J. Phys. Chem. A **2000,** *104,* 4943−4952

Spectroscopy of Hydrogen-Bonded Formanilide Clusters in a Supersonic Jet: Solvation of a Model Trans Amide

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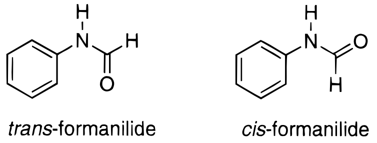
Received: December 20, 1999; In Final Form: March 17, 2000

The gas-phase structures of *trans*-formanilide (FA) clusters containing varying numbers of water and ammonia molecules have been investigated by resonant two-photon ionization spectroscopy in a supersonic jet expansion. A single structure is found for the 1:1 cluster of FA with ammonia in which the amide NH group functions as a hydrogen bond donor to the ammonia nitrogen. In contrast, vibronically resolved spectra reveal two distinct structures for the 1:1 cluster with water in which either the amide NH group functions as a hydrogen bond donor or the carbonyl oxygen functions as a hydrogen bond acceptor. The 1:1 clusters with both ammonia and water exhibit characteristic spectral shifts that depend on which amide site participates in the hydrogen bond. Three distinct types of 1:2 clusters with water have been found. Two of these can be viewed as water dimers interacting through a single hydrogen bond with either the amide NH group or the carbonyl oxygen. The third structure involves a hydrogen bond at each amide site to a separate water molecule. Ternary FA clusters containing one ammonia and one water molecule have also been investigated and found to be present in two distinct structural forms. Although each structure contains a hydrogen bond between the amide NH and one of the solvents, the structures differ with regard to which solvent serves as the acceptor of this hydrogen bond as well as in the role of the second solvent. Finally, clusters containing four water molecules have been identified, although in this case only a single cluster structure has been observed. This species is assigned to a structure containing a hydrogen-bonded chain of four water molecules forming a bridge between the NH and carbonyl oxygen binding sites on opposite sides of the trans amide. These experimental observations and structural assignment are supported by ab initio Hartree−Fock calculations.

Introduction

Hydrogen bonding plays a pivotal role in determining both the structure and activity of a wide range of biological systems.[1] Crucial to the secondary structure of proteins are the hydrogen bonds among the backbone amide groups. These hydrogen bonds form as the protein folds, with a concomitant loss of amide hydrogen bonds to the solvent. The energetics of this hydrogen bond exchange are of interest to better understand protein folding and stability.[2] In the current work, amide−water and amide−ammonia hydrogen bonds have been investigated in gas-phase clusters of a relatively simple model amide, *N*-phenylformamide or formanilide, with a particular focus on the nature of the interaction of a single amide with varying numbers of water and ammonia molecules.

The partial double-bond character of an amide C−N bond results in a nearly planar conformation of the functional group and a 15−20 kcal/mol barrier for rotation about this bond.[3] When the amide nitrogen is asymmetrically substituted, two distinct isomers are possible. For secondary amides with bulky substituents, as predominantly found in peptides and proteins, the trans isomer, in which the substituents on the carbon and nitrogen atoms adopt a trans orientation, is energetically favored. Our previous investigation of several simple *N*-phenylamides in the isolated environment of a supersonic jet expansion determined that even formanilide, with its small hydrogen atom substituent on the carbonyl group, is present in the vapor phase as the trans isomer in 94% abundance.[4] The trans isomer was additionally found to have a planar structure in both its ground and lowest-lying singlet excited states, in contrast to the cis isomer, where the phenyl ring was found rotated by approximately 40° out of the amide plane in the ground electronic state and coplanar with the amide group in the excited electronic state. The fact that the isomer populations observed in the gas phase differed significantly from the near equal abundances found in solution[5] motivated us to initiate studies on hydrogen-bonded solvent clusters of formanilide to better understand the origins of this effect.



Concurrently, Simons and co-workers also began an investigation of the hydrated clusters of formanilide.[6] In neither case have clusters of the less abundant cis isomer been observed using either single-color resonant two-photon ionization (R2PI) spectroscopy or fluorescence excitation spectroscopy. The significance of this finding lies in the fact that in the cis isomer the two hydrogen-bonding sites (amide proton and carbonyl oxygen) lie on the same side of the molecule and should permit a single water molecule to simultaneously form two strong hydrogen bonds in a cyclic arrangement, resulting in a very stable complex. These types of cyclic amide−water structures have been previously identified in 1:1 clusters of both formamide,[7] using Fourier transform microwave spectroscopy, and the cyclic cis amide 2-pyridone, using rotationally resolved

10.1021/jp994449u CCC: $19.00

fluorescence excitation spectroscopy[8] and infrared−ultraviolet double-resonance spectroscopy.[9] The reason for the failure to detect any hydrogen-bonded clusters of *cis*-formanilide is not entirely clear, although the possibility of a higher ionization potential for the cis isomer of the amide has been raised as a factor that could hinder its detection with single-color R2PI.[6]

In *trans*-formanilide (FA) the two hydrogen-bonding sites lie on opposite sides of the amide and thus prevent a single solvent molecule from interacting with both sites simultaneously. Thus two general types of 1:1 hydrogen-bonded water clusters should be possible in which the water acts as either the hydrogen bond donor or acceptor, whereas only a single 1:1 hydrogen-bonded ammonia cluster is expected in which ammonia accepts a hydrogen bond from the amide NH group. The recent study of Simons and co-workers reported spectroscopic evidence for two distinct 1:1 and two distinct 1:2 water clusters of FA and assigned specific structures to each on the basis of a combination of techniques including hole-burning spectroscopy, rotational contour analysis, and ab initio molecular orbital calculations.[6] A 1:4 (or possibly 1:5) water cluster was also reported, but no definitive structural assignment was made.

Our current work expands on the hydrated cluster work of Simons and co-workers[6] through observation and assignment of an additional 1:2 cluster and further through both stoichiometric and structural assignment of the previously observed resonance associated with a higher-order cluster. Key to these assignments are the fragmentation patterns observed after photoionization through the selected resonances as well as the spectral shifts of the electronic origins. The spectral shifts are found to be clear indicators of which amide group or groups participate in hydrogen bonding. Additionally, this work extends beyond that on purely hydrated clusters to include binary clusters containing one and two ammonia molecules as well as ternary clusters containing both one ammonia and one water molecule. The structural diversity of the ammonia clusters is expected to be considerably less than that of the water clusters because of the much greater propensity of ammonia to function as a hydrogen bond acceptor than as a hydrogen bond donor. With the ternary clusters a large number of structures are again feasible with relative stabilities that often depend on the relative strengths of solvent−solvent and solvent−amide hydrogen bonds. Assignment of the observed resonances to specific cluster structures provides insight on the relative energetics of these two types of interactions.

Experimental Section

The supersonic molecular beam apparatus used in this work has been described in detail elsewhere.[4] In brief, the seeded He carrier gas is expanded through a 1-mm pulsed nozzle and the resulting free expansion is skimmed upon entering a differentially pumped chamber containing a linear time-of-flight mass spectrometer. The resulting molecular beam is crossed orthogonally with the unfocused output of a frequency-doubled Nd:YAG pumped dye laser. Single-color R2PI occurs when the first photon is made resonant with a vibronic transition of the $S_1 \leftarrow S_0$ absorption band. The resulting ions are mass-selected and the desired ion signal is recorded as a function of laser wavelength. Fluorescein 548 was used in the dye laser to cover the spectral region of interest.

Formanilide was commercially available and used without further purification. To obtain sufficient vapor pressure, the solid sample and pulsed nozzle were heated to 100 °C. Water clusters were obtained by passing the carrier gas (typically at 3.4 atm stagnation pressure) through a mixing chamber partially filled with water at room temperature. The water content of the carrier gas is estimated to be less than 1%. Ammonia clusters were obtained in a similar manner by replacing the water in the mixing chamber with solid ammonium carbonate. The partial pressure of ammonia above the solid was sufficient to form ammonia clusters at concentrations yielding signal levels comparable with those of the water clusters. Even with only ammonium carbonate in the mixing chamber, it was still possible to observe both binary water clusters and ternary water−ammonia clusters of the amide.

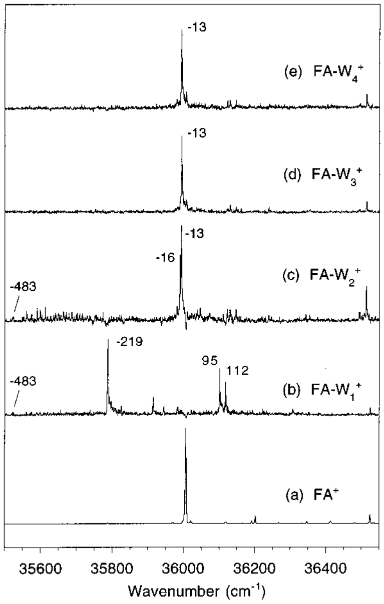


Figure 1. Mass-selected R2PI spectra of (a) FA and (b−e) its water clusters in a He supersonic jet expansion detected in the indicated mass channel. The FA origin is located at 36 006 cm^{-1}. Cluster origin shifts are given relative to that of the bare molecule.

Under the experimental conditions required to produce these water and ammonia clusters, some hydrolysis of formanilide occurred, resulting in the production of aniline as evidenced by the characteristic spectrum observed at its parent mass. This did not present significant interference to obtaining the cluster spectra due to the mass selectivity of the detection process, although some of the intense vibronic transitions of the much more volatile aniline did result in small dips in the spectra detected in the cluster mass channels.

All ab initio geometry optimizations and vibrational frequency calculations were performed at the Hartree−Fock (HF) level with 6-31G** basis sets using SPARTAN 4.0.[10]

Results and Analysis

R2PI Spectra of FA−Water Clusters. Mass-resolved, single-color R2PI spectra of FA and its clusters containing up to four water molecules are presented in Figure 1. Each spectrum was obtained under similar experimental conditions by monitoring the ionization signal resulting from ions having masses corresponding to the indicated species. The spectrum in Figure 1a was obtained by monitoring the 121-amu mass channel corresponding to unclustered FA ions. This spectrum is identical to that reported previously by Manea et al.,[4] and in this wavelength region all spectral features are associated with the trans isomer. A strong origin transition is found at 36 006 cm^{-1}, which is associated with only weak vibronic structure. In contrast, the origin of the cis isomer of formanilide is found at 34 914 cm^{-1} and displays an extended vibrational progression in a 76 cm^{-1} phenyl torsion mode.

With one exception the spectra of the water clusters of FA (Figure 1b−e) are identical to those presented previously by Simons and co-workers.[6] The spectrum obtained by monitoring the mass channel corresponding to the parent cluster ion containing a single water molecule, FA-W_1^+, shown in Figure 1b, contains three dominant features that were previously assigned to separate origin transitions shifted by −219, 95, and 112 cm^{-1} from the FA origin.[6] That these features were associated with distinct clusters was clearly shown by hole-burning spectroscopy and rotational contour analysis. Comparison of the observed rotational contours with those predicted from the structures obtained by ab initio geometry optimization also showed that the −219 and 112 cm^{-1} origins were associated with 1:1 water clusters in which the water molecule was bound at the NH and CO sites, respectively, and that the 95 cm^{-1} origin was associated with a 1:2 cluster in which the first water molecule was bound as a hydrogen bond donor to the carbonyl oxygen and the second water molecule donated a hydrogen bond to the first. This carbonyl-bound cluster undergoes very efficient fragmentation by loss of water after photoionization and hence appears exclusively in the FA-W_1^+ mass channel.

The spectrum obtained monitoring the FA-W_2^+ channel is shown in Figure 1c. Both the long progression of peaks originating −483 cm^{-1} relative to the FA origin and the higher wavenumber component of the doublet near 35 990 cm^{-1} were observed by Simons and co-workers.[6] The −483 cm^{-1} origin was assigned to another 1:2 cluster in which the first water molecule accepts a hydrogen bond from the NH group and the second water molecule accepts a hydrogen bond from the first. Associated with this origin are progressions in three vibrational modes with frequencies of 29.3, 37.7, and 51.2 cm^{-1} that were assigned to modes involving significant motion of at least one of the water molecules.[6] The −13 cm^{-1} shifted component of the doublet was assigned to a neutral cluster containing four or possibly five water molecules because the same peak also appears in spectra taken in both the FA-W_3^+ and FA-W_4^+ mass channels. Nearly all of the other weak spectral features appearing in these two higher mass channels are also identical and appear to be associated with several weakly Franck−Condon active modes with vibrational frequencies between 100 and 150 cm^{-1} and a slightly more active 532 cm^{-1} vibration that correlates with a 517 cm^{-1} mode in bare FA. Both the FA-W_4^+ and FA-W_3^+ as well as parts of the FA-W_2^+ spectra therefore appear to arise from a single species that fragments by loss of varying numbers of water molecules when ionized.

The −16 cm^{-1} shifted component of the doublet in the FA-W_2^+ channel was not previously observed. Figure 2 displays an expansion of the 35 990 cm^{-1} spectral region as detected in the FA-W_2^+, FA-W_3^+, and FA-W_4^+ mass channels. The −16 cm^{-1} peak is clearly seen to be present in only the FA-W_2^+ mass channel and therefore cannot originate from the same species responsible for the −13 cm^{-1} peak appearing in all three channels. Also in agreement with the findings of Simons and co-workers, no ions corresponding to masses greater than that of FA-W_4^+ were observed.[6]

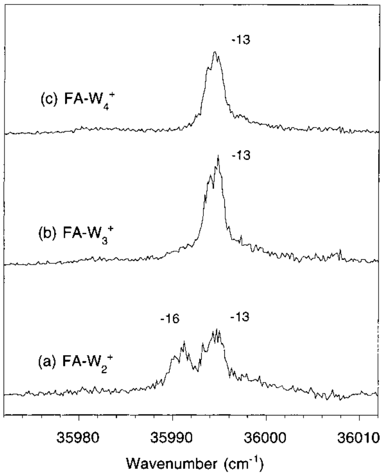


Figure 2. Comparison of R2PI spectra recorded in (a) FA-W_2^+, (b) FA-W_3^+, and (c) FA-W_4^+ mass channels in the region of the 35 990 and 35 993 cm^{-1} origins. Cluster origin shifts relative to that of the bare molecule are indicated.

TABLE 1: Relative Yields of Fragment Ions for Excitation at Different Cluster Origins and Assignments to Neutral Parent Clusters

excitation wavenumber[a] (cm^{-1})	FA^+	FA-W_1^+	FA-W_2^+	FA-W_3^+	FA-W_4^+	neutral parent cluster
−483	0.01	1.0	0.19			FA-W_2
−219	0.42	1.0				FA-W_1
−16	0.48[b]	0.65	1.0	0.70	0.21	FA-W_2
−13	0.28[b]	0.09	0.37	1.0	0.76	FA-W_4
95	0.04	1.0	0.01			FA-W_2
112	1.0	0.38				FA-W_1

[a] Excitation wavenumbers are given relative to the FA origin transition at 36 006 cm^{-1}. [b] A significant fraction of the FA^+ ions produced at these wavenumbers may arise from direct excitation of neutral FA rather than cluster fragmentation because of the small spectral shifts of these cluster resonances from the FA origin.

Fragmentation of FA−Water Cluster Ions. As an aid to assign the two origin transitions at −13 and −16 cm^{-1} to neutral clusters of specific composition, mass spectra were recorded at these two resonances as well as at all of the previously identified origins. Fragmentation of neutral clusters after ionization is well-known in the case of benzene−water and benzene−methanol clusters where loss of one or more solvent molecules occurs with near unit efficiency.[11−13] Because the extent of fragmentation after absorption of two photons resonant with the $S_1 \leftarrow S_0$ transition should vary with both the amount of excess energy deposited in the ion and the site at which the water molecules are bound, the fragmentation patterns observed with each resonance should be characteristic of the particular cluster structure. The relative abundances of the ions resulting from R2PI at each origin are summarized in Table 1.

Photoionization through the resonances assigned to 1:1 clusters, −219 and 112 cm^{-1}, produces very different fragmentation patterns, although in neither case is fragmentation complete. At −219 cm^{-1} the parent ion, FA-W_1^+, is the dominant species, whereas at 112 cm^{-1} FA^+ is predominant. Because an amide−water hydrogen bond is expected to be stronger than a pi-type hydrogen bond to benzene, the appearance of some parent ion is expected and therefore entirely consistent with the assignment of these resonances to 1:1 clusters. Excitation at both −483 and 95 cm^{-1} produces predominantly FA-W_1^+. At −483 cm^{-1} a significant fraction of parent FA-W_2^+ ions is also produced, whereas at 95 cm^{-1} less than 1% of the detected ions correspond to the parent. If this very small amount of FA-W_2^+ were overlooked, the temptation would be to assign this transition to FA-W_1. Such an assignment would then imply that essentially no fragmentation occurred after photoionization because FA^+ is produced in only a 4% relative yield. Therefore the fragmentation pattern associated with the 95 cm^{-1} transition is consistent with its assignment to a neutral 1:2 cluster whose parent ion undergoes very efficient fragmentation.

The two origins at −13 and −16 cm^{-1} also exhibit very different fragmentation patterns. In the FA-W$_2^+$ R2PI spectrum these features are considerably overlapped. As Figure 2 shows, the higher wavenumber component must correspond to a neutral cluster with at least four water molecules. The fragmentation pattern associated with this peak shows that FA-W$_3^+$ is produced in the highest yield, followed closely by FA-W$_4^+$, and that no ions of higher mass are evident. These observations suggest that the neutral parent species responsible for this resonance is indeed FA-W$_4$ and that approximately two-thirds of the parent ions fragment primarily with loss of one and two waters. It should be noted that the relative yield of FA$^+$ as shown in Table 1 is almost certainly too large because of contamination from the much more abundant neutral FA molecules that are photoionized through the wings of their strong origin transition 13 cm^{-1} to the blue. Assignment of this feature to a cluster containing more than four water molecules would make this the only cluster for which no parent ions were observed.

Excitation at −16 cm^{-1} produces FA-W$_2^+$ as the most abundant species but also results in production of some FA-W$_3^+$ and FA-W$_4^+$. However, only in the FA-W$_2^+$ mass channel does a distinct peak occur at this wavenumber. The most consistent explanation for this behavior is that the −16 cm^{-1} resonance occurs in FA-W$_2$ and that higher-order cluster ions arise from production and subsequent fragmentation of FA-W$_4^+$ via the overlapped FA-W$_4$ origin transition centered 3 cm^{-1} to the blue.

The structural assignments of Simons and co-workers[6] show that hydrogen bond donation by the aromatic amide results in a red-shifted origin transition (−218 cm^{-1} for FA-W$_1$ and −483 cm^{-1} for FA-W$_2$), whereas hydrogen bond acceptance induces a corresponding blue shift (112 cm^{-1} for FA-W$_1$ and 95 cm^{-1} for FA-W$_2$). These shifts suggest that electronic excitation results in an increase in the donating ability of the NH group and a decrease in the accepting ability of the carbonyl oxygen. This behavior is entirely consistent with ab initio configuration interaction calculations, which revealed that significant charge transfer from the amide nitrogen to the phenyl ring occurs in the excited electronic state.[6] The small spectral shifts, −13 and −16 cm^{-1}, associated with the 1:4 and 1:2 clusters can be accounted for by the competing effects when both the amide NH and CO groups are simultaneously involved in hydrogen bond formation to separate water molecules. Thus the FA-W$_2$ cluster exhibiting the −16 cm^{-1} spectral shift must have one water molecule bound at each of the amide sites. Similarly, the FA-W$_4$ species must have one water bound at the amide NH, one water bound at the carbonyl oxygen, and the third and fourth water molecules located relatively distant from the FA chromophore. This last feature is required to retain a similar spectral shift to that seen in the analogous FA-W$_2$ species.

R2PI Spectra of FA−Ammonia Clusters. Although the amide group in FA has two sites capable of participating in hydrogen bond formation, its interaction with ammonia is expected to be primarily as a hydrogen bond donor because of the much greater propensity for ammonia to serve as a hydrogen bond acceptor than as a donor. This point is clearly illustrated by the structures of the 2-pyridone−water and 2-pyridone−ammonia clusters deduced by Held and Pratt from rotationally resolved fluorescence excitation spectroscopy.[8,14] In these cyclic cis amides a single water molecule is found to interact through short hydrogen bonds of very similar length (1.96−1.97 Å) with both the NH and CO groups.[8] In contrast, the structure derived for the ammonia cluster of 2-pyridone exhibits a strong hydrogen bond with ammonia serving as the acceptor but only a weak interaction between one of the ammonia hydrogens and the carbonyl oxygen.[14] Thus the spectra of the ammonia clusters of FA are expected to be considerably simpler than those of the water clusters becaust of the presence of fewer stable species containing strong hydrogen bonds.

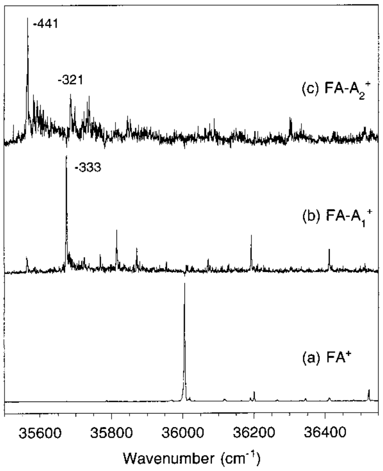


Figure 3. Mass-selected R2PI spectra of (a) FA and (b−c) its clusters with ammonia detected in the indicated mass channels. Cluster origin shifts are given relative to that of the bare molecule.

Mass-resolved, single-color R2PI spectra of FA and its clusters containing one and two ammonia molecules are presented in Figure 3. The spectrum obtained by monitoring the 138-amu mass channel is shown in Figure 3b. Here the detected species correspond to ions of FA clustered with a single ammonia molecule, FA-A$_1^+$. A strong origin transition is observed at 35 673 cm^{-1}, red-shifted 333 cm^{-1} relative to that of FA, and is assigned to the neutral 1:1 cluster FA-A$_1$. Several weaker vibronic features at 94, 140, 197, 519, and 737 cm^{-1} are also observed. The higher-frequency 197, 519, and 737 cm^{-1} peaks have counterparts in the spectrum of FA and must be associated with vibrations of the chromophore. The large red shift observed for this species is consistent with its assignment to a structure containing a hydrogen bond between the amide NH and the ammonia nitrogen. The additional 114 cm^{-1} red shift beyond that of the corresponding cluster containing a single water bound at the amide NH site arises from the increased basicity of ammonia, which provides even greater stability to the hydrogen bond in the excited state after charge reorganization.

To the red of the FA-A$_1$ origin an additional weak feature is observed that is assigned to a cluster containing two ammonia molecules that fragments by loss of ammonia after ionization. This is confirmed by the spectrum shown in Figure 3c, which was obtained by monitoring the FA-A$_2^+$ mass channel and shows a peak at 35 565 cm^{-1} coincident with the weak feature seen in the FA-A$_1^+$ channel. A mass spectrum recorded at this resonance reveals that 58% of the FA-A$_2^+$ ions fragment to produce FA-A$_1^+$ ions and that a very small fraction (<1%) fragment further to produce FA$^+$. In contrast, excitation resonant with the strong FA-A$_1$ origin produces primarily parent ions with only 12% fragmenting to produce FA$^+$. Mass spectra recorded at other resonances in the FA-A$_1^+$ mass channel spectrum show similar ratios for the production of FA-A$_1^+$ and FA$^+$. Thus there appears to be little evidence for the presence of more than one distinct 1:1 ammonia cluster.

The most intense peak in the spectrum recorded for the FA-A$_2^+$ mass channel at −441 cm^{-1} is assigned to the origin of a 1:2 cluster, FA-A$_2$. This transition exhibits an additional 108

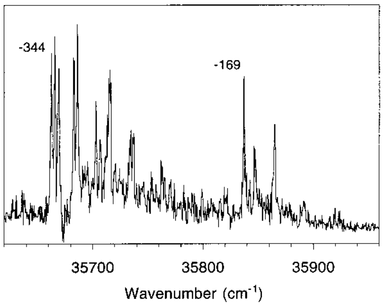


Figure 4. Mass-selected R2PI spectrum of the ternary cluster of FA containing one water and one ammonia molecule, FA-W_1A_1, detected in the parent ion mass channel of 156 amu. Cluster origin shifts are given relative to that of the bare molecule.

cm^{-1} red shift beyond the 333 cm^{-1} red shift seen in FA-A_1. A second distinct, but weaker, peak is also observed at -321 cm^{-1}, which corresponds to a 12 cm^{-1} blue shift from the FA-A_1 origin. With slight changes in the expansion conditions the relative height of this peak can be made considerably larger. Mass spectra reveal that photoionization at -321 cm^{-1} produces substantially more FA-A_1^+ than FA-A_2^+ (as opposed to the 58% yield of FA-A_2^+ at -441 cm^{-1}) and therefore suggest that this resonance be assigned to a second FA-A_2 cluster. The poorer signal-to-noise ratio obtained with this spectrum makes definitive assignment of some of the other features difficult and the presence of transitions in other FA-A_2 species or higher-order clusters that efficiently fragment cannot be ruled out. In fact, this type of fragmentation appears to be the source of much of the ion signal appearing in the spectral region between the two assigned origins. On the basis of their large red-shifts from the FA origin, both FA-A_2 species must possess a hydrogen bond between the amide NH group and an ammonia nitrogen.

R2PI Spectra of FA−Water−Ammonia Clusters. The spectrum obtained by monitoring the 156-amu mass channel, corresponding to ionic clusters containing one ammonia and one water, FA-$W_1A_1^+$, is shown in Figure 4. Two groups of peaks are found to originate with shifts of -344 and -169 cm^{-1} from the FA origin. The origin region of the red-most shifted group displays a triplet of peaks with a spacing of roughly 3 cm^{-1}. A doublet having similar spacing is found 20 cm^{-1} to the blue and appears to be associated with vibronic transitions within the same cluster. A second group of peaks is found 175 cm^{-1} to the blue. These have none of the multiplet structure seen in the first group and would therefore seem to be associated with a different cluster species. Based off of this second electronic origin are two weaker peaks that appear to be fundamental transitions of 10 and 28 cm^{-1} vibrational modes. A fairly weak overtone of the 28 cm^{-1} mode can also be discerned.

Mass spectra recorded for photoionization through the two origin transitions are shown in Figure 5. The two are quite similar and show a relatively weak peak corresponding to the parent cluster mass of 156 amu and a dominant peak at 138 amu corresponding to the production of FA-A_1^+ by loss of water. Only a very small amount of the fragmentation product resulting from loss of ammonia at 139 amu is seen. Additionally, a weak feature at the bare FA$^+$ mass is also seen in both spectra. No ions in the higher mass region corresponding to clusters containing three water or ammonia molecules (172−175 amu) are seen. This observation would appear to confirm that these two electronic origins do arise from neutral FA-W_1A_1 clusters. Despite having different structures that produce different spectral shifts, both parent ions undergo fairly efficient fragmentation to produce the same products. The relatively large red-shift of each of the cluster origins is consistent with both species having an amide NH hydrogen bond to one of the solvent molecules, although the solvent molecule accepting this hydrogen bond may differ in the two species. It might additionally be anticipated that the species with the less red-shifted origin has a second hydrogen bond in which the amide carbonyl oxygen serves as an acceptor because such interactions are seen to produce blue-shifted origins in both FA-W_1 and FA-W_2 clusters.

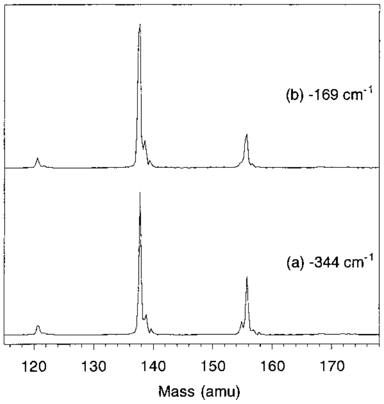


Figure 5. Time-of-flight mass spectrum for the FA-W_1A_1 cluster recorded for ionization through the indicated resonances associated with two different origin transitions. The dominant peak at 138 amu corresponds to a fragment produced by loss of water from the parent ion.

Discussion

Additional insights into the structures and properties of the hydrogen-bonded clusters of FA have been obtained from geometry optimizations and harmonic frequency calculations using ab initio HF theory. All calculations were carried out using 6-31G** basis sets. For the minimum energy structures containing one and two water molecules the effect of recalculating the electronic energies at the MP2 level while retaining the HF geometries was investigated and found to alter the relative energies by less than 0.7 kcal/mol. Differences of this magnitude would have little impact on the assignment of the observed spectral features to specific cluster structures and therefore were not carried out for the remainder of the clusters. The relative HF energies calculated for all cluster structures are summarized in Table 2, as are the energies corrected for zero-point vibration for the smaller clusters.

FA−Water Clusters. Ab initio HF geometry optimizations yield structures **1**−**4** in Figure 6 as stationary points on the FA-W_1 potential energy surface. Structures **1**−**3** correspond to local minima and were located previously by Simons and co-workers using HF theory with a 6-31G* basis set.[6] In structure **1** water serves as hydrogen bond acceptor from the NH group, whereas in structures **2** and **3** water serves as a hydrogen bond donor to the carbonyl oxygen. At the HF/6-31G** level of theory structure **1** is predicted to be 0.2 and 1.0 kcal/mol more stable than structures **2** and **3**, respectively, and 0.8 and 1.5 kcal/mol more stable when zero-point vibrational energies are included. At the MP2/6-31G*//HF/6-31G* level of theory similar relative stabilities were obtained, with **2** and **3** calculated to be 0.79 and 1.31 kcal/mol less stable, respectively, than **1** when zero-point vibrational energies were included.[6] Simons and co-workers assigned the -219 cm^{-1} shifted FA-W_1 transition to structure **1** and the 112 cm^{-1} shifted transition to structure **2**.[6] No evidence for a second FA-W_1 structure in which the water served as a hydrogen bond donor corresponding to structure **3** was observed. This would be expected if the barrier for

TABLE 2: Summary of Assignments of Cluster Structures to Observed Electronic Origins and Calculated Relative Energies

cluster	spectral shift (cm^{-1})	binding site	structure[a]	relative energy[b] (kcal/mol)	relative energy[b,c] (kcal/mol)
FA-W_1	−219	NH	1	0	0
	112	CO	2	0.2	0.8
		CO	3	1.0	1.5
		CO	4[d]	1.8	1.9
FA-W_2	−483	NH	5	0.9	0.5
	95	CO	6	0	0
	−16	NH and CO	7	2.9	1.8
FA-W_4		NH and CO	8	7.9	
	−13	NH and CO	9	0	
		CO	10	3.6	
FA-A_1	−333	NH	11	0	0
		CO	12	2.9	2.9
FA-A_2	−441	NH	13	0	0
	−321[e]	NH	see text	0.4	0.1
	−321[e]	NH and CO	14	1.2	0.6
FA-W_1A_1	−344	NH	15	0	
		CO	16	1.7	
	−169	NH and CO	17	1.8	

[a] Structures are displayed in Figures 6−10. [b] Ab initio HF geometry optimizations were carried out using 6-31G** basis sets. [c] Relative energies in this column have been corrected to include zero-point vibrational energies as calculated with 6-31G** basis sets. [d] Structure 4 is a transition state. [e] The assignment of this FA-A_2 transition is uncertain.

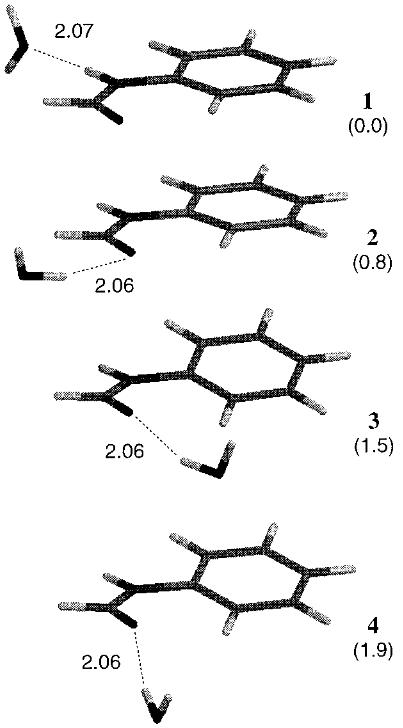


Figure 6. Structures resulting from ab initio HF geometry optimizations for FA-W_1. Hydrogen bond lengths (Å) and relative energies corrected for zero-point vibration (kcal/mol) are shown for each structure. Structure **4** was obtained by optimization of a transition state.

migration of water across the carbonyl group was quite low. Structure **4** in Figure 6 corresponds to the transition state, having a single imaginary vibrational frequency, for this migration and is calculated to lie 1.9 kcal/mol above the minimum energy structure, **1**, but only 0.5 kcal/mol above structure **3**. Thus the presence of only a single carbonyl-bound cluster is entirely consistent with these calculations. A similar barrier height of 0.9 kcal/mol has also been calculated for the analogous transition state in the cluster of formaldehyde−water.[15]

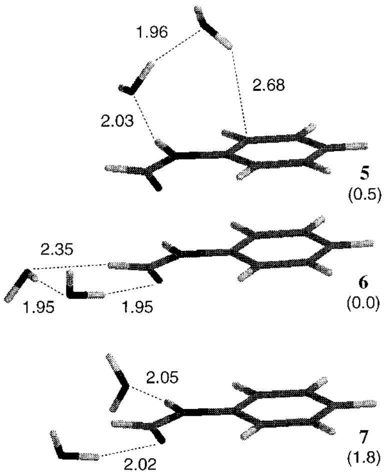


Figure 7. Structures resulting from ab initio HF geometry optimizations for FA-W_2. Hydrogen bond lengths and other relevant distances (Å) and relative energies corrected for zero-point vibration (kcal/mol) are shown for each structure.

Three selected energy-minimized structures for FA-W_2 are shown in Figure 7. Structures **5** and **6** can be viewed as water dimers interacting through one hydrogen bond with either the amide NH group or the carbonyl oxygen. The relative stabilities of these two species are reversed from what is calculated for the comparable FA-W_1 clusters where the NH-bound species is more stable. Additional interactions in these FA-W_2 clusters with either the pi electron system or the aldehyde proton appear to be present and may be responsible for the reversal of stabilities. The 95 cm^{-1} shifted transition in FA-W_2 was previously assigned to the carbonyl-bound structure, **6**, whereas the −483 cm^{-1} shifted transition was assigned to structure **5**.[6] In addition to a water−amide and water−water hydrogen bond, structure **5** also displays a short distance, 2.68 Å, between one of the water protons and the ortho carbon of the phenyl ring, indicative of a weak interaction with the pi electron system. As Simons and co-workers have pointed out, this additional interaction is responsible for the very large red-shift and extensive low-frequency vibronic activity seen in the electronic transition of this cluster.[6] The short separation between the water oxygen and aldehyde proton in **6** may also be indicative of a weak interaction. Recent MP2 calculations conducted on the clusters of formaldehyde with two water molecules having a similar structure indicate that this interaction is enhanced by the presence of the first carbonyl-bound water and that the electron density between the formaldehyde hydrogen and the second water oxygen is typical of that found in a conventional hydrogen bond.[16]

The third identified FA-W_2 isomer shows a small, −16 cm^{-1} shift in its electronic origin and is assigned to a structure where one water hydrogen bonds at each of the two amide sites. The ab initio optimized geometry of this complex is shown as structure **7** in Figure 7 and appears to be roughly a composite of the two single water clusters **1** and **2**. However, both of the hydrogen bond lengths in **7** are slightly shorter than their counterparts in **1** and **2**. Previous calculations of the total binding energy of **7** also gave a value that exceeds the sum of the binding energies in **1** and **2** by 1.1 kcal/mol.[6] These two observations are both indicative of a cooperative interaction between the two amide hydrogen-bonding sites. Similar magnitudes of the cooperative increase in the total hydrogen bond energy and decrease in the individual hydrogen bond lengths have also been calculated for the analogous cluster of *N*-methylacetamide with two water molecules.[17,18] As Figure 7 shows, an even larger cooperative decrease in the amide−water hydrogen bond lengths occurs when the second water molecule binds directly to the first, as in **5** and **6**.

At the HF/6-31G** level, structure **7** is calculated to lie 1.8 kcal/mol above the minimum energy FA-W_2 structure, **6**, when zero-point vibrational energies are included. This is lower than the value of 2.9 kcal/mol reported by Simons and co-workers at the MP2/6-31G*//HF/6-31G* level[6] and the 2.3 kcal/mol we find at the MP2/6-31G**//HF/6-31G** level. Neither value obtained with the larger basis set seems sufficiently high to rule out the presence of such a structure in the supersonic jet expansion. A number of other local minima were also located on the FA-W_2 potential surface by the previous calculations,[6] although most of these may be connected to more stable minima by low-energy transition states, as in FA-W_1, and would therefore not be observed in the expansion.

The resonance shifted by −13 cm^{-1} appearing in the FA-W_4^+, FA-W_3^+, and FA-W_2^+ mass channels is assigned to an FA-W_4 cluster. Although other resonances are seen in the FA-W_2^+ mass channel that can be assigned to FA-W_2 clusters, no additional distinct transitions are seen in the FA-W_3^+ mass channel that can be associated with a neutral FA-W_3 cluster. Careful scrutiny of the spectrum in Figure 2b does reveal a weak tail on the red side of the strong FA-W_4 origin transition but it is not clear if this arises from FA-W_3. In any case, the FA-W_4 cluster appears to be unusually stable, such that during cluster growth in the expansion the majority of any FA-W_3 that is formed is readily converted to FA-W_4 by addition of water. Further, this stability appears to be associated with only a single cluster structure despite the fact that a number of hydrogen-bonded structures could be produced having different numbers of hydrogen-bonded water molecules at each of the two amide binding sites.

Because the FA-W_4 origin transition is red-shifted only 13 cm^{-1} from that of FA and blue-shifted only 3 cm^{-1} from that of the FA-W_2 cluster having a hydrogen-bonded water molecule at both the amide NH and CO sites, it also is assigned to a structure where the both the amide proton and carbonyl oxygen participate in hydrogen bonds. The additional two water molecules must be hydrogen bonded to the water molecules interacting directly with the amide in a manner that locates them remotely to the phenyl chromophore.

A number of cluster geometries having these characteristics were investigated by ab initio geometry optimizations. The most stable is shown as structure **9** in Figure 8 and possesses a hydrogen-bonded bridge of four water molecules anchored at each end by a hydrogen bond to the amide. For comparison, structure **8**, which is essentially a composite of the two FA-W_2 structures **5** and **6,** contains two noninteracting water dimers hydrogen bonded to separate amide sites and is found as a local potential minimum lying 7.9 kcal/mol higher in energy. Of course, the composite structure **8** contains only four strong hydrogen bonds compared with the five that are found in the bridged structure **9**.

Beyond the number of hydrogen bonds, some insight into the increased stability of **9** can be obtained by comparing the calculated hydrogen bond lengths with those obtained for some of the other clusters. In **9** the C═O···H and N−H···O hydrogen bond lengths are 1.88 and 1.97 Å, respectively. These values correspond to decreases of 0.08 and 0.14 Å from the analogous bond lengths in the FA-W_2 cluster, **7**, which as mentioned previously are shorter than those present in the FA-W_1 clusters, **1** and **2**. Additionally, the hydrogen bond lengths between the four water molecules range from 1.86 to 1.88 Å, whereas in the two FA-W_2 clusters, **5** and **6**, the water−water hydrogen bond lengths are 1.95 to 1.96 Å. The pattern of hydrogen bonds in the bridged structure **9**, where each water serves as both a hydrogen bond donor and acceptor, leads to a cooperative enhancement of all four of the hydrogen bonds. An ab initio study on similar-sized water clusters was previously undertaken at the MP2 and MP4 levels to determine the magnitude of the cooperative or many-body terms to the total interaction energy.[19] In the most stable water pentamer, which has the same number and pattern of hydrogen bonds as **9**, the cooperative terms were found to account for 19.5% of the total interaction energy, with three-body interactions making the dominant (18.9%) contribution.

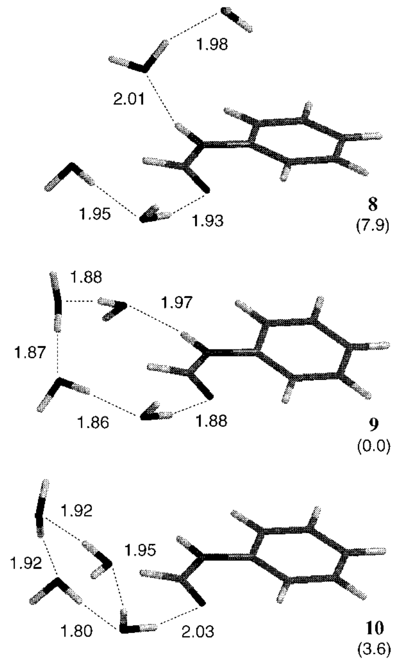


Figure 8. Structures resulting from ab initio HF geometry optimizations for FA-W_4. Hydrogen bond lengths (Å) and relative energies (kcal/mol) are shown for each structure.

Previous spectroscopic work on water clusters of benzene has focused on the structures of clusters containing up to eight water molecules.[12,20] The cluster containing four water molecules was deduced to contain a cyclic water tetramer that was able to serve as a proton donor to the pi electron cloud. In this case, the hydrocarbon solute did not appreciably alter the structure of the water tetramer from that calculated to be the lowest-energy structure of the isolated cluster[21] or from that observed with far-infrared vibration−rotation-tunneling spectroscopy.[22] If the FA-W_4 cluster contained a cyclic water tetramer, the interaction with the amide would most likely be as a hydrogen bond donor to the carbonyl oxygen. This interaction would be expected to blue shift the electronic origin, contrary to what is observed. Nevertheless, such a structure does contain five hydrogen bonds and would therefore be expected to be more stable than other noncyclic structures. Ab initio geometry optimizations were also carried out on a structure containing such a water tetramer built up by addition of two water molecules to the optimized FA-W_2 structure **6**. The resulting optimized structure **10** is shown in Figure 8. This local minimum lies 3.6 kcal/mol above that of **9**. The C═O···H hydrogen bond length is 0.15 Å longer in this structure than in **9**, as might be expected because the interacting water functions as a double

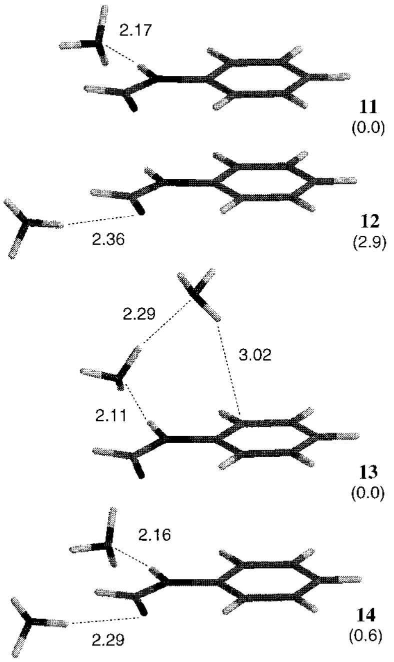


Figure 9. Structures resulting from ab initio HF geometry optimizations for FA-A$_1$ and FA-A$_2$. Hydrogen bond lengths and other relevant distances (Å) and relative energies corrected for zero-point vibration (kcal/mol) are shown for each structure.

hydrogen bond donor. Although structure **10** does appear to retain an interaction between the aldehyde hydrogen and a water oxygen, it lacks any cooperativity between the two amide sites. This and the requirement that one of the waters serve as a double donor appear to be responsible for the decreased stability of **10** relative to **9**.

Clusters containing chains of up to four water molecules have also been recently observed by Bach and Leutwyler.[23] In their work, the bifunctional hydrogen-bonding molecule 7-hydroxyquinoline was used as the chromophore. Structures containing chains of two, three, and four water molecules stretched between the hydroxy donor and the pyridine nitrogen acceptor were assigned on the basis of spectral shifts, ultraviolet hole-burning experiments, and comparison with ab initio HF calculations. In contrast to the case with FA-W$_4$, the bridged 7-hydroxyquinoline clusters exhibited very red-shifted origins (exceeding 1600 cm^{-1}), and two bridged and three nonbridged structures were identified for the cluster containing four water molecules.

FA−Ammonia Clusters. In comparison with water, ammonia is expected to function as a stronger hydrogen bond acceptor and a much weaker hydrogen bond donor. As evidence for the former, one can compare the calculated binding energy of the ammonia−water cluster, 6.28 kcal/mol,[24] with that of the water dimer, 5.0 kcal/mol,[25] and for the latter one can compare the calculated ammonia dimer binding energy of 2.81−2.98 kcal/mol[26,27] with that of the ammonia−water cluster.[24] Figure 9 displays two of the energy-minimized structures for FA-A$_1$ at the HF/6-31G** level of theory. As expected, the structure in which ammonia functions as a hydrogen bond acceptor of the amide NH, **11**, is calculated to lie 2.9 kcal/mol lower in energy than the structure in which the ammonia functions as a hydrogen bond donor to the carbonyl oxygen, **12**. Thus the assignment of a single origin transition in the spectrum of FA-A$_1$ is entirely consistent with the presence of only the more stable species in the expansion. The hydrogen bond length in **11** is calculated to be 2.17 Å and the N−H···N angle is calculated to be 172°. The orientation of the ammonia hydrogens is such to give the complex essentially C_s symmetry even though symmetry constraints were not applied during the optimization. Internal rotation of the ammonia about the hydrogen bond appears to occur over a very small barrier. Structures optimized under C_s symmetry constraints differing in their ammonia torsional angles by 60° were calculated to differ in energy by only 16 cm^{-1}.

As with the FA-W$_1$ cluster, in which water serves as a hydrogen bond acceptor, the observed red shift of the electronic origin is indicative of the increased stability of the amide N−H···N(O) hydrogen bond in the excited electronic state because of the charge reorganization associated with the electronic transition. The fact that the magnitude of the red shift in the ammonia cluster exceeds that of the water cluster gives further confirmation of the stronger hydrogen-bonding interaction associated with an ammonia acceptor than with a water acceptor. Similar results have also been reported for the spectral shifts observed for clusters of carbazole with water and ammonia.[28] Here the carbazole NH functions as a hydrogen bond donor to the heteroatom of the solvent, resulting in a 491 cm^{-1} red-shift for water and a 709 cm^{-1} red-shift for ammonia. The larger red shifts for the carbazole clusters indicates that a much larger enhancement of the hydrogen bond strength occurs in their S$_1$ states than in the S$_1$ states of the FA clusters.

Both origin transitions observed in FA-A$_2$ are red-shifted relative to FA and therefore must contain a hydrogen bond between the amide NH and one of the ammonia nitrogens. The two species differ in the location of the second ammonia molecule. The most red-shifted origin, −441 cm^{-1}, lies 108 cm^{-1} to the red of that of FA-A$_1$. In analogy to the FA-W$_2$ cluster with the −483 cm^{-1} origin, this FA-A$_2$ cluster is assigned to the energy-minimized structure **13** in Figure 9. Here the second ammonia accepts a hydrogen bond from the first and has one of its hydrogens located 3.02 Å above the ortho phenyl carbon. Two factors account for the increased red-shift in such a structure. First, the hydrogen bond between the two ammonias enhances the accepting ability of the first ammonia interacting with amide NH group, and second, the location of one of the hydrogens on the other ammonia is characteristic of a weak interaction with the pi electron system. This interaction must be considerably weaker than that present in the analogous water cluster, **5**, because ammonia is a much weaker donor than water, and is confirmed by the larger distance between the interacting proton and the phenyl ring.

Figure 9 also displays an alternative energy-minimized structure, **14**, in which the second ammonia functions as a hydrogen bond donor to the carbonyl oxygen. This structure is calculated to lie 0.6 kcal/mol higher in energy than structure **13** when zero-point vibrational energies are included. The additional hydrogen-bonding interaction with the carbonyl acceptor should result in a blue shift of the electronic origin relative to FA-A$_1$. Experimentally, a second FA-A$_2$ origin is found 12 cm^{-1} to the blue of the FA-A$_1$ origin that might be reasonably assigned to **14**. However, ab initio geometry optimizations also yield a third structure similar to **13** except that the second ammonia accepts a hydrogen bond from the N−H of the first ammonia that eclipses the amide's aldehyde hydrogen. This more extended structure is calculated to lie only 0.1 kcal/mol above **13** and exhibits no interaction between the second ammonia and the pi electron system. It would therefore be expected to exhibit a smaller red-shift than **13**, although the hydrogen bond between the first ammonia and the amide NH would still be enhanced by the presence of the ammonia−ammonia hydrogen bond, further red-shifting the electronic

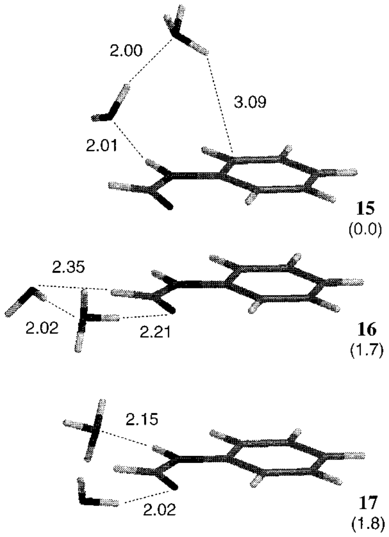


Figure 10. Structures resulting from ab initio HF geometry optimizations for FA-W_1A_1. Hydrogen bond lengths and other relevant distances (Å) and relative energies (kcal/mol) are shown for each structure.

transition from that of FA-A_1, **11**. Although this extended structure is calculated to be slightly more stable than **14**, a harmonic frequency analysis reveals a single imaginary frequency, characteristic of a first-order transition state. Coupled with the knowledge that rotation of a single ammonia about its hydrogen bond to the amide NH occurs essentially freely, it is not clear whether such an extended structure corresponds to a true local minimum or, if it does, whether the zero-point level lies below the barrier separating it from structure **13**. Thus it remains difficult to make a definitive assignment to the second FA-A_2 origin at -321 cm^{-1}.

FA−Ammonia−Water Clusters. Many more distinct stationary points are expected to appear on the potential energy surface of FA-W_1A_1 than on that of either FA-W_2 or FA-A_2 because corresponding to any identified structure is usually another that differs by interchange of the two distinct solvents. Figure 10 displays the minimum energy FA-W_1A_1 structure, **15**, and the two other structures, **16** and **17**, which lie within 2 kcal/mol of the minimum. All other located minima lie at least 1 kcal/mol above **16** and **17**. In structure **15** water serves as a hydrogen bond acceptor from the amide NH and simultaneously donates a hydrogen bond to ammonia. Geometry optimization of the related cluster having the positions of the ammonia and water solvents interchanged produces a local minimum lying 2.9 kcal/mol higher in energy. Such a structure contains a much weaker ammonia−water hydrogen bond in which ammonia serves as the donor. Structure **16** also contains an ammonia−water hydrogen bond having the preferred orientation as well as a second hydrogen bond in which ammonia functions as a donor to the carbonyl oxygen. This weaker interaction with the amide group lowers the stability of **16** relative to **15** by 1.7 kcal/mol. The analogous ternary cluster of formaldehyde has recently been studied theoretically and estimated to have a total binding energy of 10.1 kcal/mol,[16] which appears to also include a stabilizing interaction between the water oxygen and the aldehyde hydrogen, as evidenced by their rather small separation. Interchanging the solvent positions in **16** and reoptimizing the geometry destabilizes the cluster by 1.1 kcal/mol. The third relatively low-energy minimum corresponds to structure **17**, in which water serves as a hydrogen bond donor to the carbonyl oxygen and ammonia functions as a hydrogen bond acceptor from the amide NH. This structure, which lacks an ammonia−water hydrogen bond, is calculated to lie 1.8 kcal/mol above **15**, and interchanging the solvents results in a further 3.3 kcal/mol destabilization by requiring ammonia to serve as the hydrogen bond donor to the carbonyl oxygen.

Experimentally, Figure 4 reveals the presence of two distinct clusters that both have electronic transitions red-shifted from that of the bare molecule. On the basis of all the results from the binary clusters, this observation requires the presence of a hydrogen bond in which the amide NH group serves as a donor to the solvent and eliminates **16** from consideration for assignment to either of the two observed origins. Furthermore, the similarity of FA-W_1A_1 structure **16** to FA-W_2 structure **6** would lead one to expect similar fragmentation patterns after resonant photoionization. This particular FA-W_2 cluster, in which a water dimer serves as a single hydrogen bond donor to the carbonyl oxygen, undergoes very efficient ionic fragmentation such that the parent ion appears in only 1% abundance. Thus if an FA-W_1A_1 cluster having structure **16** were present in the expansion, its spectral signature would be expected to appear in one of the fragmentation channels (FA-A_1^+ or FA-W_1^+) and not in the channel corresponding to the parent mass.

The red-most shifted origin of FA-W_1A_1, -344 cm^{-1}, is most logically assigned to structure **15**. The magnitude of its red-shift is larger than that of the 1:1 water cluster hydrogen-bonded at the amide NH because of the enhancement of the amide−water hydrogen bond by the presence of the ammonia. Additionally, its red shift is not as large as that of the analogous 1:2 water cluster, **5**, in which the second water appears to interact via a pi-type hydrogen bond with phenyl group. Although structures **5** and **15** are generally similar, the analogous separation between the second solvent molecule's hydrogen and the ortho phenyl carbon increases from 2.68 to 3.02 Å on going from FA-W_2 to FA-W_1A_1. This is exactly what would be expected because water is a much stronger hydrogen bond donor than ammonia and the result of this weaker interaction with the pi system would be a decrease in the magnitude of the origin red-shift. Furthermore, the -344 cm^{-1} FA-W_1A_1 origin is associated with fairly strong low-frequency vibronic activity, much as is the origin of the analogous FA-W_2 cluster. The only FA-W_2 cluster origin displaying such vibronic activity is associated with the cluster having the pi-type hydrogen bond, which lends additional support of the -344 cm^{-1} FA-W_1A_1 origin to structure **15**.

Assignment of the second FA-W_1A_1 origin at -169 cm^{-1} to structure **17** is also consistent with the results obtained with the water and ammonia binary clusters. This FA-W_1A_1 resonance is blue-shifted 164 cm^{-1} from that of the FA-A_1 cluster, which also has a strong hydrogen bond between the amide NH and the ammonia. Therefore addition of a second hydrogen-bonding interaction between water and the carbonyl oxygen appears to be responsible for the blue shift. In the case of the binary water clusters, addition of a second water molecule having a hydrogen bond with the carbonyl oxygen to the 1:1 NH bound cluster produces a 203 cm^{-1} blue shift of the electronic origin.

Despite the assignment of the two FA-W_1A_1 origins to quite different cluster structures, the fragmentation patterns after photoionization are quite similar. As Figure 5 shows, both fragment by loss of one solvent to a fairly similar extent and in both cases the solvent lost is almost exclusively water. Whereas such an observation might be expected for structure **17**, where the water would be lost from the carbonyl group, the loss of water from structure **15** clearly requires extensive reorganization because the water is hydrogen bonded to both FA and ammonia. Ionization of FA is expected to increase the hydrogen bond donating ability of the amide NH group but decrease the accepting ability of the carbonyl group. Thus in both cases ionic fragmentation appears to proceed in a manner that produces the species expected to have the strongest hydrogen bond, FA-A_1^+.

Summary

The previous work of Simons and co-workers[6] on the hydrated clusters of *trans*-FA has been extended to include binary ammonia clusters as well as ternary ammonia−water clusters. In agreement with this earlier work, two distinct 1:1 water clusters are observed in which water interacts at either the amide NH or carbonyl sites. Besides the two earlier reported 1:2 clusters containing a water dimer singly hydrogen-bonded to one of the two amide sites, a third 1:2 cluster has also been observed in which each water forms a hydrogen bond with the two sites on opposite sides of the trans amide. Ab initio calculations on such a structure reveal evidence for a small degree of cooperativity between the two amide sites. The very small spectral shift of the electronic origin of this particular 1:2 cluster from that of the bare molecule (-16 cm^{-1}) arises from a cancellation of the perturbative effects associated with hydrogen bond donation and hydrogen bond acceptance by the aromatic amide.

A higher-order water cluster, also previously observed,[6] has been assigned to have a 1:4 stoichioimetry and contain a chain of four hydrogen-bonded water molecules bridging the two amide binding sites. Key to the structural assignment of this cluster is the small (3 cm^{-1}) spectral shift of its electronic origin from that of the 1:2 cluster with hydrogen bonds at both amide sites. The hydrogen-bonding pattern in this cyclic structure, with each water and the amide serving as both a donor and an acceptor, appears to lead to a large cooperative stabilization. Unlike the smaller hydrated clusters, the 1:4 species appears to be present only in one particularly stable structural form.

The 1:1 and 1:2 binary ammonia clusters are found to exhibit less structural diversity than do the binary water clusters because of the decreased ability of ammonia to serve as a hydrogen bond donor. Thus only a single 1:1 cluster is found in which ammonia accepts a hydrogen bond from the amide NH. Two distinct 1:2 clusters are found that both have one ammonia accepting a hydrogen bond from the amide but differ in the location of the second ammonia. In one of these, the second ammonia accepts a hydrogen bond from the first and interacts weakly with the phenyl pi electron system.

Ternary clusters containing both an ammonia and a water molecule have also been investigated. Despite the large number of local minima on the potential energy surface that arise from interchange of the two distinct solvent molecules, only three structures are calculated to lie within 2.7 kcal/mol of the global minimum and only two of these have been observed experimentally. In the most stable structure, the water and the ammonia form a strong hydrogen bond, with ammonia serving as the acceptor, and the water in turn accepts a hydrogen bond from the amide NH. In the other structure observed, the two solvent molecules interact independent of each other at the two distinct amide binding sites, with ammonia serving as an acceptor at the amide NH and water serving as a donor to the carbonyl oxygen.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (CHE-9727527) for this research.

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