

Photoionization and Vibrational Spectroscopy of the Aniline–Methanol Clusters

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Aniline–methanol mixed clusters are ionized by single photon vacuum ultraviolet (VUV, 118 nm) radiation with which absorption to an excited intermediate S_1 state is not required. Aniline ion (An^+), a series of $(An)_n^+-(CH_3OH)_m$ ($n = 1, 2$) cluster ions, and their hydrogenated cluster ions, $(An)_n^+-(CH_3OH)_mH$ ($n = 1, 2$) are observed by mass spectrometry. Infrared (IR) absorption spectra of aniline–methanol cluster cations and neutrals are measured through IR and VUV (118 nm) “ion dip” spectroscopy in the range 2500–4000 cm^{-1} . The observed mid-IR spectrum of the An^+-CH_3OH has two sharp absorption bands, at 3438 and 3668 cm^{-1} , which are assigned to the free NH stretch vibration of the aniline cation and the free OH stretch vibration of methanol, respectively. Calculations demonstrated that a change in the charges on the nitrogen atom of the amine group upon ionization of the neutral to the cluster cation alters the role of aniline from hydrogen acceptor to hydrogen donor in its interaction with methanol. Theoretical and experimental results suggest that a hydrogen bond forms between one of the H atoms of the aniline amine group and the lone pair of electrons of the methanol oxygen atom in the aniline–methanol cluster cation. Measured IR spectra and theoretical results for neutral clusters suggest that the H atom of the methanol OH moiety is bonded to the aniline amine group lone pair electrons for the neutral ground state aniline–methanol cluster.

I. Introduction

The supersonic expansion technique provides a pathway for the synthesis of molecular clusters in the gas phase. Combined with multiphoton ionization mass spectrometry and vibrational and electronic spectroscopy, this experimental technique has led to a deeper understanding of intra- and intermolecular interactions, and reactions such as hydrogen transfer.^{1,2} Clusters consisting of aromatic molecules and hydrogen-donating molecules, such as water or methanol, have been widely studied since they can serve as models of solvated biomolecules.³ Aniline is the simplest amine with an aromatic ring, and should be a generally good model for hydrogen bonding through an NH_2 or NH group. A number of spectroscopic studies on aniline and its clusters with various solvent systems have appeared.^{4–7}

In this paper, we present experimental and theoretical results on clusters consisting of aniline and methanol. A previous report reveals that the aniline–methanol complex ($An-Me$) has an $S_1 \leftarrow S_0$ resonance enhanced multiphoton ionization (REMPI) spectrum consisting of a broad absorption starting at ~ 600 cm^{-1} to the red of the origin transition of the aniline monomer.⁸ This broad absorption is due to the shift between the potential energy surfaces of the ground and excited electronic states of the complex. The Franck–Condon allowed region from the ground state zero-point level would be to the outer wall of the potential energy surface of the excited electronic state (the binding increases in the S_1 state with respect to that in the S_0 state), producing a distribution of absorption over a broad energy region of the $An-Me$ van der Waals modes. In the present research, this complex is ionized by a single photon of VUV (118 nm) radiation in a single step, for which absorption to the excited

intermediate S_1 state is not required: the relatively low vacuum ultraviolet (VUV, 118 nm, 10.5 eV) photon flux has sufficient photon energy to ionize the neutral complex by single photon ionization. The infrared (IR) absorption spectra of the neutral and cation of the aniline–methanol complex in the gas phase are measured by employing IR and VUV “ion dip” spectroscopy in the region 2500–4000 cm^{-1} . All IR spectra observed in the various aniline–(methanol)_n ($n = 1, 2$) mass channels are negative in nature and thus relate to the specific mass channel observed and not to larger mass cluster fragmentation. IR signals observed in the hydrogenated cluster mass channels (e.g., aniline⁺–(CH₃OH)H) are associated with the next larger aniline–methanol cluster (e.g., aniline–(CH₃OH)₂), in like manner. For these clusters, absorption of IR photons will cause fragmentation of the clusters, and thereby will cause a decrease in the ion signal for the parent cluster mass channel observed in the absence of IR radiation. The present technique of IR absorption plus single photon VUV ionization for detection bypasses the intermediate state employed for IR absorption plus REMPI,⁸ and enables even hydrogen bonded and strongly bound clusters to be studied. Calculation of the neutral and ionic $An-Me$ cluster structures enables these spectra to be assigned, thus verifying the nature and extent of the methanol–aromatic amine hydrogen bond and the $An-Me$ cluster's charge distribution.

II. Procedures

A. Experimental. The experimental apparatus used to record VUV time-of-flight (TOF) mass and IR spectra has been described in detail previously.⁹ Commercial samples (Aldrich) of all chemicals are used without additional purification. The aniline liquid is placed close to the valve body (Parker General Valve series 9) and is heated slightly to increase its vapor pressure. The sample and the entire nozzle body are heated to

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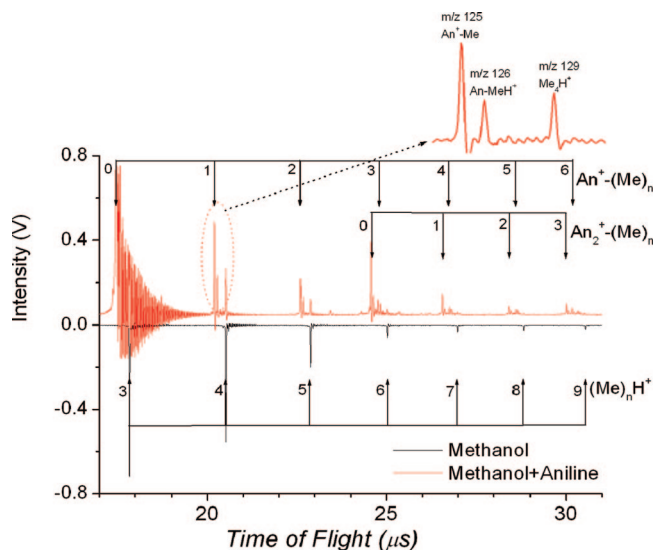


Figure 1. Mass spectra for An-Me clusters ionized by VUV (118 nm) light. The upper trace (in red) represents the mass spectrum of aniline-methanol mixed clusters and the lower trace represents the mass spectrum of the methanol clusters (in black). $\text{An}^+(\text{Me})_n$ and $(\text{An})_2^+(\text{Me})_n$ indicate sequences of cation clusters with one and two aniline molecules and n methanol molecules, respectively; $(\text{Me})_n\text{H}^+$ indicates sequences of hydrogenated methanol cluster cations.

a temperature not higher than 50 °C to avoid decomposition or reaction of the sample gas mixture before it is expanded into the vacuum. Gaseous methanol is seeded into a neon/helium gas mixture (70%/30%, total pressure of 2 atm) by passing the carrier gas above a methanol liquid surface. The final gaseous mixture is expanded into a high vacuum chamber by the pulsed supersonic nozzle with a pulse width of $\sim 150 \mu\text{s}$ duration. After passing through a skimmer, the generated molecular beam interacts with pulsed VUV and IR laser beams in the ionization region of a time-of-flight mass spectrometer. The generated ions are mass analyzed and detected by a pair of microchannel plates.

Generation of the VUV 118 nm light and IR laser light is similar to that described earlier.⁹ The 118 nm radiation is the ninth harmonic of the fundamental output of a Nd^{3+} /yttrium aluminum garnet (YAG) laser at 1064 nm. The 355 nm radiation (third harmonic) is focused into a cell with Xe/Ar at a ratio of 1:10 at ca. 200 Torr total pressure. A MgF_2 lens focuses the 118 nm light in the ionization region of the TOFMS and disperses the remaining 355 nm light. The IR radiation is generated by a Laser Vision Parametric Converter pumped by the fundamental of a seeded Nd^{3+} /YAG laser. Tunable IR light output in the range of 2500 to 4000 cm^{-1} has a pulse energy of 3–5 mJ/pulse and a bandwidth of $\sim 2 \text{ cm}^{-1}$.

B. Computational. To predict structures, energies, and vibrational frequencies of the neutral and cation An-Me cluster, DFT calculations are performed with the Gaussian 03W program package¹⁰ at the B3LYP/aug-cc-pVDZ level. Frequency calculations are used to determine the nature of stationary points found by a geometry optimization.

III. Results and Discussion

A. Mass Spectra and Structure Predictions by DFT Calculations. Figure 1 (the upper trace in red) presents the time-of-flight mass spectrum of $(\text{An})_n-(\text{CH}_3\text{OH})_m$ clusters generated through VUV (118 nm) single photon ionization. An^+ ions, $(\text{An})_n^+(\text{CH}_3\text{OH})_m$ ($n = 1, 2$), cluster ions, and their hydrogenated cluster ions, $(\text{An})_n^+(\text{CH}_3\text{OH})_m\text{H}$ ($n = 1, 2$) can be seen in the mass spectrum. The dominant cluster cation series

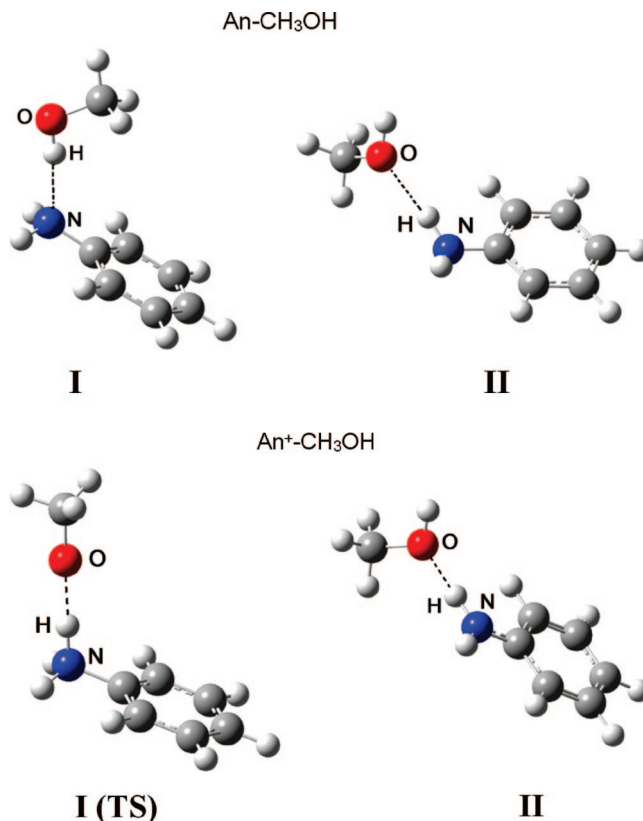


Figure 2. Structures of An- CH_3OH and $\text{An}^+-\text{CH}_3\text{OH}$ clusters optimized at the B3LYP/aug-cc-pVDZ level. Two stable isomers for the aniline-methanol 1:1 neutral complex are found; the structure (isomer I) with the hydrogen of the OH group of methanol bound to the nitrogen of the amine group of aniline is the most stable one. These structures for the 1:1 cluster differ in energy by ca. 180 cm^{-1} . Only one stable structure for the complex 1:1 cation is obtained, for which the oxygen of methanol is bonded to a hydrogen of the aniline amine group. The structure $\text{An}^+-\text{CH}_3\text{OH}$ I(TS) with the hydrogen of methanol bonded to the nitrogen of the amine group is a saddle point for the ion, not a minimum.

observed is the nonhydrogenated one. To distinguish and assign the features in the spectra, the mass spectrum of the pure methanol clusters (lower trace in black) is also presented in the figure. The series of hydrogenated methanol clusters can be assigned in both spectra. Since the VUV (10.5 eV) single photon energy is larger than the aniline molecule ionization energy (IE, $\sim 7.7 \text{ eV}$),¹¹ $(\text{An})_n^+(\text{CH}_3\text{OH})_m$ ($n = 1, 2$) cluster cations can be generated by either direct ionization of neutral clusters or photodissociative ionization of larger clusters, $(\text{An})_{n'}-(\text{CH}_3\text{OH})_{m'}$ ($n' > n$ and $m' > m$). Hydrogenated cluster ions are generated by a rearrangement reaction induced by the difference between vertical and adiabatic ionization energies. The results are consistent with recently published studies in which aniline-methanol cations are generated through two-photo absorption at 266 nm.¹²

DFT calculational results predict two isomers for the An- CH_3OH neutral complex shown in Figure 2. The structure (isomer I) with the hydrogen of the methanol OH group bound to the nitrogen of the aniline amine group is the most stable one, while that (isomer II) with the oxygen of methanol bound to the hydrogen of the aniline amine group is the next most stable. Similar to aniline- H_2O clusters,¹³ isomers with methanol above the aromatic ring or attached to the hydrogen of the aniline aromatic ring are energetically less favorable.¹³ For the complex cation, two structures can be obtained from energy minimization calculations (see Figure 2); however, vibrational mode frequency calculational results reveal the structure,

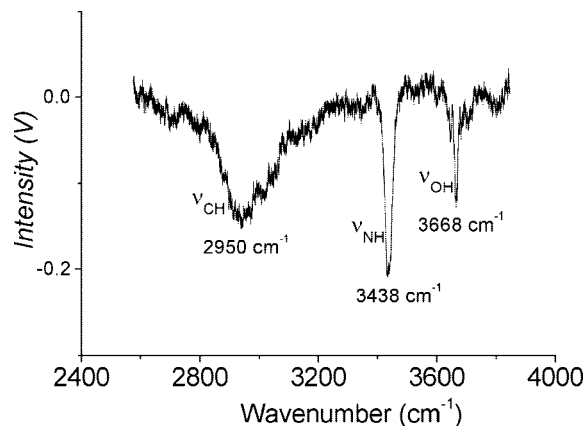


Figure 3. IR spectrum for the $\text{An}^+-\text{CH}_3\text{OH}$ complex, observed at the $\text{An}^+-\text{CH}_3\text{OH}$ mass channel, m/z 125. The features at 3438 and 3668 cm^{-1} are assigned to the free NH stretching vibration of the aniline molecule and the free OH stretching vibration of methanol, respectively.

$\text{An}^+-\text{CH}_3\text{OH}$ I(TS), with the OH hydrogen of methanol bound to the nitrogen of the amine group (in which that hydrogen is close to the amine group), has three imaginary frequencies, which indicate that structure is a saddle point, not a minimum. Thus, the structure for the An^+-Me ion with the oxygen of methanol bound to the hydrogen of the amine group is the only stable structure. Structures of the larger neutral and cation clusters of aniline and methanol have been presented by Song and Park in their recent publication.¹² Our calculations for the one-to-one neutral and cation complexes agree with theirs.

B. IR Spectra of $\text{An}-\text{Me}$ Cluster Cations. The infrared spectra of cluster cations can be measured by using depletion of the cluster ion signal in the mass spectrum, due most likely to infrared multiphoton dissociation (IRMPD) following cluster cation generation by VUV (118 nm) single photon ionization of the neutral cluster. This technique has been applied previously to obtain the CH and OH vibrational spectra of the methanol clusters.¹² The infrared spectrum of the $\text{An}^+-\text{CH}_3\text{OH}$ cation can thereby be obtained in the region 2500–3800 cm^{-1} and is presented in Figure 3. These spectra indicate a decrease in the mass spectrum signal in the aniline $^+-\text{CH}_3\text{OH}$ mass channel upon IR absorption. If larger clusters, which have lower concentrations in the molecular beam, contributed to these spectra we would observe positive signals for the IR spectrum.^{14,15} Thus, while some fragmentation due to IR multiphoton absorption for the ion is possible, it apparently does not obscure the IR spectrum due to the anticipated aniline– CH_3OH cluster negative signal at mass channel 125 amu. Two sharp “ion dips” at 3438 and 3668 cm^{-1} and a broad dip at ~ 2950 cm^{-1} can be observed in the presented spectrum. Table 1 gives the summary of frequencies of observed absorption bands and assignments based on the calculational results. The fine structure observed in the 3668 cm^{-1} band may be due to water vapor remaining in the optical path.¹³ The sharp absorption band at 3668 cm^{-1} can be assigned to the OH stretching vibration of methanol in the cluster cation. The frequency shift of this band from that of neutral methanol is ca. -16 cm^{-1} .^{14,15} Methanol seems to be neutral in the 1:1 complex cation. If the cluster positive charge were located on methanol, the frequency of the OH stretching vibration would be lower than 3500 cm^{-1} ;¹⁶ thus, the frequency shift would be much larger than the value obtained in this study.

Only one sharp absorption band is observed in the NH aniline stretching vibration region. The absorption is at ca. 3438 cm^{-1} , which is about the average of the two stretching vibration

energies of the aniline monomer cation.¹⁷ The aniline monomer has two equivalent NH bonds, and the NH stretching vibrations for this moiety yield two vibrational modes, a symmetric (at ca. 3394 cm^{-1}) and an antisymmetric (at ca. 3488 cm^{-1}) stretch. If a bond forms between one of the two NH hydrogens of the amine group and the lone pair of electrons on the oxygen atom of methanol, this hydrogen-bonding interaction will cause a large red shift for one of the stretching modes of the NH_2 moiety. One of two NH modes described above will broaden and red shift in energy, and the NH stretching mode of the free NH bond will be observed near its original position (ca. 3440 cm^{-1}).¹³ The observed mode with energy at 3438 cm^{-1} is comparable to that obtained in the study of the aniline– H_2O complex cation.¹³ The stretching mode energy of the methanol oxygen bonded NH is probably shifted to the CH stretch region and this mode overlaps and interacts with the free CH stretching modes of aniline and methanol.^{13,18} The spectrum of Figure 3 shows an unresolved broadband from ca. 2600 to ca. 3350 cm^{-1} consistent with these interaction and mode coupling assumptions.¹⁸

Ab initio calculations at the B3LYP/aug-cc-pVDZ level of the Mulliken charges for the complex cation and neutral are shown in Figure 4. A negative (ca. $-0.3e$) charge is located on the neutral amine group nitrogen, while in the complex cation, this charge has changed to $+0.2e$. Therefore, in the neutral complex, the aniline is a hydrogen acceptor and the methanol is a hydrogen donor: the two molecules are then connected by an $\text{N}\cdots\text{H}-\text{O}$ hydrogen bond. On the other hand, for the cation, the amine group nitrogen atom is not a favorable hydrogen acceptor site for the methanol OH group, and as a result, the oxygen of methanol tends to be bonded to a hydrogen atom of the amine group ($\text{N}-\text{H}\cdots\text{O}$). The optimized structures and the predictions of the Mulliken charges on the complex support this analysis (see Figures 2 and 4).

C. IR Spectra of Neutral $\text{An}-\text{Me}$ Clusters. By using IR plus VUV nonresonant ionization and fragmentation detection spectroscopy, IR spectra of the series neutral clusters of alcohols,¹⁴ organic acids,⁹ and amino acids¹⁹ can be obtained by monitoring the signal intensities of related cations. Such IR spectra have provided structural information for their respective clusters. One fundamental common property these molecules have is that their vertical ionization energies (VIE) are close to the single photon VUV energy, i.e. 10.5 eV. If this were not the case, the cluster cations observed in mass spectra might not correlate to a single neutral precursor; assignment of the features in the IR spectrum, to specific cluster species and specific cluster and molecules, would then be less certain. Nonetheless, the most likely result even in this latter instance is that the photoionized electron removes photon energy in excess of the cluster or molecule VIE in the form of kinetic energy.²⁰

The IE of aniline is 7.72 eV.¹¹ For $(\text{An})_n-(\text{CH}_3\text{OH})_m$ clusters having lower ionization energy than the aniline monomer, the internal energies of $(\text{An})_n^+-\text{CH}_3\text{OH}_m$ cluster cations could be large enough to cause some fragmentation upon VUV (118 nm) single photon ionization of the neutral clusters. Moreover, neutral clusters tend to be less strongly bound than ionic ones and the IR energy adsorbed by them could result in more extensive fragmentation for neutral species than for the ionic ones. The IR spectra of neutral cluster species obtained by monitoring the An^+-Me cation mass channel at m/z 125 and the An^+-MeH cation mass channel at m/z 126 are presented in Figure 5. These spectra are most probably associated with aniline– $(\text{CH}_3\text{OH})_{1,2}$ neutral clusters, respectively, because they both represent respective intensity loss in their appropriate mass

TABLE 1: Observed and Calculated Vibrational Energies of the Aniline⁺-CH₃OH Cluster Cation and the Aniline-(CH₃OH)_n Neutral Clusters for n = 1, 2 (in cm⁻¹)

	obsd	calcd ^a	assignment
An-CH ₃ OH ⁺	unresolved, broadband, band center at 2950 cm ⁻¹	2923	CH sym stretch (ν_3) ¹² of methanol
		2949	bond NH stretch of aniline
		3005, 3028	CH antisym stretch (ν_2 and ν_9) ¹² of methanol
		3066, 3074, 3079, 3087, 3092	CH sym and antisym stretch of the aromatic ring of aniline
		3438	3444
3668	3659	free OH stretch of methanol	
An-CH ₃ OH	unresolved, broadband, band center at 3444 cm ⁻¹	3380, 3471	NH sym and antisym stretch of aniline
An-(CH ₃ OH) ₂	unresolved, broadband, band center at 3413 cm ⁻¹	3307, 3449	bonded OH stretch of methanol
		3350, 3424	NH sym and antisym stretch of aniline bonded OH stretch of methanol

^a Theory level B3LYP/aug-cc-pVDZ. A frequency factor of 0.96 is employed.

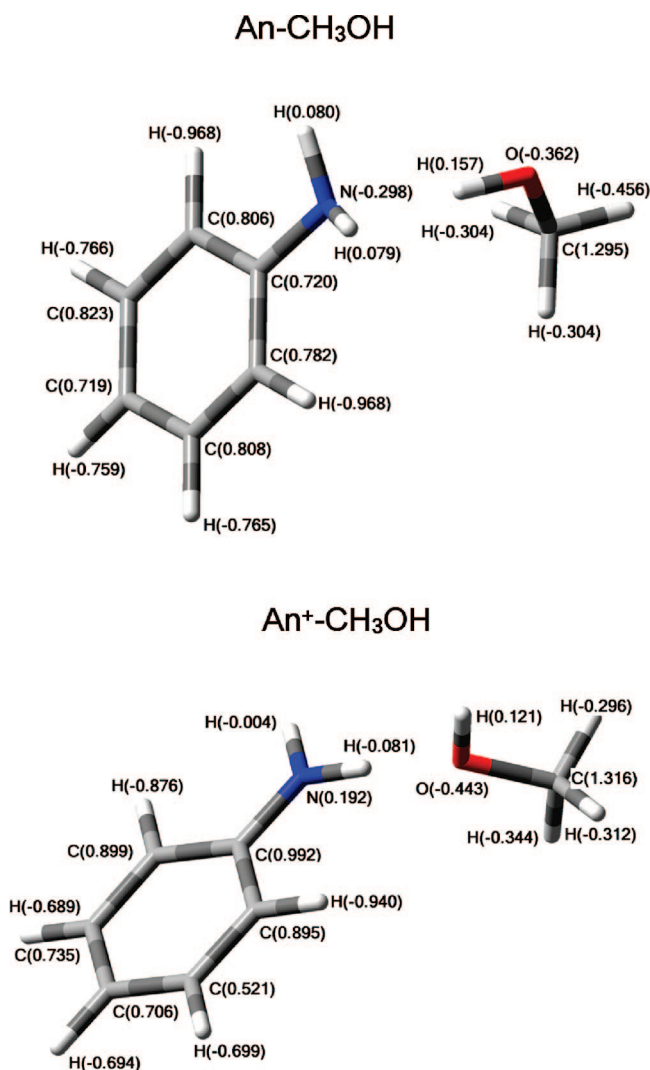


Figure 4. The Mulliken charges for the aniline-methanol neutral and cation complex, predicted by ab initio calculations at the B3LYP/aug-cc-pVDZ level. The change in the charges from ca. $-0.3e$ to $+0.2e$ on the nitrogen atom of the amine group in the complex between the neutral and cation clusters alters the role of the aniline from a hydrogen acceptor to a hydrogen donor in interaction between methanol and aniline.

channels. The upper trace (in red) in Figure 5 represents the IR spectrum measured in the An⁺-Me cation mass channel, while the lower trace (in black) represents the IR spectrum measured in the An⁺-MeH mass channel. One tentative conclusion can be reached from these results: the OH groups of methanol in these neutral clusters are hydrogen bonded, and hydrogen bonding networks are probably involved in the cluster struc-

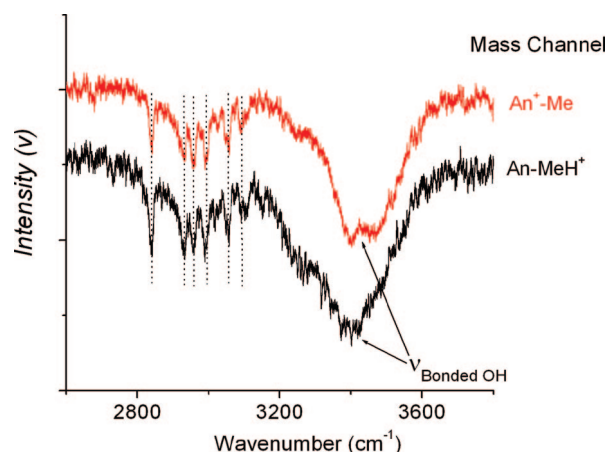


Figure 5. IR spectra for aniline-CH₃OH neutral clusters, observed at the An⁺-CH₃OH (m/z 125 amu) and An-CH₃OH₂⁺ (m/z 126 amu) mass channels. The absence of free OH stretching bands in these spectra indicates that the OH groups of methanol are hydrogen bonded; no shift for the CH features between the two traces suggests that the CH groups are unlikely involved in the interaction between molecules in these clusters.

tures.¹⁴ The vibrational mode energy predictions for An-(Me)_{1,2} are consistent with this assumption (see Table 1). The calculation results show that the IR spectrum measured at the An-Me⁺ (125 amu) mass channel is associated with the neutral complex An-Me while that detected at the An-MeH⁺ mass channel correlates to the neutral An-(Me)₂ cluster. Broad dips at ca. 3400 cm⁻¹ (3200 to 3600 cm⁻¹) are correlated with overlap of the hydrogen-bonded OH (N \cdots H-O) and free NH stretch modes.¹⁴ In the CH mode region (ca. 2900 cm⁻¹), features representing CH stretch modes in the two IR spectra correspond to each other very well; this similarity for the IR absorption detected in the two mass channels (for An-(Me)_{1,2}) suggests that the CH groups are not involved in the interaction between molecules in the clusters. Features with frequencies higher than ca. 3000 cm⁻¹ are probably associated with the aromatic CH stretch vibrations of the aniline molecule,²¹ while those lower than ca. 3000 cm⁻¹ are probably related to the CH stretch of methanol.¹⁴

As mentioned in the Introduction, the aniline-methanol 1:1 complex has a REMPI spectrum consisting of a broad, structureless absorption.⁸ Infrared depletion spectroscopy (IRDS) combined with spectroscopically selected REMPI of a particular cluster size is inapplicable in this instance. Our above results suggest that IR-VUV single photon, soft ionization spectroscopy is an excellent approach to the study of hydrogen-bonded clusters.^{9,22} Cluster fragmentation can be a problem for these systems and a tunable VUV source could be of some use in

this instance. Nonetheless, rearrangement reactions on the ion ground electronic state potential energy surface are probably the major initiator of such fragmentation reactions.^{19,21} The free electron can remove a substantial fraction of the excess cluster energy ($h\nu$ -VIE) in the form of kinetic energy, but (VIE-AIE + ΔH_{react}) will still remain in the cluster and can be employed for cluster fragmentation.

The broad absorption features found for the neutral clusters (Figure 5) could possibly obscure sharp features from minority structures in the expansion. The combined data from both theory and experiment make this possibility unlikely because of the unique structures calculated and the good agreement between the two data sets. Additionally, as pointed out above, many reasons can be suggested for the broad nature of the observed neutral cluster spectra.

IV. Conclusions

Aniline–methanol mixed clusters ionized by the single photon of VUV (118 nm) radiation in a single step have been detected by linear TOF mass spectrometry. Absorption to an excited intermediate state for 1+1 REMPI is not required. The results indicate that single photon ionization is an excellent technique to detect those solute–solvent systems for which a REMPI approach is not possible or inapplicable. The obtained vibrational spectrum of the An^+ - CH_3OH cation in the 2500–3800 cm^{-1} region shows two sharp features at 3438 and 3668 cm^{-1} , which are assigned to the free NH stretching vibration of the aniline cation and the free OH stretching vibration of methanol, respectively. Calculational results demonstrate that the change in the charge on the amine group nitrogen atom in the An–Me complex upon ionization alters the role of aniline in the complex from an acceptor to a donor in the hydrogen bonding interaction with methanol. Theoretical and experimental results suggest that a hydrogen bond is formed between one of the NH hydrogen atoms of aniline and a lone pair of electrons on the oxygen atom of methanol in the aniline–methanol complex cation. IR spectra of neutral clusters suggest that all the OH groups of methanol in these clusters are involved in hydrogen bonding.

These changes in IR spectra for the aniline– CH_3OH neutral and ionic clusters are generated by an ionization-induced cluster ion rearrangement reaction. The vertical–adiabatic ionization energy difference drives this reaction. This reaction and its energy release in the cluster generates the fragmentation $\text{aniline}^+(\text{CH}_3\text{OH})_n \rightarrow \text{aniline}^+(\text{CH}_3\text{OH})_{n-1}\text{H} + \text{CH}_3\text{O}^+$. We are presently calculating this potential energy surface and exploring possible conical intersections that facilitate such reactions.

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