van der Waals Complex and Solvatochromism Studies of Substituted Benzenes and Naphthalenes

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Laser induced fluorescence (LIF) and resonantly enhanced multiphoton ionization (REMPI) studies of van der Waals complexes of aniline and 4-aminobenzonitrile (4-ABN) with some polar solvents are reported. The 1+1 clusters of aniline with methanol, acetone, and water do not fluoresce. The REMPI spectrum of 1+1 cluster of aniline with methanol shows only a broad band, which indicates a large change in geometry between ground and excited states. For complexes of aniline with acetone or water, the 1+1 signals in the mass spectra are from the dissociation of larger clusters. The molecule 4-aminobenzonitrile forms fluorescent 1+1 clusters with methanol and acetonitrile which have emission spectra similar to that of uncomplexed 4-aminobenzonitrile. In the complexes, the broad background that appears in the emission spectrum occurs at lower excess energy. Solvatochromism studies of 4-fluorobenzonitrile (4-FBN), aniline, 4-ABN, 1-cyanonaphthalene (1-CNN), 1-aminonaphthalene (1-AMN), and 1-amino-4-cyanonaphthalene (*p*-AMCNN) are also reported. The solvatochromism study shows that those molecules giving rise to broad emission in the gas phase (aniline, 4-ABN, 1-AMN, and *p*-AMCNN) have a large solvatochromic shift, implying that in solution their emitting excited states have larger dipole moments than those of the ground states. The molecules with sharp gas-phase spectra, 4-FBN and 1-CNN, have little or no solvatochromic shift in solution.

1. Introduction

In our previous paper[1] (paper I), we reported laser induced fluorescence (LIF) studies of seven derivatives of substituted benzenes and naphthalenes. The molecules are 4-fluorobenzonitrile (4-FBN), *p*-dicyanobenzene (*p*-DCB), aniline, and 4-aminobenzonitrile (4-ABN) for the benzene system, and 1-cyanonaphthalene (1-CNN), 1-aminonaphthalene (1-AMN), and 1-amino-4-cyanonaphthalene (*p*-AMCNN) for the naphthalene system. The molecules are chosen to have one electron-donating or -withdrawing group attached to the ring (aniline, 1-AMN, and 1-CNN), two electron-withdrawing groups attached to the para position (4-FBN, *p*-DCB), or one donating and one withdrawing group attached to the para position (4-ABN, *p*-AMCNN).

Dual fluorescence had been observed at excess excitation energy in aniline, 4-ABN, 1-AMN, and *p*-AMCNN. The fluorescence contained a sharp component from a locally excited state (the L_b state) and an unstructured, red-shifted background. In aniline and 4-ABN, the broad background only appeared at excess excitation energy, while in 1-AMN and *p*-AMCNN it was observed from all vibronic levels including the origin. The broad emission was the only observable feature in emission spectra at high excess excitation energy. In paper I we proposed that the broad emission was due to emission from a second electronic excited state, perhaps with charge-transfer (CT) character, which was populated by internal conversion from the locally excited state. One possible such state was an L_a/CT state, a combination of the L_a state and the ring to constituent charge-transfer state.

In this paper we report the results of studies on van der Waals complexes of aniline and 4-ABN with polar solvents formed in a supersonic jet and of solvatochromism studies of all the substituted benzenes and naphthalenes mentioned above (except *p*-dicyanobenzene which has no dipole moment).

For van der Waals complexes with polar partners, the more polar L_a/CT state may be lower in energy, and the crossing between the L_b and the L_a/CT states may be lower in the complex than in the bare molecule. If this were the case, the broad, red-shifted background would be observed at lower excess energy. However, caution needs to be used in pursuing this argument. In the gas phase, it has been established that the binding energy of small clusters is not determined solely by the polarity but is also sensitive to the local environment of the binding site.[2,3]

In solution, a more polar electronic state is usually stabilized more than a less polar state by a polar solvent. As reported in paper I, the energy barrier between L_b and the second state was about 1800 cm^{-1} in aniline, 1500 cm^{-1} in 4-ABN, and 800−900 cm^{-1} in 1-AMN and *p*-AMCNN. If the second state is more polar, level inversion may occur in a polar solvent so that the lowest excited state is no longer the L_b state. A solvatochromism study allowed us to measure the differences between the ground- and excited-state dipole moments.

2. Experimental Section

The LIF study of van der Waals complexes uses the same apparatus as that used in paper I. In the resonantly enhanced multiphonon ionization (REMPI) experiment on aniline with polar solvents, one-color−two photon ionization spectra were recorded by skimming the free jet expansion and ionizing the resultant molecular beam with a dye laser. The photoions were analyzed by a Mclaren−Wiley[4] type time-of-flight mass spectrometer operated in the reflectron mode. Mass selective excitation spectra were recorded by scanning the excitation/ionization laser and monitoring the current produced by ions of a particular mass.

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In the solvatochromism study, steady-state fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer, Model LS50B, with a 2.5 nm excitation and emission bandpass. The absorption spectra were obtained with an HP 8453 UV/vis spectrometer. All solutes (4-FBN, aniline, 4-ABN, 1-CNN, 1-AMN, and *p*-AMCNN) and solvents (*n*-heptane, chloroform, *n*-butyl ether, diethyl ether, ethyl acetate, ethyl formate, *n*-butanol, glycerol, methanol, and acetonitrile) were purchased from Aldrich and were used without further purification. The concentration of the solution was 10^{-4} M.

3. Results and Discussion

3.1. van der Waals Complexes between Aniline and 4-ABN with Polar Solvents. *3.1.1. Aniline/Polar Solvents.* In LIF experiments, when a small amount of methanol, water, or acetone was introduced into a supersonic expansion of aniline, the fluorescence of the aniline monomer was decreased. However, no sharp features from the 1+1 complexes were observed. The single exception was the observation of a very weak peak about 300 cm^{-1} to the red of the aniline origin when methanol was used. The new peak was too weak to produce an observable dispersed fluorescence spectrum. Increasing the concentration of the solvent in the expansion resulted in the formation of larger complexes, observed as a decrease of intensity of the fluorescence excitation features of bare aniline and the rise of a broad background. Complexes of aniline and solvent molecules were formed in the expansion, but their fluorescence quantum yields were low, producing only weak and broad signals. van der Waals complexes between aniline with nonpolar solvents have been previously studied using LIF or REMPI/time-of-flight mass spectroscopy (TOFMS), but studies of complexes between aniline and more polar solvent molecules have been rare.[5]

We also used REMPI and mass spectroscopy to study the cluster formation between aniline and various polar solvents.

(a) Aniline with Methanol. Mass spectra are shown in Figure 1a,b. The intense signal at $m/e = 93$ is from the aniline monomer, and the signals at m/e values less than 93 are fragments of the aniline monomer. The small peak at $m/e = 125$ is assigned to the 1+1 complex of aniline and methanol because its intensity increases linearly as the concentration of the methanol in the mixture increases, and it is observable at low power density of the excitation laser. The peak at $m/e = 186$ is the aniline dimer, and the very weak peak at $m/e = 218$ is the complex of the aniline dimer and methanol. The peaks at higher m/e values are not assigned.

The REMPI spectrum of the $m/e = 125$ ions in the region to the red of the origin transition of aniline monomer is shown in Figure 1c. The spectrum is broad and structureless, similar to the spectrum in solution, and no other features appear at lower energy.

(b) Aniline with Acetone. The mass spectra of this system are shown in Figure 2a,b. The difference between the two spectra is the power density of the laser, the power density of (b) being 10 times higher than that of (a). In Figure 2a only $m/e = 93$ and lighter ions are observable, these being from the aniline monomer and its fragments. A very weak peak at $m/e = 186$ is due to the aniline dimer. In Figure 2b, at higher power density, some new peaks are observed. The new peaks with m/e less than 93 are extra fragments, the peak at $m/e = 151$ is the signal from the 1+1 complex of aniline and acetone, and the peak at $m/e = 209$ is the signal from the 1+2 complex of aniline and acetone. The fact that signals from the complex only appear at high power density indicates that they originate from dissociation
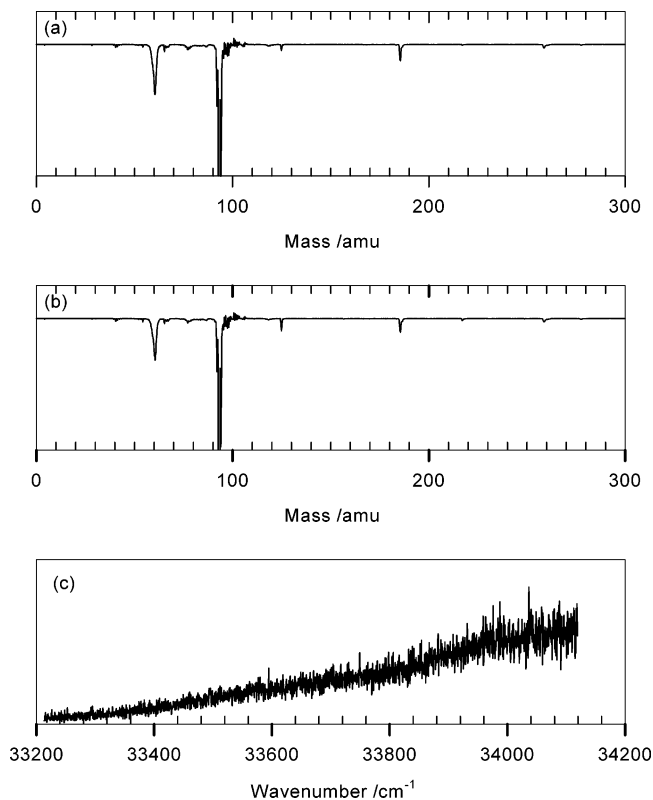

Figure 1. Mass and REMPI spectra of aniline/methanol. (a) Mass spectrum: the excitation laser wavelength is 2937 Å; the peak power density is ~2.5 MW/cm²; the relative ratio between aniline and methanol is 1:2. (b) Same as (a) except that the relative ratio between aniline and methanol is 1:4. (c) REMPI spectrum: monitoring $m/e = 125$ (93 + 32); the relative ratio between aniline and methanol is 1:4.

products of higher aniline—acetone complexes or from multiphoton processes.

The REMPI spectrum of the $m/e = 151$ ion to the red of the origin transition of the aniline monomer is shown in Figure 2c. Only a broad background is observable.

(c) Aniline with Water. The results of studies of complexes between aniline and water are similar to those of aniline with acetone and agree with the report of Nakanaga et al.[5b] The signal of the 1+1 complex is weak and is only observable at high concentration of water and high power density. The REMPI spectrum from m/e 111 (93 + 18) has only a broad feature similar to that in the spectrum of Figure 2c.

3.1.2. 4-ABN/Polar Solvents. Fluorescence studies of 4-ABN and its complexes with acetonitrile and methanol have been reported,[6] and our studies agree with those results. However, no vibronic assignment or dispersed fluorescence spectra were given in the previous study. The fluorescence excitation spectra of 4-ABN in the presence of methanol in a supersonic jet expansion are displayed in Figure 3. The fluorescence excitation spectra of uncomplexed 4-ABN are also shown for comparison. Unlike aniline, when methanol is added to the expansion several new sharp features appear between 0 and 300 cm^{-1} to the blue of the origin of bare 4-ABN. The concentration dependence of these signals indicates they are from 1+1 complexes of 4-ABN and methanol. The two strongest ones at +210 and +304 cm^{-1} are assigned as origin transitions of complexes with different conformations.[6] The proof lies in their dispersed fluorescence spectra shown in Figures 4a and 5a. The two spectra have a similar pattern with an energy shift of about 90 cm^{-1}, which is exactly the difference between the excitation energies. The conformer with the origin transition at +210 cm^{-1} is designated

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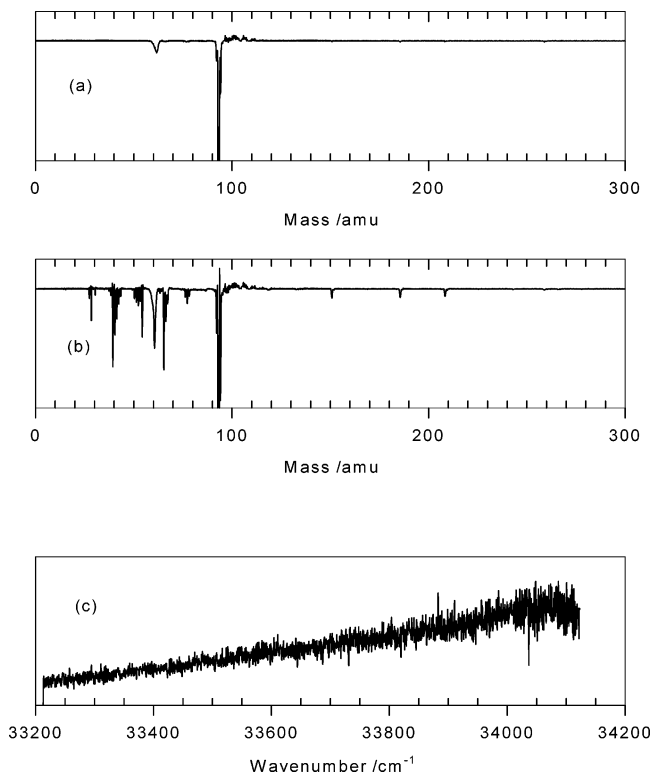

Figure 2. Mass and REMPI spectra of aniline/acetone. (a) Mass spectrum: the excitation laser wavelength is 2937 Å; the peak power density is ~2.5 MW/cm^2; the relative ratio between aniline and acetone is 1:8. (b) Same as (a) except that the peak power density is ~25 MW/cm^2. (c) REMPI spectrum: monitoring $m/e = 151$ (93 + 58).

Figure 3. Fluorescence excitation spectra of 4-ABN/methanol. (a) Spectrum of the 33 400−34 400 cm^{-1} region. The top trace is the fluorescence excitation spectrum of 4-ABN only; the lower trace is 4-ABN with methanol. The ratio between 4-ABN and methanol in the system is ~1:4. (b) Spectrum of the 34 200−35 000 cm^{-1} region. The sensitivity of the lower trace is twice that of (a). A and B indicate the conformers that give rise to the transition. The asterisks indicate the transitions from other unassigned conformers.

conformer A, and that at +304 cm^{-1} is designated conformer B. Other weak features in this energy region at +91, +215, +239, and +249 cm^{-1} and marked with an asterisk in Figure 3a were previously assigned as origin transitions of other conformers.[6] In the higher excitation energy region, the features arising from the 1+1 complexes are vibronic transitions of conformers A and B. Their assignments are given in Tables 1 and 2. The assignment is based on their dispersed fluorescence pattern, especially the position of the $\Delta\nu = 0$ band, and comparison with frequencies of the vibrational modes of bare 4-ABN. However, the assignment of the higher energy bands of the complexes is less certain because of the slight red shift or complete disappearance of the $\Delta\nu = 0$ band in the emission spectra and the complicated vibronic structure of bare 4-ABN in a similar energy region. No features of the complexes could be distinguished at more than 1500 cm^{-1} above the origin transition of bare 4-ABN.

The dispersed fluorescence spectra of complexes A and B are shown in Figures 4 and 5, respectively. At low excitation energies the spectra of both complexes are similar to those of bare 4-ABN and are dominated by sharp features arising from the progression of the 6a mode, as shown in spectra a and b in both Figures 4 and 5. However, at higher excitation energies, the two complexes behave differently. With more than +800 cm^{-1} excess energy, the sharp features are almost completely lost in the emission spectra of complex A, and a broad band is the most prominent feature [see Figure 4d]. In the emission spectra of complex B, as shown in (c)−(e) of Figure 5, the resonance features are broadened compared to those of bare 4-ABN at similar excess energy but can still be observed easily. It is apparent that the energy barrier to state crossing is lower in complex A at around +800 cm^{-1} and higher in complex B
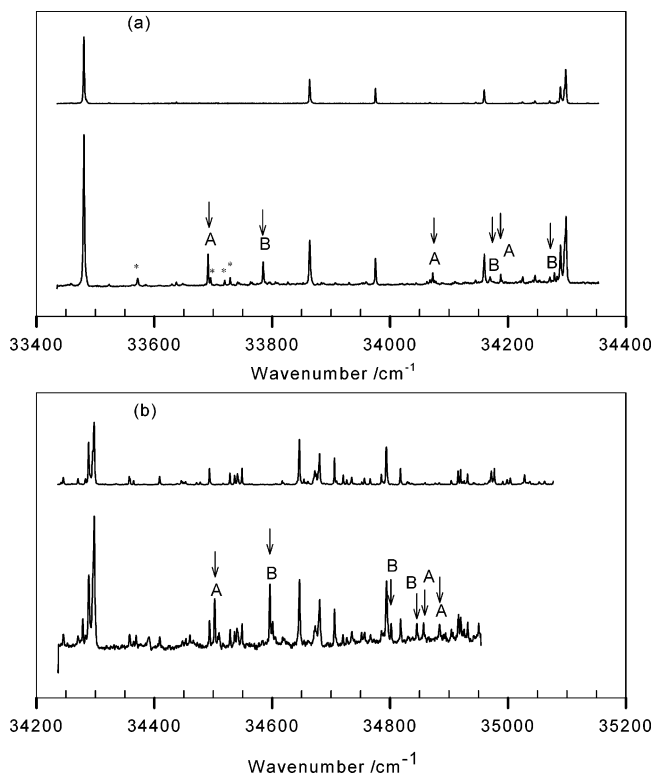
above +1060 cm^{-1}. Both are lower compared to +1500 cm^{-1} in bare 4-ABN.

Figure 6 displays the fluorescence excitation spectrum of 4-ABN in the presence of acetonitrile. Several new features originating from the 1+1 complex appear in the first 1500 cm^{-1} to the blue of the origin transition of 4-ABN. The peak at 33 717 cm^{-1} is assigned as the origin transition of the complex, 236 cm^{-1} above the origin transition of bare 4-ABN. The features at higher energies are assigned to vibronic excitations built on this origin. Unlike the case of methanol, no other conformers were found. The vibronic assignments of these features are given in Table 3. The +72 cm^{-1} is probably an intermolecular vibration. The +1061 cm^{-1} peak is not assigned due to lack of a corresponding transition in the bare 4-ABN, but a similar peak exists in complex B between 4-ABN and methanol (Table 2).

The dispersed fluorescence spectra of the acetonitrile complexes are shown in Figure 7. The emission spectra shown in Figure 7a−c from the origin, +72 cm^{-1}, and the 6a^1 mode at +383 cm^{-1} are similar to the corresponding ones of the bare 4-ABN and the 1+1 4-ABN + MeOH complexes. The emission from +72 cm^{-1} has the $\Delta\nu = 0$ band positioned at the origin excitation energy. This indicates that it is a vibronic transition built on that origin instead of the origin of another conformer. The appearance of a broad, red-shifted band and the loss of sharp progressions starting at +500 cm^{-1} excess energy is shown in Figure 7d. This is an indication of the onset of state mixing, the energy barrier in this complex being only about 500−600 cm^{-1}.

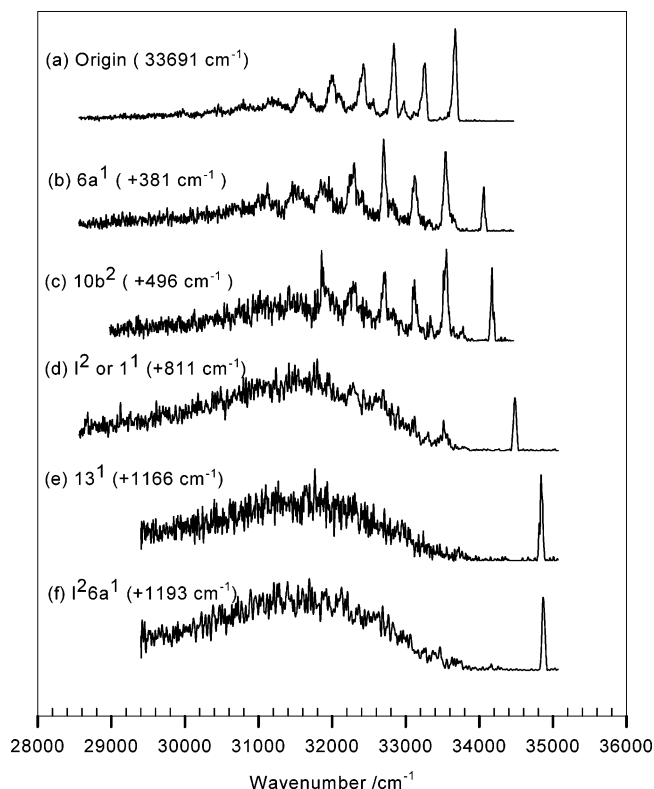*3.1.3. Discussion of van der Waals Complexes.* The lack of fluorescence emission from aniline 1+1 complexes with polar

Figure 4. Dispersed fluorescence spectra of 4-ABN/methanol, conformer A. Scattered light levels at excitation energies: (a) ~10%; (b) >50%; (c) >50%; (d)−(f) ~100%.

TABLE 1: Vibronic Assignment of Complex A, 4-ABN/Methanol

ν_{vac}/cm^{-1} (S$_1$)	$\Delta\nu/cm^{-1}$ from 0−0[a]	ν in 4-ABN	assignment
33 691	0		
34 072	+381	+383	6a^1
34 187	+496	+494	10b^2
34 502	+811	+808 or +817	I^2 or 1^1
34 857	+1166	+1165	13^1
34 884	+1193	+1191	I^{2}6a^1

[a] The origin of complex A, which is +210 cm^{-1} blue of the origin of bare 4-ABN.

TABLE 2: Vibronic Assignment of Complex B, 4-ABN/Methanol

ν_{vac}/cm^{-1} (S$_1$)	$\Delta\nu/cm^{-1}$ from 0−0[a]	ν in 4-ABN	assignment
33 785	0		
34 170	+385	+383	6a^1
34 279	+494	+494	10b^2
34 596	+811	+808 or +817	I^2 or 1^1
34 802	+1017	+1013	6a^{1}6b^1
34 846	+1061		

[a] The origin of complex B, which is +304 cm^{-1} blue of the origin of bare 4-ABN.

solvents is striking, especially compared to their fluorescence behavior in solution. Also, the broad background in the fluorescence excitation spectra at higher concentrations of polar solvent vapor indicates that larger complexes do emit. The paradox is why the small complexes do not emit while larger ones do. The REMPI studies of the system show some interesting aspects of the excited electronic states of the complexes.

The aniline−methanol 1+1 complex has a REMPI spectrum consisting of a broad absorption band starting at ~600 cm^{-1} to the red of the origin transition of the aniline monomer. The extensive broadening cannot be lifetime broadening since the
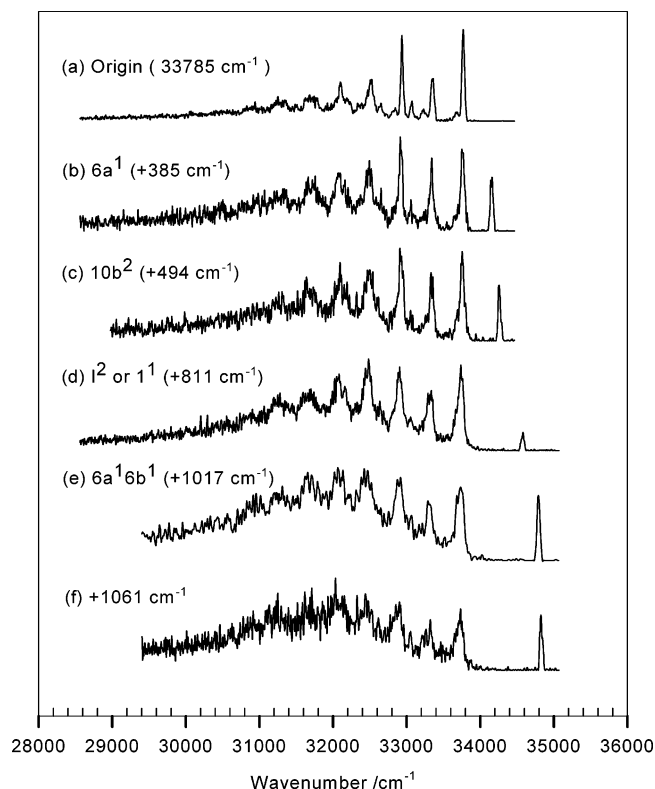

Figure 5. Dispersed fluorescence spectra of 4-ABN/methanol, conformer B. Scattered light levels at excitation energies: (a) ~10%; (b) >50%; (c) >50%; (d)−(f) ~100%.

lifetime required for such broadening would be in the femtosecond range and would be too fast to produce two-photon ionization signals. The broad absorption is probably due to a shift between the potential energy surfaces of the ground and excited electronic states in the 1+1 complex. The Franck−Condon allowed region from the ground-state zero-point level would be to the inner wall of the potential energy surface of the excited electronic state, producing a distribution of absorption over a broad energy region. This combined with a low fluorescence quantum yield would make the observation of the 1+1 complex signal in LIF very difficult.

The 1+1 complexes of aniline−acetone and aniline−water do not give rise to either an LIF or a REMPI spectrum. The 1+1 ion signal observed under these conditions originates from multiphoton dissociation of higher complexes. No ion signals directly arising from the 1+1 complexes are observed.[5]

The 1+1 complexes of 4-ABN and polar solvents have sharp fluorescence excitation spectra. In contrast to aniline, the solvent molecule can attach to the cyano end of 4-ABN, which is the conclusion of previous studies.[3,6] Acetonitrile complexes with 4-ABN show only one conformer in their fluorescence excitation spectra, while methanol shows several conformers. This is because of hydrogen bonding between the hydroxyl hydrogen in methanol and 4-ABN.

All the complexes have lower energy barriers for state crossing than that of bare 4-ABN. Because the S$_2$ state has a larger dipole moment than the S$_1$ (L$_b$) state, it will be stabilized more in the complexes. However, the binding energy of small clusters can also be sensitive to the local environment of the binding site.[2,3] For some binding sites the electronic transition between the ground state and S$_1$ (L$_b$) state in the complexes can be blue shifted even though the S$_1$ state has a large dipole moment. The reason for not observing any red-shifted features from the 1+1 complex is possibly that these types of conformers
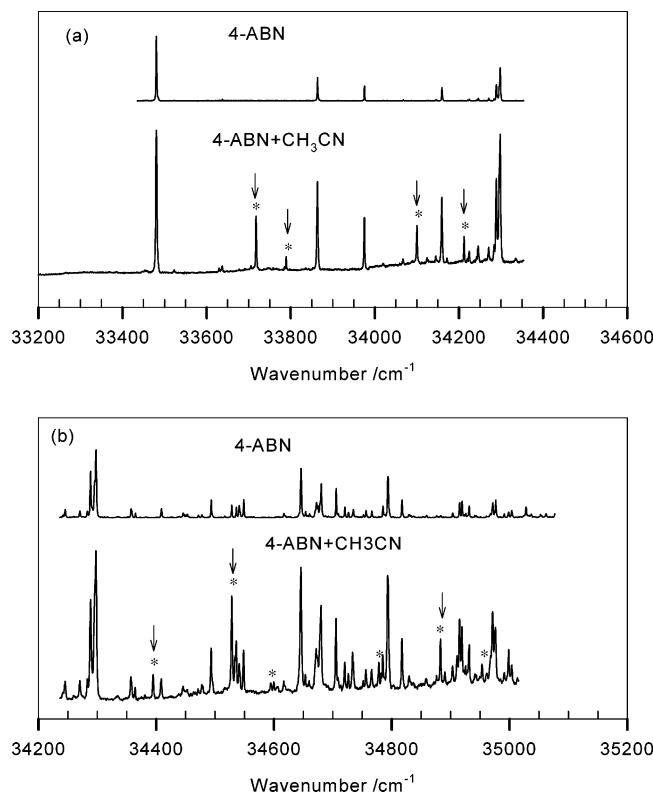
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Figure 6. Fluorescence excitation spectra of 4-ABN/acetonitrile. (a) Spectrum of the 33 200−34 400 cm^{-1} region. The top trace is the fluorescence excitation spectrum of 4-ABN only; the lower trace is 4-ABN with acetonitrile. The ratio between 4-ABN and acetonitrile in the system is ~1:4. (b) Spectrum of the 34 200−35 200 cm^{-1} region. The sensitivity of the lower trace is 1.5 times that of (a). The asterisks indicate the transitions from the 1+1 4-ABN−acetonitrile complex.

TABLE 3: Vibronic Assignment of 4-ABN/Acetonitrile

ν_{vac}/cm^{-1} (S$_1$)	$\Delta\nu$/cm^{-1} from 0−0^a	ν in 4-ABN	assignment
33 717	0		
33 789	+72		intermolecular
34 100	+383	+383	6a^1
34 212	+495	+494	10b^2
34 395	+678	+679	12^1
34 528	+811	+808 or +817	I^2 or 1^1
34 595	+877	+877	6a^{1}10b^2
34 778	+1061		
34 883	+1166	+1165	13^1
34 943	+1236	+1225	3^1

^{a} The origin of the complex, it is +236 cm^{-1} blue to the origin of bare 4-ABN.

do not emit as is the case for aniline−solvent complexes. Similar behavior was observed in the study of complexes between 4-DMABN (*N,N*-dimethylaminobenzonitrile) and polar solvents, where LIF only showed blue-shifted features.[2,7] REMPI spectra revealed red-shifted features, and this type of conformer is attributed to the binding of solvent molecules to the amino group of 4-DMABN.[3b]

3.2. Solvatochromism Study. *3.2.1. Theoretical Model.* Several theoretical models describing the effect of the solvent on electronic spectra have been developed over the past 40 years.[8] The model of Amos and Burrows[8a] has a minimal number of approximations and is easy to compare with experiment. We use this model to analyze solution spectra of several molecules related to the gas-phase complexes described above. This allows us to estimate their excited-state dipole moments.

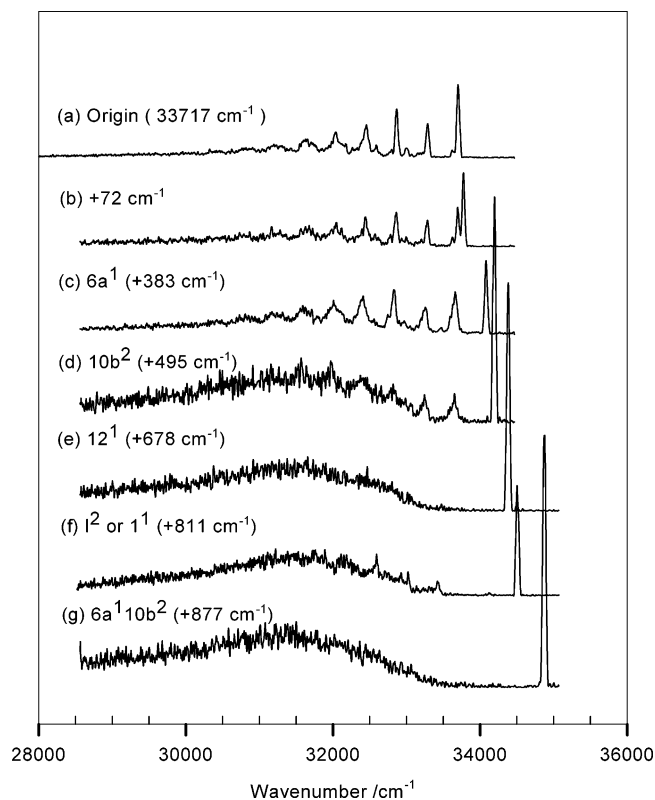We make the usual approximations made when using the

Figure 7. Dispersed fluorescence spectra of 4-ABN/acetonitrile. Scattered light levels at excitation energies: (a) ~10%; (b) ~20%; (c) ~20%; (d)−(g) ~100%.

Amos and Burrows model: we neglect the variance of refraction indexes of the solvents, the difference in polarizabilities of the solute molecule in the excited and ground states, and the difference in dispersion interaction between the excited and ground solute molecules with the solvents. All of these neglected terms are expected to be small. With these approximations, the solvent-dependent wavenumber shift, $\Delta\nu_f$ (the shift of the maximum of the emission spectrum in solution relative to that in the gas phase) will be proportional to the solvent polarity function $f(D,n)$:

$$hc\Delta\nu_f \propto \frac{-\boldsymbol{\mu}_e^u \cdot (\boldsymbol{\mu}_e^u - \boldsymbol{\mu}_g^u)}{a^3} f(D,n) \qquad (1)$$

with $f(D,n) = 2\{[(D-1)/(D+2)] - [(n^2-1)/(n^2+2)]\}$. Here $\boldsymbol{\mu}_g^u$ and $\boldsymbol{\mu}_e^u$ are the dipole moments for the solute molecule (superscript "u") in its ground or excited state (subscripts "g", "e"); D is the static dielectric constant of the solvent; n is the solvent refractive index extrapolated to zero frequency; a is the cavity radius in Onsager's theory of the reaction field. It is therefore meaningful to plot $\Delta\nu_f$ against $f(D,n)$. The plot should be a line with a slope proportional to $\boldsymbol{\mu}_e^u \cdot (\boldsymbol{\mu}_e^u - \boldsymbol{\mu}_g^u)$. If the dipole moment of the ground state is known, the dipole moment of the excited state can be calculated. If we assume the dipole moments of the ground and excited states are parallel, which is probably true for these substituted aromatic molecules, then the vector product in eq 1 becomes an arithmetic product.

3.2.2. Results and Discussion of the Solvatochromism Study. The emission spectra of 4-fluorobenzonitrile (4-FBN) and 1-amino-4-cyanonaphthalene (*p*-AMCNN) in various solvents of different $f(D,n)$ values are shown in Figure 8. Other molecules we studied fall into two classes typified by the spectra of 4-FBN and *p*-AMCNN. Molecules that give rise to broad background
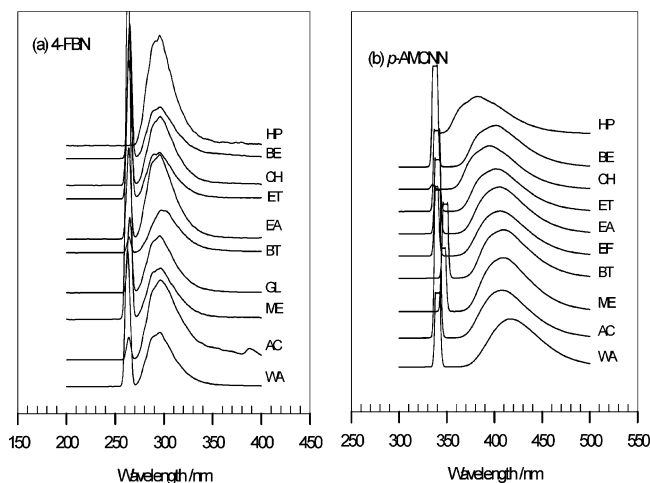
Figure 8. Fluorescence emission spectra of (a) 4-fluorobenzonitrile (4-FBN) and (b) 1-amino-4-cyanonaphthalene (*p*-AMCNN) in various solvents. The solvents are *n*-heptane (HP), *n*-butyl ether (BE), chloroform (CH), diethyl ether (ET), ethyl acetate (EA), ethyl formate (EF), butanol (BT), glycerol (GL), methanol (ME), acetonitrile (AC), and water (WA). The sharp bands at the blue end in both spectra are scattered light.

emission in a supersonic jet expansion such as aniline, 4-aminobenzonitrile (4-ABN), and 1-aminonaphthalene (1-AMN) have emission spectra in solution that are similar to that of *p*-AMCNN. All of these molecules have emission spectra that shift to the red as the polarity of the solvent increases. Molecules that have sharp emission in a supersonic jet such as 1-cyanonaphthalene (1-CNN) have emission spectra that are similar to that of 4-FBN. These spectra are almost invariant to the polarity of the solvent. The solvatochromism study shows that aniline, 4-ABN, 1-AMN, and *p*-AMCNN have much larger excited-state dipole moments than those of the ground states. The dipole moments in the ground and excited states are almost same in 4-FBN and 1-CNN.

Plots of $\Delta\nu_f$ against $f(D,n)$ are shown in Figure 9. In the calculation of $\Delta\nu_f = \nu_f - \nu_f^0$ the origin transitions of the supersonic jet spectra were used as ν_f^0 despite the fact that the emitting states in solution and in a supersonic expansion may not be same. The choice of ν_f^0 does not affect the slope of $\Delta\nu_f$ against $f(D,n)$ and will not affect the evaluation of the dipole moment of a molecule in its excited state.

From the slope of the linear regression of the plots and the known values of the ground-state dipole moments, the excited-state dipole moments can be calculated and are shown in Table 4. As seen in Figure 9, the fluorescence shifts of various solute molecules in acetonitrile are far off the linear regression line. The reason for this is unclear. In the estimation of the slopes of $\Delta\nu_f$ vs $f(D,n)$, the data points of molecules in acetonitrile were omitted. For *p*-AMCNN, no evaluations of the dipole moments are given since the value in the ground state is not reported in the literature.

In the calculation of $|\mu_e|$, the value of a, the cavity radius in Onsager's theory of the reaction field, was estimated as[8a]

$$a = r_\mu + \frac{1}{2}r_v \qquad (2)$$

where $r_{\mu(v)} = [3/(4\pi\rho_{\mu(v)})]^{1/3}$ is the radius of the solute (μ) or solvent (v) molecules, and $\rho = A(d/M)$ is the number density (A is Avogadro's number, d is the density, and M is the molecular weight of the solvent). The values of r_v range from 4 Å for butyl ether to 2 Å for water. The average value over
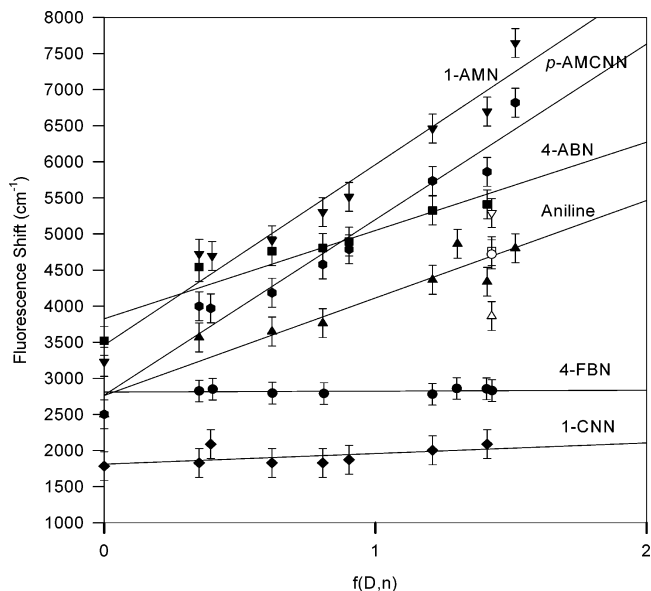

Figure 9. Plots of $\Delta\nu_f$ vs $f(D,n)$. ▼, 1-aminonaphthalene (1-AMN); ⬢, 1-amino-4-cyanonaphthalene (*p*-AMCNN); ■, 4-aminobenzonitrile (4-ABN); ▲, aniline; ●, 4-fluorobenzonitrile (4-FBN); ◆, 1-cyanonaphthalene. (1-CNN). The data points of 1-AMN, *p*-AMCNN, 4-ABN, and aniline in acetonitrile have the same symbol as each individual plot but with blank fill.

TABLE 4: Estimated Dipole Moments from Solvatochromism Studies

molecule	$|\mu_g|$ (D)	$[\mu_e\cdot(\mu_e - \mu_g)]/hca^3$ (cm^{-1})	a (Å)	$|\mu_e|$ (D)	$|\mu_e|$
4-FBN	2.7[a]	22	4	2.8	
aniline	1.49[b]	1350	4	5.0	
4-ABN	6.6[c]	1223	4	8.4	8.0[c]
	(5.96)[d]				8.3[c]
	(6.46)[d]				8.5[c]
1-CNN	3.99[e]	147	4	4.4	
1-AMN	1.5[f]	2501	4	6.5	6.7[g]
					6.1[g]
p-AMCNN		2432			

^{a} See ref 9. ^{b} See ref 10. ^{c} See ref 11. ^{d} See ref 12. ^{e} See ref 13. ^{f} See ref 14. ^{g} See ref 15.

the various solvents used in the experiments, 3.2 Å, is used in the estimation of a. However, the values of a determined in this way are larger than the values used in previous studies, such as 3.0−3.4 Å in the study of indoles by Lami et al.[16] and 3.0 Å in the study of aminonaphthalenes by Lim et al.[15] As a result, the excited-state dipole moments of 4-ABN and 1-AMN calculated using these larger a values are larger than the values measured or estimated in previous studies. If the value of a is taken to be 4 Å, the dipole moments are similar to those of the previous studies. The uncertainty in the value of a is a major uncertainty in the estimation of dipole moments using solvatochromism. The theoretical model is based on the reaction field theory of classical electrostatics, where a field arises from the interaction between a dipole and a homogeneous polarizable dielectric. Therefore, it cannot account for special solute−solvent interactions such as hydrogen bonding between the solute and solvent molecules. Despite the limitations of the model, a plot of $\Delta\nu_f$ against $f(D,n)$ is quasi-linear, and the estimates of the dipole moments in the excited state agree very well with the literature.

There is a consistency between the solution results and the supersonic jet results. Those molecules that showed broad red-shifted emission from the L$_a$/CT state (aniline, 4-ABN, 1-AMN, and *p*-AMCNN) had solution fluorescence spectra with a strong

solvent dependence. For these molecules, it is likely that in solution the L_a/CT state is the lowest excited state, and thus the emitting state. This would account for the larger dipole moment difference between the ground and the emitting states. Molecules in which emission is seen from a locally excited state in the supersonic expansion (4-FBN and 1-CNN) have similar dipole moments in the ground and excited states.

References and Notes

(1) Jiang, S.;Levy, D. H. *J. Phys. Chem. A* **2002**, *106*, 8590, and references therein.

(2) (a) Kobayashi, T.; Futakami, M.; Kajimoto, O. *Chem. Phys. Lett.* **1986**, *130*, 63. (b) Kobayashi, T.; Futakami, M.; Kajimoto, O. *Chem. Phys. Lett.* **1987**, *141*, 450. (c) Kajimoto, O.; Nayuki, T.; Koboyashi, T. *Chem. Phys. Lett.* **1993**, *209*, 357.

(3) (a) Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1988**, *88*, 871. (b) Grassian, V. H.; Warren, J. A.; Bernstein, E. R. *J. Chem. Phys.* **1989**, *90*, 3994.

(4) Wiley, W. C.; Mclaren, I. H. *Rev. Sci. Instrum.* **1955**, *26*, 1150.

(5) Aniline and water complexes had been studied recently using infrared depletion spectroscopy. See: (a) Nakanage, T.; Piracha, N. K.; Ito, F. *J. Phys. Chem. A* **2001**, *105*, 4211. (b) Takanaga, T.; Kawamata, K.; Ito, F. *Chem. Phys. Lett.* **1997**, *279*, 309.

(6) Gibson, E. M.; Jones, A. C.; Taylor, A. G.; Bouwman, W. G.; Phillips, D.; Sandell, J. *J. Phys. Chem.* **1988**, *92*, 5449.

(7) Peng, L. W.; Dantus, M.; Zewail, A. H.; Kemnitz, K.; Hicks, J. M.; Eisenthal, K. *J. Phys. Chem.* **1987**, *91*, 6162.

(8) (a) Amos, A. T.; Burrows, B. L. *Adv. Quantum Chem.* **1973**, *7*, 289. (b) Lippert, E. Z. *Elektrochem.* **1957**, *61*, 962. (c) Mataga, N.; Keifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 456. (d) Bakhshiev, N. G. *Opt. Spectrosc. (USSR)* **1962**, *13*, 24 and 104.

(9) Carsey, T. P.; Findley, G. L.; McGlynn, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 4502.

(10) Nagakura, S.; Baba, H. *J. Am. Chem. Soc.* **1952**, *74*, 5693.

(11) Schuddeboom, W.; Jonker, S. A.; Warman, J.; Leinhos, U.; Kuhnle, W.; Zachariasse, K. A. *J. Phys. Chem.* **1992**, *96*, 10809.

(12) Curran; Estok. *J. Am. Chem. Soc.* **1950**, *72*, 4575.

(13) Le Fèvre, R. J. W.; Sundaram, A. *J. Chem. Soc.* **1962**, 4756.

(14) (a) Cowley, E. G.; Partington, J. R. *J. Chem. Soc.* **1938**, 1598. (b) Richards, J. H.; Walker, S. *Tetrahedron.* **1964**, *20*, 841.

(15) Dresner, J.; Modiano, S. H.; Lim, E. C. *J. Phys. Chem.* **1992**, *96*, 4310.

(16) Lami, H.; Glasser, N. *J. Chem. Phys.* **1986**, *84*, 597.