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Investigation of the N−H Stretching Vibrations of the Aniline−Pyrrole Binary Complex and Its Cation by Infrared Depletion Spectroscopy

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The vibrational spectra of the aniline−pyrrole complex and the corresponding complex cation have been measured in the region of the NH stretching vibration using a mass-selective IR−UV double-resonance technique. In the spectrum of the neutral complex, there are three absorption bands at 3393, 3464, and 3496 cm^{-1}, which have been assigned to the symmetric and antisymmetric stretching vibrations of the aniline NH_2 group and the NH stretching vibration of pyrrole, respectively. The positions of the first two bands are close to those found in the aniline dimer and aniline−benzene complexes, suggesting that the neutral aniline−pyrrole complex has a similar parallel configuration. In the spectrum of the complex cation, three absorption bands have been observed at 3293, 3435, and 3498 cm^{-1}. In this case, the first two bands appeared at the same positions as those of the aniline−benzene cation, which indicates that there is a hydrogen bond between one of the NH bonds of the aniline cation and the π-electron system of pyrrole. These structures of the aniline−pyrrole complexes and its cation have been confirmed by ab initio MO calculations.

Introduction

Recently, the investigation of small clusters has attracted our attention. The reactions and properties of these clusters are defined by their degree of aggregation. They are expected to show a behavior that is very different from that found in the condensed phase and that seen in isolated atoms or molecules.[1−3] The ability to study reactions and properties of the clusters in a well-defined environment offers new insights into the intermolecular interactions acting between them. Furthermore, the possibility is given for the development of new functional materials which are quite different from bulk systems.

Vibrational spectroscopy offers important information about hydrogen-bond interactions. Recently, the hydrogen-bond interactions in several hydrated clusters have been investigated in the region of the OH stretching vibration by a new spectroscopic technique which utilizes an IR−UV double-resonance technique and REMPI mass spectrometry.[4,5] This technique was first applied to the benzene dimer by Page et al.[6] and has been applied to various clusters since it is a sensitive and mass-selective method.[7,8] The Raman spectra of clusters can also be measured using the stimulated Raman effect instead of infrared absorption.[9−16] As far as cationic species are concerned, a similar depletion technique has been applied to them which utilizes infrared predissociation or infrared multiphoton decomposition and mass spectrometry.[17−25]

Since the hydrogen-bond interaction through the NH bond plays an important role in various biological systems, it is necessary to investigate the interactions of the NH group with other functional groups in an isolated setting where the number of molecules involved can be limited. Aniline seems to be a good probe to investigate the hydrogen bonding of the NH bond in isolated clusters, because it is the simplest amine with an aromatic ring. This is underlined by the many studies of its complexes in supersonic jet expansions which have been reported in the literature.[26−32] Recently, we reported the hydrogen-bond interactions between the amino group in aniline and countermolecule,[33−35] and two different types of hydrogen-bond interactions were observed. One is the hydrogen bond with an aromatic ring (NH−π system), and the other is that with a nonbonding electron pair (NH−X system). It is well-known that the frequency shift of the NH stretching vibration of the hydrogen donor is correlated with pK_a values or proton affinities of the proton acceptor in NH−X systems. An interesting point is whether these relations can be applied to the NH−π-type hydrogen-bond interactions.

The principal interaction in the aniline−pyrrole complex is expected to be the NH−π-type hydrogen bond, since the pK_a value of pyrrole is negative[36] and the NH part of pyrrole may act as a very weak acid. The absorption intensity of the NH stretching bond of pyrrole is strong compared with that of aniline; one can expect to observe this band in the spectrum and gain further information about the structure of the complex. In this study, the infrared spectra of the NH stretching vibrations of the aniline−pyrrole complex and the aniline−pyrrole complex cation have been measured using infrared depletion spectroscopy. The structures of these complexes will be discussed, taking into account the infrared spectra and the results of ab intio MO calculations.

Experimental Section

Figure 1 shows a schematic diagram of the experimental setup.[37] The complexes formed in the molecular beam were ionized by one-color, two-photon absorption (REMPI) using the vibrationless $S_1 \leftarrow S_0$ transition of the aniline complex and detected after passing through a linear TOF mass spectrometer.

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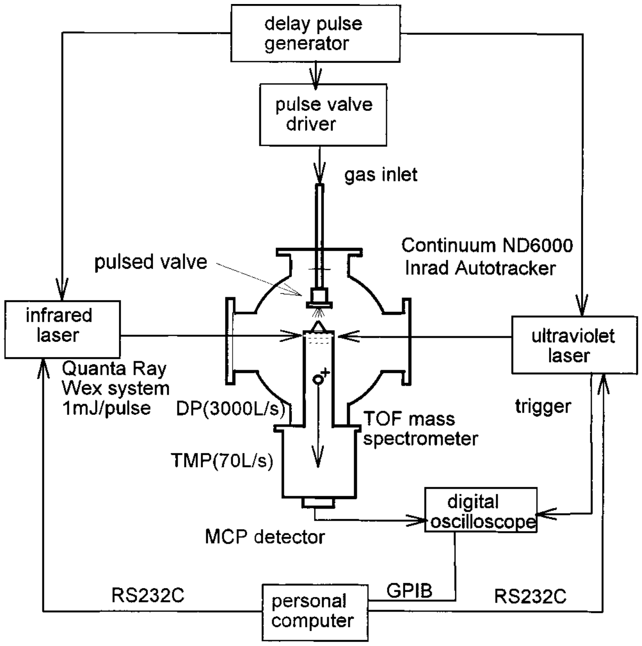

Figure 1. Schematic diagram of the experimental setup.

The ion signals were accumulated using a digital storage oscilloscope (Tectronics, TDS320) and transferred to a personal computer (Epson 486SE) through a GPIB interface. Mass resolution was about 200 at $m/e = 100$. The UV laser light was generated by frequency doubling of the output of a dye laser (Continuum ND6000) with a KDP crystal (Auto-tracker, Inrad Co). The pulse duration and the line width of this laser were 5 ns and 0.1 cm^{-1}, respectively. The incident power of the UV laser was reduced to less than a hundred microjoules/pulse with a glass filter to minimize the fragmentation of the aniline complexes.

The aniline−pyrrole complex was formed in a supersonic expansion of a gaseous mixture of aniline, pyrrole, and He at room temperature. The gas mixture was prepared by bubbling the He through a solution of pyrrole in aniline. The vapor pressure of the pyrrole was controlled by the concentration of pyrrole in the solution, which was usually less than 10%. If the concentration of pyrrole was higher than 20%, the UV excitation spectrum became featureless. The gas mixture was expanded through a pulsed valve (General Valve, $d = 0.8$ mm) which was operated at 10 Hz, and the pulse duration time was set to 250 μs. The backing pressure was set to 1.5 bar. The molecular beam was passed into the ionization region through a skimmer (1-mm diameter). The ions were separated in a linear TOF mass spectrometer and detected by a MCP detector.

The infrared spectra of the aniline−pyrrole complex and corresponding complex cation were measured by infrared depletion spectroscopy combined with REMPI-TOF mass spectrometry. Figure 2 shows the principles of the infrared depletion spectroscopy adopted in this experiment for the neutral complex (Figure 2a) and the complex cation (Figure 2b). The wavelength of the UV laser was fixed to the 0−0 band of the S_1-S_0 electronic transition of the complex in both cases. The ultraviolet and the infrared lasers were focused at the center of the ionization region of the TOF mass spectrometer using concave mirrors ($R = 700$ mm).

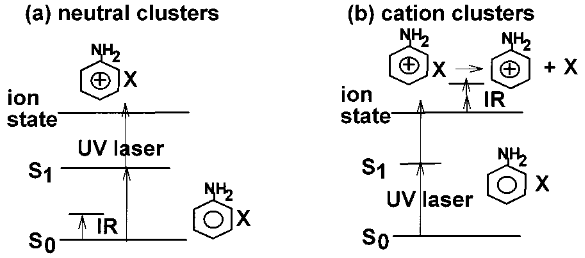

Figure 2. Principles of infrared depletion spectroscopy combined with the REMPI-TOF method. (a) Infrared spectra of neutral clusters (aniline−X) are obtained as a decrease of the REMPI signal due to depopulation of the ground state induced by IR laser absorption. (b) Infrared spectra of cluster cations are obtained as a decrease of the cation signal induced by the IR laser.

The infrared depletion spectrum of the neutral complex was recorded by means of the decrease of the REMPI signal strength of the 0−0 transition. To achieve this, the molecular beam was first irradiated by the infrared laser (Spectra Physics Wex system, 1.5 mJ/pulse at $\lambda = 3$ μm) and then after 50 ns by the UV laser. Since only the complexes in the ground vibrational state can be ionized by the REMPI process, the depletion of a specific type of cluster in the ground state results in the decrease of the ion signal from that cluster complex. The vibrational spectrum of the complex can therefore be obtained by scanning the wavelength of the infrared laser, which will cause the depletion of a specific cluster type only when it absorbs an infrared photon.

The infrared spectrum of the cation was obtained utilizing infrared predissociation or infrared multiphoton decomposition (Figure 2b), whereby the complex cation which absorbed the infrared photons dissociates into its constituents. This causes a decrease of the ion signal of the complex cation. By monitoring the ion signal and varying the infrared wavelength, the IR spectrum of the cluster cation is obtained. In the present work, the complex cation was generated by the same technique that was used for the neutral clusters, with the exception being that the molecular beam was first irradiated by the UV laser and then by the infrared laser 50 ns later. All other parameters remained the same.

The infrared laser light was obtained by difference frequency generation of the fundamental of a Nd:YAG laser with the output of a dye laser (QuantaRay Wex system) in a $LiNbO_3$ crystal. The power of the IR laser was about 1.5 mJ/pulse at 3500 cm^{-1}. The output became weaker in the lower wavenumber region (0.3 mJ/pulse at 3200 cm^{-1}). The wavelength of the infrared laser was calibrated by monitoring the wavelength of the dye laser using a wave meter (Burleigh WA4500), and for the Nd:YAG laser, the wavelength value $\lambda = 1064.45$ nm was used in the calculation. The accuracy and the resolution of the infrared laser were estimated to be about 1 cm^{-1}, being limited by the stability of the Nd:YAG laser.

Results and Discussion

Excitation Spectrum of the Aniline−Pyrrole Complex. Figure 3 shows the UV excitation spectrum of the aniline−pyrrole complex measured by the REMPI technique. Two progressions whose intervals are about 10 and 60 cm^{-1} can be seen in the spectrum. Table 1 lists the observed bands. The 0−0 band of the aniline−pyrrole complex has been determined to be at 33 684 cm^{-1}. The origin of the 0−0 band is shifted by 345 cm^{-1} to the red from that of the aniline monomer (34 029 cm^{-1}). This value is about half of that observed in the aniline dimer (672 cm^{-1}).[33]

The peaks observed at 33 681 and 33 705 cm^{-1} in Figure 3 were found to be hot bands, which was confirmed as follows. The effective temperature of the complex can be controlled by changing the time interval between the injection of the sample

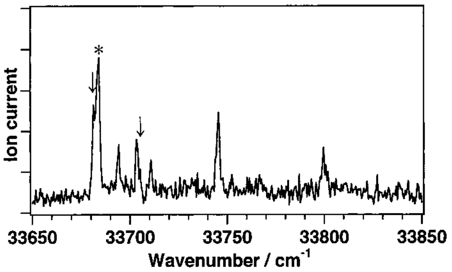

Figure 3. REMPI spectrum of the aniline−pyrrole cluster. The 0−0 band is indicated with an *. The bands indicated with arrows were assigned to hot bands.

TABLE 1: List of the Observed Bands in the REMPI Spectrum of the Aniline−Pyrrole Cluster

mode	x/cm^{-1}	Δx/cm^{-1} [a]
ν_0	33 684	
$\nu_0 + \nu_a$	33 694	10
$\nu_0 + 2\nu_a$	33 703	19
$\nu_0 + 3\nu_a$	33 711	27
$\nu_0 + \nu_b$	33 745	61
$\nu_0 + 2\nu_b$	33 800	116

[a] The values of Δx are defined as $\Delta x = x - \nu_0$.

from the pulsed nozzle and the irradiation by the UV laser. The excitation spectra were measured with different timings between the pulsed valve and the UV laser (which translates into different effective cluster temperatures), and hot bands can then be distinguished by comparing the relative intensities of the observed bands. The intensity of the above two bands changed greatly from one spectrum to the other because of the temperature variation along the cluster pulse. The coldest clusters are encountered in the center of the pulse, while those probed in the beginning or at the end of the pulse are warmer. Another possibility is that the band at 33 681 cm^{-1} could be due to an isomeric complex. However, this was denied by measuring the infrared depletion spectrum while exciting this band. The spectrum was identical to that obtained exciting the peak at 33 684 cm^{-1}.

The progression with an interval of 10 cm^{-1} was cited as ν_a in Table 1 and tentatively assigned to the intermolecular sliding mode in which each molecule translates along the a axis; this is supported by the results of the ab initio MO calculations mentioned below. In the same way, that with an interval of about 60 cm^{-1} was cited as ν_b in Table 1 and tentatively assigned to the intermolecular stretching mode.

Infrared Depletion Spectrum of the Neutral Aniline−Pyrrole Complex. Figure 4 shows the infrared depletion spectrum in the region of the NH stretching vibration. The wavelength of the UV laser was fixed on the 0−0 band of the complex. Three vibrational bands are observed at 3393, 3464, and 3496 cm^{-1} which are cited as a, b, and c in Figure 4, respectively. Band a at 3393 cm^{-1} has been assigned to the symmetric stretching vibration and b at 3464 cm^{-1} to the antisymmetric stretching vibration of the NH_2 group.[33] This assignment gives a red shift of 29 cm^{-1} for a and 44 cm^{-1} for b compared to those found for the free aniline monomer. This leaves band c at 3496 cm^{-1} to be assigned to the NH stretching vibration of pyrrole. This assignment was chosen for the following reasons. Bands a and b would then have frequency shifts which are practically identical to those observed in the aniline dimer and the aniline−benzene complexes,[33,39] indicating a similar interaction between the NH_2 group and the pyrrole π system. This also means that the NH stretching band c of pyrrole is red-shifted compared to that of the free pyrrole monomer (3530.5 cm^{-1})[40] by 35 cm^{-1}, a reasonable value if we postulate a hydrogen-bonding interaction between the pyrrole NH group and the aniline π system.

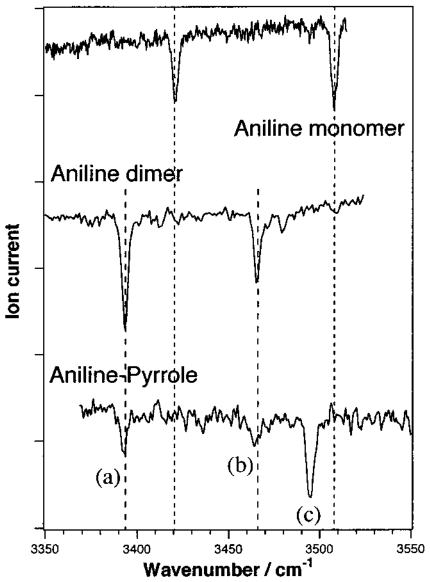

Figure 4. Infrared depletion spectra of the aniline monomer, aniline dimer, and aniline−pyrrole neutral clusters in the reagion of the NH_2 stretching vibration. UV laser was fixed to the 0−0 band of the S_1-S_0 transition to monitor the population of the ground state. In the case of aniline−pyrrole, a binomial smoothing method was used.[38]

TABLE 2: Red Shifts of the NH_2 Symmetric and Antisymmetric Stretching Vibrations and That of the 0−0 Bands of the S_1-S_0 Band of Aniline Clusters as Measured from the Aniline Monomer

	red shift/cm^{-1} [a]		
	NH_2 sym str	NH_2 antisym str	0−0 band
aniline dimer[b]	28	42	672
aniline−Benzene[c]	29	41	438
aniline−Pyrrole[d]	29	44	348

[a] Reference 37. The original values of the aniline monomer are 3422, 3508, and 34 029 cm^{-1}, respectively. [b] Reference 33. [c] Reference 39. [d] This work.

If either band a or band b were assigned to the NH stretching vibration of pyrrole, difficulties will occur in the assignment of the NH_2 stretching vibrations of aniline. If band a were assigned to the pyrrole NH stretching vibration, the red shifts of the NH_2 stretching vibrations of aniline would be −42 (blue-shifted) and 12 cm^{-1}. This would suggest an abnormally large blue shift for the symmetric stretching vibration of aniline. If band b were assigned to pyrrole, bands a and c would be assigned to aniline. By doing this, one obtains red shifts of 29 and 12 cm^{-1}. The red shift of the symmetric stretching mode becomes larger than that of the antisymmetric mode. This kind of frequency shift occurs when one of the NH bonds interacts with the acceptor. Since the absorption band of a hydrogen donor gets much stronger than that of a non-hydrogen-bonding XH group, this contradicts the experimental result to the extent that the intensity of band c is stronger than that of band a. The present assignment of the vibrational modes was confirmed by ab initio MO calculations, which will be discussed later.

Table 2 shows the assignments of the observed vibrational bands of the aniline−pyrrole complex and compares them with those of the aniline dimer[33] and the aniline−benzene complexes.[39] It is interesting that the frequencies of the NH_2 stretching vibrations of these three complexes agree so well with each other. This result implies that the origins of the interactions

TABLE 3: Observed and Calculated Red Shifts (in cm^{-1}) with Respect to the Aniline Monomer and IR Intensities (in km/mol) of the NH_2 Symmetric and Antisymmetric Stretching Vibrations and the NH Stretching Vibration

	red shift (IR intensity)		
	NH_2 sym str	NH_2 antisym str	NH str
obsd	29 (m)	44 (w)	35 (vs)
RHF/4-31G**			
NH−N	26 (27)	32 (17)	103 (444)
NH−π	−1 (26)	−2 (18)	14 (180)
parallel	4 (26)	15 (12)	10 (88)
MP2/4-31G** [a]			
NH−N	23 (32)	29 (13)	174 (497)
parallel	18 (18)	34 (8)	49 (89)

[a] See Figure 5 for the detailed structures.

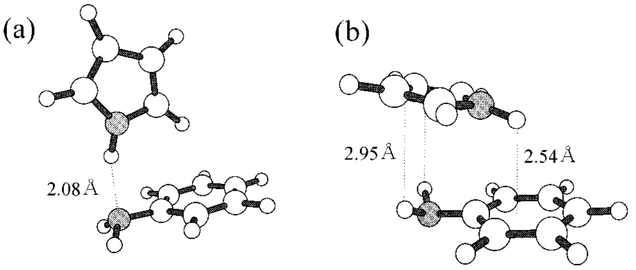

Figure 5. Structures for the aniline−pyrrole neutral cluster. Calculated with the MP2/4-31G** basis set.

of these three complexes are basically the same; that is, a hydrogen bond is formed between the NH_2 group and the aromatic ring. The structure of the aniline dimer is considered to have a parallel arrangement of the rings, with each amino group interacting with the other ring by a NH_2−π-type hydrogen bond. This was concluded from the experimental fact that only two absorption bands were found in the region of the NH stretching vibration, which suggested a high symmetry.

Ab initio molecular orbital calculations were performed using the GAUSSIAN 94 program package on a CRAY computer in order to discuss the structures of the complexes further.[41] At first, various configurations of the aniline−pyrrole complex were examined using a RHF/4-31G** basis set. Then, the stabilization energies and vibrational frequencies, as well as their intensities, of the stable configurations including the parallel one were calculated analytically by the standard procedures built into the program. The stabilization energy is calculated using the same level of calculation for the monomer and cluster:

$$E_s = E(\text{aniline}) + E(\text{countermolecule}) - E(\text{cluster})$$

where E is the total energy corrected for the zero-point energy.

The results are summarized in Table 3. Higher level calculations using a MP2/4-31G** basis set were carried out for the two cluster structures which gave the largest stabilization energy (NH−N configuration) and reasonable red shifts for the NH stretching vibrations (parallel configuration). The optimized structures were obtained by using a standard procedure of the program. The IR frequencies and intensities were computed numerically. In one structure, the main interaction is a hydrogen bond between the NH bond of pyrrole and the nitrogen atom of aniline (Figure 5a, NH−N configuration) and, in the other, a parallel structure which resembles that of the aniline dimer (Figure 5b, parallel configuration). The structure shown in Figure 5a gives an extremely large red shift for the NH stretching vibration of pyrrole and a small red shift for both stretching vibrations of the aniline NH_2 group; therefore, it cannot be said that the result of this calculation reproduces the observed values. On the other hand, in the case of the parallel structure (Figure 5b), the calculations seem to reproduce the experimental results much better.

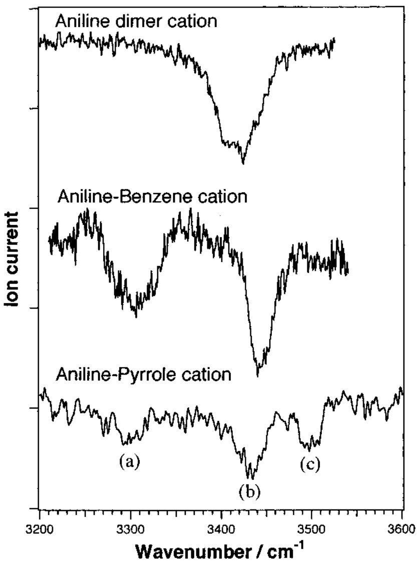

Figure 6. Infrared depletion spectra of the aniline dimer, aniline−benzene and aniline−pyrrole cluster cations in the region of the NH_2 stretching vibration. The cation was produced by the REMPI ionization of the aniline−pyrrole neutral cluster using the 0−0 band of the S_1−S_0 transition. In the case of aniline−pyrrole, a binomial smoothing method was used.[38]

TABLE 4: Observed and Calculated Vibrational Frequencies, Red Shifts, and Binding Energies (in cm^{-1}) of the Aniline Dimer and Aniline−Benzene and Aniline−Pyrrole Cation Clusters Using the UHF/6-31G Basis Set (in cm^{-1})**

	obsd freq	red shift[a]	calcd freq[b]	red shift[a]	E_b[d]
aniline dimer cation[c]					
NH_2 sym str		2985	399		
NH_2 antisym str		3447	62		
aniline−benzene cation[c]					5300
NH_2 sym str	3305	90	3323	61	
NH_2 antisym str	3440	48	3469	40	
aniline−pyrrole cation					4760
NH_2 sym str	3293	98	3256	128	
NH_2 antisym str	3435	51	3464	45	
N−H str (pyrrole)	3498	33	3521	23	

[a] Red shift from aniline cation[37] or neutral pyrrole.[40] [b] Scaled by a frequency factor of 0.90. [c] Reference 42. [d] Binding energy was calculated using the same level of calculations for the monomers and cluster: $E_b = E(\text{aniline}) + E(\text{countermolecule}) - E(\text{cluster})$, where E is the total energy corrected for the zero-point energy.

Infrared Depletion Spectrum of the Aniline−Pyrrole Complex Cation. Figure 6 shows the infrared depletion spectrum of the aniline−pyrrole complex cation. The complex cation was obtained by REMPI of the aniline−pyrrole complex. Three broad bands are observed at 3293, 3435, and 3498 cm^{-1} and have been assigned to the NH_2 symmetric stretching vibration, the NH_2 antisymmetric stretching vibration of aniline, and the NH stretching vibration of pyrrole, respectively, for the same reasons given in the previous section. Table 4 summarizes the observed frequencies and the assignments for the aniline−pyrrole complex cation with those of the aniline dimer cation and aniline−benzene complex cation.[42]

It is apparent that the bandwidths of the vibrational modes in Figure 6 are much larger than those observed in the neutral

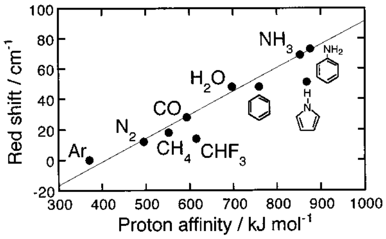

Figure 7. Relationship between the red shift of ν_{antisym} of the aniline cation cluster (aniline$^+$−X) and the proton affinity of the interacting molecules (X).

complex (Figure 4). The main cause of this increased bandwidth seems to be the internal vibrational relaxation of the complex cation into intermolecular vibrational modes. The complex cation generated by the REMPI process is thought to have an excess energy of about 5000 cm^{-1}; this estimate is made by assuming that the ionization potential of the aniline is at most 7.68 eV for the complex.[43] A fraction of the excess energy is partitioned into the intermolecular vibrational modes of the cation statistically. Although the structure of the cluster in the ionic state is different from that in the ground state, transitions from the resulting excited vibrational states may overlap with transitions from the ground state.

As seen in Table 4, the frequency shift of the NH_2 symmetric stretching vibration of the aniline−pyrrole cation is larger than that of the antisymmetric stretching vibration. Although this behavior is reversed from that found in the neutral complex, it matches that of the aniline−benzene complex cation. This frequency shift suggests that only one of the NH bonds of aniline interacts with the pyrrole molecule in the complex cation.

It is apparent that the frequency shifts of the NH stretching vibrations of the aniline complex cations are highly correlated with the proton affinity of the acceptor molecules. In fact, a linear relationship between the red shift of the higher energy stretching mode of the amino group in aniline complex cations and the proton affinities of the interacting molecules was reported.[35] However, the frequency shift of the aniline−pyrrole complex cation makes an exception here, as is shown in Figure 7. It is interesting that the red shift of the aniline−benzene complex cation also deviates slightly from the linear relationship. These complexes gave identical frequency shifts for both the symmetric and the antisymmetric stretching vibrations of the NH_2 group, although the proton affinities of benzene and pyrrole are quite different. A similar tendency in the frequency shift is observed in neutral complexes with NH_2−π-type hydrogen-bond interactions.

Two explanations can be postulated: (i) The formation of the hydrogen bond reduces the symmetry of the NH_2 groups and also the splitting between the symmetric (NH-bonded) and antisymmetric (NH-free) NH stretching vibrations of aniline. This leads to the red shift of the antisymmetric (NH-free) stretching vibration. (ii) When the charge transfer in the hydrogen bond X−H−N takes place, this causes a small frequency shift to the red of the adjacent free NH bond as well as a large frequency shift for the interacting bond. In Figure 7, these two effects apparently coincide with each other by chance. This relationship may indicate similarities in the structures and interactions between protonated molecules (XH$^+$) and aniline−X cations. The deviation of the red shifts of the aniline−pyrrole and aniline−benzene cations from this relationship can be understood by the structural difference.

Figure 8 shows the calculated structure of the aniline−pyrrole complex cation which was obtained by using an UHF/6-31G** basis set with the standard procedure incorporated in the program GAUSSIAN 94. The positive charge was found to be localized mostly in the aniline molecule. The calculated frequencies shown in Table 4 almost reproduced the observed ones for the NH stretching vibration of pyrrole and the NH_2 stretching vibrations of aniline. This result confirms the discussions about the experimental results.

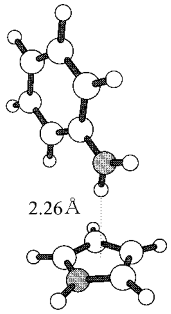

Figure 8. Structure of the aniline−pyrrole cluster cation calculated with an UHF/6-31G** basis set.

Conclusions

The vibrational spectra of the NH stretching region of the aniline−pyrrole complex and the corresponding complex cation were measured by an infrared depletion technique combined with REMPI-TOF mass spectrometry, which allowed a highly sensitive and selective detection of each complex.

The analysis of the infrared spectra and ab initio MO calculations with the MP2/4-31G** basis set showed that the aniline−pyrrole complex has a parallel conformation which was also found in the aniline dimer. The main intermolecular interactions in the complex were found to be a NH−π-type hydrogen bond between the NH_2 group of aniline and the aromatic ring of pyrrole and a similar bond between the NH group of pyrrole and the aromatic ring of aniline.

On the other hand, the main interaction in the aniline−pyrrole complex cation was determined to be a hydrogen bond between one of the NH groups of the aniline cation with the aromatic ring of pyrrole.

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