions; however, experimentally observed solvent effects on the intramolecular CT reaction suggest that these reactions are solvent assisted and thus not purely intramolecular. Polar solvents have the ability to stabilize the charge transfer state and can consequently lower the barrier to reaction. A considerable amount of interest has been generated in the solution phase emission studies of molecules which undergo such behavior because they exhibit anamolous dual fluorescence in polar solvents (e.g., acetonitrile) and normal fluorescence in nonpolar solvents (e.g., hexane).[1–10] The dual fluorescence is attributed to "normal" fluorescence from S_1 and red-shifted emission from a CT state.

The nature of the charge transfer state has been the subject of some debate. Grabowski and co-workers[1–3] have suggested a twisted intramolecular charge transfer (TICT) state to explain the supposed viscosity dependence of the dual fluorescence of molecules such as 4-dimethylaminobenzonitrile (4-DMABN). They postulated that after excitation, 4-DMABN undergoes electron transfer from the dimethylamino group to the benzonitrile group with a concommitent 90° twist of the dimethylamino group. The complete loss of conjugation between the dimethylamino group and the benzonitrile group (due to the proposed 90° twist) would prohibit electron transfer from proceeding in the reverse direction. This intramolecular charge transfer state is stabilized by solvent interactions in polar solvents. Eisenthal and co-workers have carefully studied the role of the solvent on the kinetics in the formation of the TICT state,[5,6] and find that the viscosity dependence of the fluorescence is an experimental artifact. Thus the original basis for the TICT mechanism no longer appears to be valid, although this TICT mechanism is still invoked to rationalize the presence of the low lying CT state of 4-DMABN in polar solvents.

Recently we have published a spectroscopic study of jet-cooled 4-DMABN both isolated and clustered with polar and nonpolar solvents.[11] These studies were undertaken in hopes of providing some insight into the solution phase behavior of 4-DMABN and related molecules which exhibit dual fluorescence in polar solvents. The correlation between the monosolvated clusters, formed in the supersonic jet expansion, and the solution phase behavior is quite good. Similar to what is observed in solution, we were able to identify spectroscopically two distinct regions in the time-of-flight mass spectrum (TOFMS-mass resolved excitation spectrum) of monosolvated 4-DMABN when clustered with polar solvents such as acetonitrile, acetone, and dichloromethane. The TOFMS of 4-DMABN clustered with these three polar solvents shows a broad red-shifted (with respect to the 4-DMABN spectral origin) peak which we associate with

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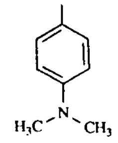
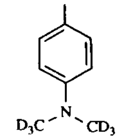
the "anomalous" emission found in solution phase and a slightly blue shifted (again with respect to the 4-DMABN origin) set of spectrally sharp features which we attribute to normal cluster emission. These spectra were suggested to arise from clusters of different configurations and therefore clusters with different degrees of CT state stabilization. The frequency shift of the broad peak is proportional to the dipole moment of the solvent as is expected for a CT state. Although other workers have published fluorescence excitation studies on jet-cooled 4-DMABN clustered with various solvents they did not detect the broad, relatively weak red-shifted features associated with the charge transfer state.[12–14]

The solution phase spectra are broad with little or no sharp features present. The jet-cooled cluster species are preferable to study spectroscopically because they yield relatively uncongested spectra.[15] Although several studies on jet-cooled 4-DMABN have appeared in the literature, the spectrum has yet to be assigned. The full analysis of the spectrum for 4-DMABN and some of its chemical analogs is the subject of this paper. Assignment of the TOFMS (or the fluorescence excitation spectra which are identical, *vide infra*) for jet-cooled 4-DMABN is of course an important first step in understanding the excited state potential energy surface of the isolated molecule. The spectrum for jet-cooled 4-DMABN displays a Franck–Condon envelope clearly evident in the origin region. We attribute these features to a twist of the dimethylamino group upon excitation of the molecule from S_0 to S_1. This implies the molecule is already in a twisted form in the S_1 state before the solvent assisted charge transfer occurs. The degree to which the amino group twists for isolated 4-DMABN in S_1 and its relation to the TICT state is discussed in this paper.

In this study we present TOFMS for dimethylaniline (DMA), *N*, *N*-dimethyl-4-(trifluoromethyl)aniline (4-CF_3-DMA), and the specifically labeled d_6-4-DMABN (deuterated methyl groups), as well as the TOFMS for 3- and 4-DMABN. These chemical analogs of 4-DMABN are studied so as to aid in the assignment of the spectrum. We have analyzed the spectra in terms of the dimethylamino torsional motion about the C–N bond, i.e., the twist coordinate, and the dimethylamino inversion motion. The similarity in the spectra of all these closely related molecules near the origin region shows that the low frequency peaks can be solely attributed to motions of the dimethylamino group. Since only 4-DMABN, of this set of molecules, evidences a low lying charge transfer state in solution and in clusters, we can conclude that the twisting motion in S_1 is not mechanistically related to the charge transfer mechanism.


4-DMABN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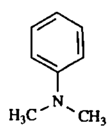
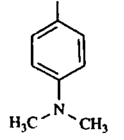

DMA


4-CF_3-DMA

II. EXPERIMENTAL PROCEDURE

The time-of-flight system has been described previously.[16] The supersonic jet expansion is generated by a pulsed R.M. Jordan valve. The supersonic beam is skimmed before it interacts with the laser beams in the ionization region of the TOFMS. The jet-cooled molecules are excited to S_1 and photoionized with the same laser frequency in these one-color experiments. The doubled output of a Nd:YAG laser (532 nm) is used to pump a dye laser. The dye (DCM for 4-DMABN, 4-CF_3-DMA, and d_6-4-DMABN; and LDS 698 for 3-DMABN) output is frequency doubled by a KDP crystal. The laser beam and the skimmed, molecular beam cross at right angles. The ions that are formed from the one-photon resonant, two-photon ionization process are accelerated into the flight tube and detected by a microchannel plate.

4-DMABN was purchased from Aldrich Chemical Co., and used without further purification. 3-DMABN was prepared as described previously.[11] The synthesis of d_6-4-DMABN and 4-CF_3-DMA are described in the supplementary material for this report.[20]

III. THEORY

A. Torsional analysis (dimethylamino twist)

The observed torsional energy levels of the dimethylamino group are fitted with a one-dimensional potential of the general form

$$V(\tau) = \frac{1}{2}\sum_n V_n(1 - \cos n\tau), \tag{1}$$

in which τ is the torsion angle. The eigenvalues and eigenvectors of this torsional motion are calculated from the equation

$$\left[-B\frac{\partial^2}{\partial\tau^2} + V(\tau)\right]\Psi(\tau) = E(\tau)\Psi(\tau) \tag{2}$$

by expanding the wave function $\psi(\tau)$ in 71 free-rotor basis functions which have the form

$$\Phi_m(\tau) = e^{im\tau} \tag{3}$$

with $m = 0, \pm 1, \pm 2, \ldots$. The eigenvalues are computed by numerically diagonalizing the Hamiltonian. The free-rigid rotor case with $V(\tau) = 0$ leads to energy values of $E = m^2B$. The parameters B, V_2, and V_4 are adjusted to correspond to the best fit of the experimental data: B is not directly calculated because the exact molecular structure in both electronic states is not known.

B. Inversion motion of the dimethylamino group

The inversion motion of the dimethylamino group requires a double minimum potential function for its modeling and the form we have chosen consists of a superimposed Gaussian and a harmonic oscillator function. We use here the three parameter double minimum potential developed by Coon, Naugle, and McKenzie.[18] This potential has the form

$$V(q) = \tfrac{1}{2}kq^2 + Ae^{-a^2q^2} \tag{4}$$

with

$$a^2 = \frac{e^{\rho}\lambda}{2A} \tag{5}$$

and

$$\lambda = (2\pi c \nu_0)^2. \quad (6)$$

The parameters ρ and ν_0 (the harmonic frequency) are adjusted to fit the experimental data. The barrier height b (in cm^{-1}) is defined as

$$bhc = V(0) - V(Q_m) = \frac{A^{(e^\rho - \rho - 1)}}{e^\rho} \quad (7)$$

in which Q_m is the positon of the minima and is given by

$$Q_m^2 = \frac{2\rho}{e^\rho - \rho - 1} \frac{hb}{(2\pi\nu_0)^2 c}. \quad (8)$$

C. Franck–Condon analysis

An estimate of the displacement in the dimethylamino twist coordinate ϕ in the excited state can be made by a Franck–Condon intensity profile analysis. The eigenvectors can be written as $\psi(\tau)$ and $\psi(\tau + \Delta\tau)$ for the ground and excited states, respectively. The Franck–Condon factors for transitions from the zero-point level in the ground state potential well to the torsional levels of the excited state potential surface can be written as

$$\langle \psi_e(\tau + \Delta\tau) | \psi_g(\tau) \rangle \quad (9)$$

$$= \langle \sum_m C_m^e \, \phi_m(\tau + \Delta\tau) | \sum_m C_m^g \, \phi_m(\tau) \rangle \quad (10)$$

$$= \sum_m C_m^e \, C_m^g \, \langle \phi_m(\tau + \Delta\tau) | \phi_m(\tau) \rangle \quad (11)$$

$$= \sum_m C_m^e \, C_m^g \cos m(\Delta\tau), \quad (12)$$

$$m = \pm 1, \pm 2, \pm 3, \ldots .$$

IV. RESULTS

A. TOFMS of jet-cooled 4-DMABN, DMA, 3-DMABN, and 4-CF$_3$-DMA

Figure 1 shows the one-color TOFMS obtained within ~250 cm^{-1} of the spectral origin, the $S_1 \leftarrow S_0$ 0_0^0 transition, for jet cooled 4-DMABN, DMA, 3-DMABN, and 4-CF$_3$-DMA. The spectra are displayed in Fig. 1 with aligned 0_0^0 transition of the different molecules. The actual frequencies of the 0_0^0 transition are listed in Table I. DMA has the greatest $S_1 \leftarrow S_0$ transition energy and the spectral origin for the substituted dimethylanilines are all red-shifted with respect to the DMA origin. The fluorescence excitation spectrum of jet cooled 4-DMABN published in Refs. 12–14, and reproduced in this laboratory, is identical to the TOFMS depicted in Fig. 1.

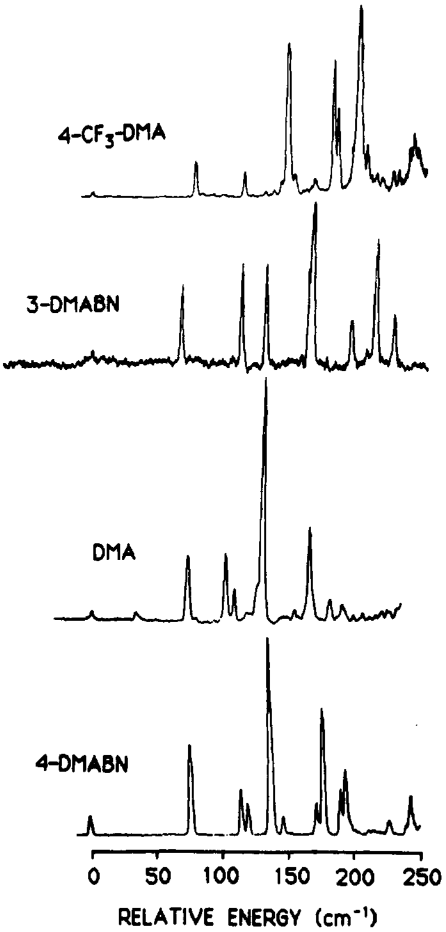


FIG. 1. The one-color TOFMS of 4-DMABN, DMA, 2-DMABN, and 4-CF$_3$-DMABN at the origin region. The spectroscopic origins have been aligned in this figure so as to compare the low frequency modes. The actual frequencies of 0_0^0 transition are listed in Table I.

The similarity in the spectrum of DMA and 4-DMABN (as well as 3-DMABN and 4-CF$_3$-DMA) indicate that the low frequency peaks in the spectra are due to motions of the dimethylamino group. The intensity of the 0_0^0 transitions is relatively weak for all of these dimethylaminobenzenes. In addition, the spectra all exhibit a Franck–Condon intensity envelope for the low frequency mode progression. These spectra clearly demonstrate that the position of the dimethylamino group is being displaced in the excited state relative to that in the ground state. A complete analysis of the spectra is discussed in detail in the next section.

Figure 2 shows the TOFMS of d_6-4-DMABN compared to the spectrum of 4-DMABN. The frequency of the 0_0^0 transition for d_6-4-DMABN (listed in Table I) is 85 cm^{-1} higher in energy than 4-DMABN. The transitions have been aligned in Fig. 2 for these two isotopes of 4-DMABN so that the effect of deuteration on these low frequency peaks can be readily seen. A significant shift in frequency of the peaks clearly demonstrates that the spectrum is properly assigned to the dimethylamino group. This is, of course, consistent with the above observation that the spectra for DMA and 4-DMABN (Fig. 1) are quite similar.

TABLE I. The energy of the 0_0^0 transitions for the molecular species studied in this work.

Molecule	0_0^0 transition (cm^{-1})
4-Dimethylaminobenzonitrile (4-DMABN)	32 255.5
d_6-4-Dimethylaminobenzonitrile (d_6-4-DMABN)	32 340.4
Dimethylaniline (DMA)	32 895.8
3-Dimethylaminobenzonitrile (3-DMABN)	30 076.1
4-Trifluoromethyldimethylaniline (4-CF$_3$-DMA)	32 829.2

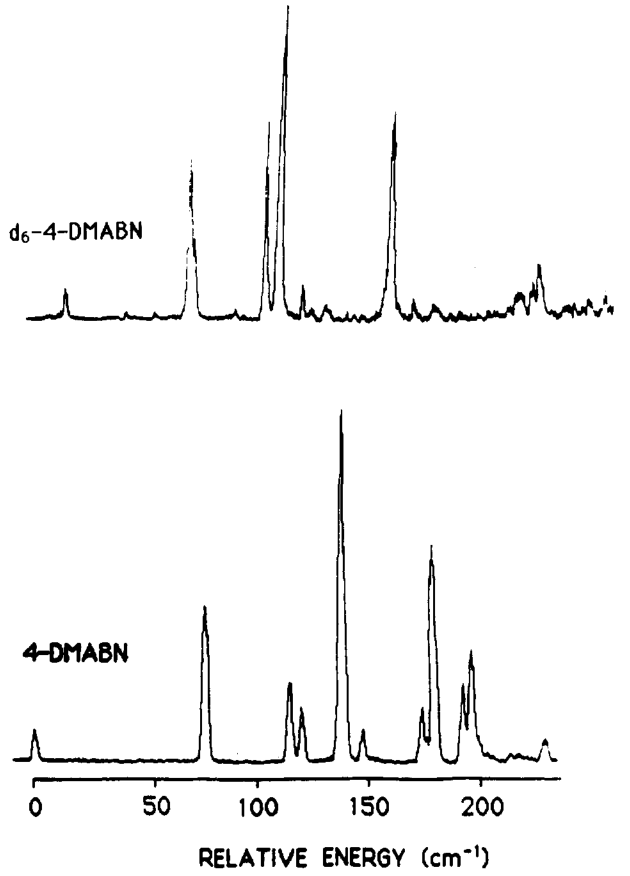


FIG. 2. The one-color TOFMS of d_6-4-DMABN in the origin region. The spectrum for 4-DMABN is also shown for comparison. See Table I for the 0_0^0 absolute energies.

B. Summary of cluster results: 4-DMABN $(X)_1$, X = H_2O, CH_4, CH_3CN, $(CH_3)_2CO$, CH_2Cl_2

In a recent publication[11] we reported the results of 4-DMABN clustered with H_20, CH_4, CH_3CN, $(CH_3)_2CO$, and CH_2Cl_2. Methane and water clusters give "normal" cluster spectra with sharp spectral features and small cluster shifts. The origin for 4-DMABN$(CH_4)_1$ is red shifted by 63 cm^{-1} with respect to the origin for the isolated molecule. The DMABN (H_2O) spectra consist of two cluster origins both blue shifted, by 114 and 199 cm^{-1} with respect to that of the bare molecule.

Of a more interesting nature are the spectra of DMABN clustered with CH_3CN, $(CH_3)_2CO$, and CH_2Cl_2.[11] The spectra are shown in Fig. 3. Acetonitrite and acetone, when clustered with 4-DMABN, exhibit two types of cluster spectra: "normal" cluster spectra, with sharp blue shifted spectral features (closely related to those of the isolated molecule); and cluster spectra that are broad and significantly red shifted with respect to the isolated molecule spectrum. These two different spectra are associated with different cluster solvation configurations.[11] Only the red-shifted broad spectrum is observed for the 4-DMABN dichloromethane cluster.

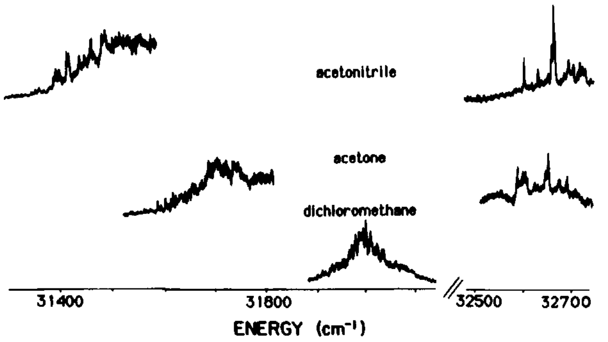


FIG. 3. Two-color TOFMS cluster spectra of 4-DMABN with CH_3CN, $(CH_3)_2CO$, and CH_2Cl_2. The spectra for CH_3CN and $(CH_3)_2CO$ exhibit two distinct regions: a lower energy broad peak and sharp features ~1000 cm^{-1} higher in energy.

V. DISCUSSION

A. Analysis of the dimethylamino twist and inversion for isolated 4-DMABN, 3-DMABN, DMA, and 4-CF_3-DMA

The methods detailed in Sec. III are employed to analyze the TOFMS for the series of dimethylaniline derivatives: DMA, 3-DMABN, 4-DMABN, and 4-CF_3-DMA. The similarity in the spectra of DMA and 4-DMABN as well as the significant shift of the peaks in the spectrum d_6-4-DMABN leaves little doubt that the low frequency peaks in the TOFMS are due to motions of the dimethylamino group. The two motions whose features dominate these spectra are the rotation of the dimethylamino group about the C_{ispo}–N bond and the inversion of the dimethylamino group. The first step in the analysis is determining which peaks can be assigned to the rotational motion.

The spectrum of 4-DMABN contains a progression with an energy level spacing on the order of 65 cm^{-1}. The most intense peak in the 4-DMABN spectrum, at 136.4 cm^{-1} from the origin, is the third member in the progression. In the DMA spectrum, the third peak in the progression is also the most intense, whereas for 3-DMABN and 4-CF_3-DMA the fourth member of the progression has the greatest intensity. The spacings observed here are very close to those observed in the far-infrared spectrum of ground state DMA[19] which are assigned to the dimethylamino rotation about the C–N bond. In analogy to the ground state assignment,[18] we assign this progression to the dimethylamino twist.

The calculated values corresponding to the best fit of the data for the torsional motion about the C–N bond, i.e., the twist, are listed in Table II. The potential parameters V_2, V_4, and B are quite similar for DMA and 4-DMABN.

The doublet in the 4-DMABN spectrum near 115 cm^{-1} (112 and 118 cm^{-1}) and the doublet near 195 cm^{-1} (191 and 198 cm^{-1}) are not members of the above progression and are assigned to the inversion motion. In the DMA spectrum, both sets of features for the inversion motion are also present, near 105 and 197 cm^{-1}. The doublet nature of these peaks is what would be expected from the splitting which

TABLE II. Calculated and observed energy levels for the dimethylamino rotation in S_1 for 4-DMABN, DMA, 3-DMABN, and 4-CF_3-DMA (in cm^{-1}).

4-DMABN[a]		DMA[b]		3-DMABN[c]		4-CF_3-DMA[d]	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	0	0	0	0	0	0	0
75.3	70.8	75.5	70.1	75.4	71.0	79.4	75.3
136.3	143.2	136.4	141.6	146.4	143.8	151.9	153.6
176.6	172.0	172.0	171.9	184.9	184.7	208.5	211.4
227	219.9	212.0	217.2	214.2	220.9	251.8	238.0

[a] $V_2 = 175$, $V_4 = 525$, and $B = 0.564\ cm^{-1}$.
[b] $V_2 = 175$, $V_4 = 515$, and $B = 0.564\ cm^{-1}$.
[c] $V_2 = 188$, $V_4 = 525$, and $B = 0.564\ cm^{-1}$.
[d] $V_2 = 215$, $V_4 = 580$, and $B = 0.564\ cm^{-1}$.

occurs for energy levels which are below the barrier of a double well potential. The features associated with the inversion motion of the dimethylamino group for 3-DMABN and 4-CF_3-DMA are not as obvious but can be determined by comparison with the DMA and 4-DMABN spectra. The peak at 122.0 and 123.0 cm^{-1} for 3-DMABN and 4-CF_3-DMA, respectively, are assigned to the first transition for this inversion motion. These features are no longer doublets, however, indicating the barrier to inversion and perhaps the shape of the potential well are somewhat different in these latter systems.

The calculated energy levels for the inversion motion are given in Table III along with the experimentally measured values. The calculated and observed energy levels for this motion agree quite well for 3-DMABN and DMA. The agreement between theory and experiment is not nearly as good for 4-DMABN and 4-CF_3-DMA; however, the anharmonicity of this inversion motion is much greater for these para-substituted aromatics. The inclusion of an x^4 term in the potential would be necessary to describe the anharmonicity of this motion for 4-DMABN and 4-CF_3-DMA.

B. Franck–Condon calculations

The displacement in the dimethylamino twist is calculated to be the same in 4-DMABN and DMA. A value of $\sim 30°$ is derived from the Franck–Condon analysis of these two spectra for which the maximum intensity occurs at the third peak in the progression. The value of the twist angle upon excitation is slightly larger for 3-DMABN and 4-CF_3-DMA and is calculated to be $\sim 40°$. The maximum intensity occurs at the fourth peak position for these latter two molecules. The ground state of 4-DMABN is pseudoplanar with the nitrogen lone pair orbital nearly perpendicular to the plane of the aromatic π system.

TABLE III. Calculated and observed energy levels for the dimethylamino inversion in S_1 for 4-DMABN, DMA, 3-DMABN, and 4-CF_3-DMA (in cm^{-1}).

4-DMABN[a]		DMA[b]		3-DMABN[c]		4-CF_3-DMA[d]	
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
113.3	107.2	104.9	104.3	127.0	127.7	118.0	106.9
118	109.3	111.5	105.6	127.0	128.4	118.0	107.7
190	187.4	189.0	185.0	233.0	235.6	188.1	188.0
194	210.0	198.7	202.2	248.2	246.7	193.5	205.0

[a] $\rho = 0.65$, $\nu_0 = 105\ cm^{-1}$, and $b = 250\ cm^{-1}$.
[b] $\rho = 0.55$, $\nu_0 = 110\ cm^{-1}$, and $b = 255\ cm^{-1}$.
[c] $\rho = 0.95$, $\nu_0 = 100\ cm^{-1}$, and $b = 350\ cm^{-1}$.
[d] $\rho = 0.41$, $\nu_0 = 130\ cm^{-1}$, and $b = 260\ cm^{-1}$.

C. Analysis of the cluster spectra: 4-DMABN $(X)_1$, $X = CH_3CN$, $(CH_3)_2CO$, CH_2Cl_2, CH_4, and H_2O

The monosolvate clusters of 4-DMABN with acetonitrile and acetone exhibit two distinct regions in the TOFMS. Spectral features which are blue shifted with respect to those of the isolated 4-DMABN are sharp and exhibit structure which resembles the bare molecule. Table IV lists the most prominent features in the cluster spectra for this region, as well as those observed for methane and water. The assignment of these features in the cluster spectra can be readily made by direct comparison of the frequency and intensity of these peaks to those of the bare molecule. The Franck–Condon intensity profile for both cluster and bare molecule spectra is similar indicating a twist of $\sim 30°$ for the dimethylamino group: the peaks in the cluster spectra can be assigned to the dimethylamino group rotation about the C–N bond. The potential parameters for this motion in the cluster spectra are nearly identical to those of the bare molecule, suggesting that the solvent molecule in the cluster is not in close proximity to the dimethylamino group. In addition, Lennard-Jones potential energy calculations show that one of the coordination sites for solvent molecules is at the cyano group.

Consider now the more interesting region in the spectra of 4-DMABN clustered with CH_3CN, $(CH_3)_2CO$, and CH_2Cl_2: the one containing the broad red-shifted feature. The red shift for these clusters is proportional to the static dipole moment of the solvent. These spectra do not evidence the rotation and inversion motion of the previously discussed clusters. The solvent may now be coordinated to the other bonding sites (as suggested by the calculations) afforded by these molecules: the ring and the dimethylamino group. The ring binding site would probably tend to stabilize the CT state most effectively. The red-shifted CT-like cluster spectra can be associated with clusters for which polar aprotic solvent molecules bind to the 4-DMABN at the aromatic ring position rather than at the cyano group.

D. Relationship between TICT and S_1 twist

Since the equilibrium angle is displaced 30° in S_1 for 4-DMABN, the bare molecule itself would appear to be moving toward a TICT conformation, i.e., a full 90° twist, upon excitation. The same is true, however, for the other three molecules studied: DMA, 3-DMABN, and 4-CF_3-DMA. While solution phase emission studies for 4-CF_3-DMA have yet to be done, DMA and 3-DMABN in solution do not exhibit TICT behavior, i.e., dual fluorescence in polar solvents.[11] Since these molecules which do not exhibit TICT behavior are also twisted in S_1 at least as much as 4-DMABN, one must strongly question the relationship

TABLE IV. The rotational dimethylamino group progression for the various clusters of 4-DMABN with the indicated solvents and the 0^0_0 transition shift for the clusters with respect to the 4-DMABN bare molecule (in cm^{-1}).

	4-DMABN	$\cdot CH_4$	$\cdot H_2O$[a]	$\cdot H_2O$	$\cdot CH_3CN$	$\cdot (CH_3)_2CO$	Calculated[b]
Cluster 0^0_0 shift	0	−63	+14	+199	+252	+260	
	0	0	0	0	0	0	0
	75.3	74	74	78	71	76	70.8
	136.3	133	140	136	138	139	143.2
	176.6	173	180	175	179	178	172.0

[a] Coordination of the water solvent to the aromatic ring. In all other clusters, coordination of the solvent is calculated to be to the cyano group.

[b] $B = 0.564$, $V_2 = 175$, and $V_4 = 525\ \mathrm{cm}^{-1}$.

between the twist in S_1 and the TICT state mechanism: recall that the viscosity data upon which the original TICT mechanistic suggestion was based has been shown to be invalid.[5,6]

VI. CONCLUSIONS

Molecular jet spectroscopy has been used to determine potential parameters for the dimethylamino group motions in 4-DMABN and some of its chemical analogs. The rotation and inversion motion of the dimethylamino group dominate the spectrum of these molecules in the origin region. The potential parameters for the twist coordinate using a one-dimensional rotor analysis are calculated to be $B = 0.546$, $V_2 = 175$, $V_4 = 525\ \mathrm{cm}^{-1}$. A Franck–Condon analysis yields a displacement angle of 30° for the twist coordinate in S_1 for 4-DMABN. Potential parameters for the inversion motion are given in Table III.

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