Investigations on the Hydrogen Bond Interaction in the Aniline−Furan Complex and Its Cation by Infrared Depletion Spectroscopy

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The vibrational spectra of the NH_2 stretching modes of the aniline−furan complex and its cation in a supersonic jet have been measured by infrared depletion spectroscopic methods. Two absorption bands have been observed at 3409 and 3497 cm^{-1} in the spectrum of the neutral aniline−furan complex, which is red-shifted from the corresponding bands of aniline monomer by 12 and 11 cm^{-1}, respectively. The main intermolecular interaction of the complex has been found to be a weak hydrogen bond between the NH bond of aniline and the lone pair of the oxygen atom of furan. As for the aniline−furan cation complex, two strong absorption bands have been observed at 3315 and 3446 cm^{-1} in the infrared spectrum. In this case, the main intermolecular interaction has been found to be the NH-π type hydrogen bond between one of the NH bonds and the π-electron of the aromatic ring of furan. The difference between the interactions of the neutral and the cation complexes has been discussed.

Introduction

The hydrogen bond plays important roles in various systems, and there are plenty of research works on the hydrogen bond in bulk phases, especially by infrared spectroscopy.[1] Recent progress in the cluster science has made it possible to study the nature of the hydrogen bond by observing the infrared spectrum of the cluster in a supersonic jet in which the number of interacting molecules is well-defined.[2−6] Among the new spectroscopic methods, infrared depletion spectroscopy, which utilizes the IR−UV double resonance and REMPI-TOF mass spectrometry, enables us to measure the infrared spectrum of the hydrogen-bonded clusters with relatively high sensitivity and mass selectivity.[7,8]

Aniline has been used as a model molecule to study the hydrogen bond interaction through the NH bond by infrared depletion spectroscopy since it is the simplest amine with an aromatic ring and it is easy to measure its REMPI spectrum. There are two kinds of hydrogen bonds that have been observed in the aniline complexes. One is the hydrogen bond with a lone pair (σ-electron),[9−12] and the other is that with an aromatic ring (π-electron).[12−15] There is also a significant difference between the infrared spectra of the two. Hereafter, the former case will be referred to as NH-σ type and the latter NH-π type.

Since aniline has two equivalent NH bonds, there are two NH stretching modes, the NH_2 symmetric stretching (ν_{sym}) and the NH_2 antisymmetric stretching ($\nu_{antisym}$) modes. When one of the NH bonds interacts with an acceptor, the local symmetry disappears and they should be called the stretching mode of the interacting NH bond (ν_{H-bond}) and that of the free NH bond (ν_{H-free}). On the other hand, van der Waals (vdW) or NH_2-π type complexes have local symmetry around the NH_2 group and the notation should be the same as in the monomer. In this paper, the red shift will be defined as $\Delta\nu_S = \nu_{sym} - \nu_2$ and $\Delta\nu_A = \nu_{antisym} - \nu_1$, where ν_{sym} and $\nu_{antisym}$ are the frequency of the NH_2 symmetric and antisymmetric stretching modes of the aniline monomer, respectively, and ν_1 and ν_2 are the frequencies of the NH stretching modes of the aniline complex ($\nu_1 > \nu_2$). The correlation between the vibrational modes for the NH-σ type interaction will be discussed later.

When the NH bond interacts with the lone pair of the acceptor molecule, the NH stretching vibration shows a large red shift that strongly depends on the types and the strength of the intermolecular interaction. This effect appears as a correlation between the frequency shift and the basicity of the acceptor molecule such as the proton affinity or pK_a value. This correlation is especially significant in the aniline complex cation. The red shift of the stretching mode of the free NH bond, $\Delta\nu_A$, shows a linear correlation with the value of the proton affinity of the acceptor molecule in the range 300−900 kJ/mol.[12]

On the other hand, the infrared spectrum of the aniline complexes whose main interaction is the NH-π type hydrogen bond is quite different from that of the NH-σ type interaction. Until now, the infrared spectra of three neutral complexes and two complex cations of the NH-π type interaction have been reported.[12−15] In the case of the neutral complex, the NH_2 group interacts with the aromatic ring, and the frequency shifts of the NH_2 stretching vibrations do not depend on the acceptor molecule. In the case of the cation complex, one NH bond interacts with the aromatic ring, and the observed shifts were $\Delta\nu_A \approx 40$ cm^{-1} and $\Delta\nu_S \approx 80$ cm^{-1}.[16] In both cases, the red shifts do not seem to depend on the nature of the acceptor molecule.

Furan is a simple heterocyclic aromatic ring molecule and has the isoelectronic structure with pyrrole whose aniline complex has already been investigated by the infrared depletion spectroscopy. Since the atomic orbital of the lone pair of the oxygen atom is only partially mixed with the π-orbital of the ring, the aromaticity of furan is not as strong as pyrrole, and the oxygen atom can act as the acceptor. For this reason, it is difficult to say whether the main interaction is the NH-π type or the NH-σ type in the aniline−furan complex. In the present work, the vibrational spectra of the NH_2 stretching vibrations of aniline−furan complex and aniline−furan complex cation have been measured using the infrared depletion spectroscopic

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technique, and the structure and the nature of the intermolecular interaction of these complexes has been discussed.

Experimental Section

The infrared spectra of the aniline−furan complexes were measured using the ion depletion technique, which utilizes the IR−UV double resonance or infrared predissociation. The details of the experimental apparatus are given elsewhere.[17]

The aniline−furan complex was prepared in a supersonic expansion of a mixture of aniline (the vapor pressure at room temperature), furan (100−400 Pa), and He (150 kPa). The higher partial pressure of furan made the UV excitation spectrum poor. The gas mixture was injected into a vacuum chamber through a pulse valve (General Valve, 0.8 mm o.d.). It operates at 10 Hz, and the opening time was set to 250 μs. The cluster beam was introduced into an ionization room through a molecular beam skimmer (1 mm o.d.). The clusters were ionized by resonant two-photon ionization (REMPI) by an ultraviolet pulse laser (duration time ~5 ns) and detected by a linear TOF mass spectrometer. The S_1 state of the aniline−furan complex was used as an intermediate state of the REMPI process. The power of the UV laser was reduced to less than 100 μJ/pulse by using a filter in order to minimize the fragmentation of aniline clusters.

The infrared laser was generated by a difference frequency mixing of the Nd:YAG fundamental and a dye laser (~780 nm). The wavelength of the infrared laser was calibrated by monitoring the wavenumber of the dye laser using a wave meter (Burley WA4500). The reliability of the frequency value was estimated to be better than 1 cm^{-1}.

The infrared spectra of the aniline−furan complex and the aniline−furan complex cation were measured using the infrared depletion spectroscopy. In the case of the neutral complex, infrared absorption was measured as the ion depletion induced by the vibrational excitation or the vibrational predissociation of the complex with an infrared photon. The complex beam was irradiated with an infrared laser (Spectra Physics Wex system, 1.5 mJ/pulse at 3 μm) 50 ns before the UV laser for the detection of the neutral complex. If the complex absorbs the infrared photon, it will be excited into the vibrationally excited state. This depletes the complex in the ground state, and the REMPI signal will decrease.

The infrared spectrum of the cation complex was measured by detecting the decrease of the ion current caused by the infrared predissociation of the complex cation. In this case, the infrared laser was irradiated 50 ns after the UV laser pulse.

Results and Discussion

UV Excitation Spectrum of Aniline−Furan Complex. The UV excitation spectrum of the aniline−furan complex was measured in the region of 295−300 nm by monitoring the mass signal of the aniline−furan cation ($m/z = 161$). Figure 1 shows a part of the excitation spectrum of the aniline−furan complex. The partial pressure of furan was about 100 Pa. A band structure was clearly observed in the region of 33 700−33 900 cm^{-1}. There are several series of peaks in the spectrum near the band origin. Two band progressions are clearly seen in the spectrum with $\Delta\omega = 16$ and 23 cm^{-1}. The sharp peak observed at 33 744 cm^{-1} has been assigned to the 0−0 band of the aniline−furan complex, and other peaks have been assigned to the vibrational structure of the S_1 state of the complex. The assignment of these peaks to a single aniline−furan complex has also been confirmed by the infrared hole-burning spectroscopy. Details of the infrared hole burning spectrum of the aniline−furan complex will be given later.

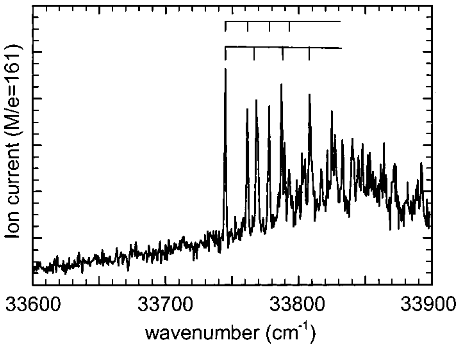

Figure 1. UV excitation spectrum of the aniline−furan complex in a supersonic jet.

TABLE 1: Red Shifts of the Band Origin of the S_1-S_0 Transition and the NH_2 Stretching Vibrations, $\Delta\nu_S$ and $\Delta\nu_A$, of Neutral Aniline Complexes (in cm^{-1})

molecule	$\Delta\nu(S_1-S_0)$[a]	$\Delta\nu_S$[ab]	$\Delta\nu_A$[b]
Aniline−Furan Complex			
C_4H_4O	277	12	11
vdW Complexes			
CH_4	79	0	0
N_2	128	1	3
CO	348	6	10
NH-π Type Hydrogen Bond Complexes			
aniline-dimer	672	28	42
benzene	436	29	41
pyrrole	345	29	44
NH-σ Type Hydrogen Bond Complexes			
$(CH_3)_2O$	666	40	23
NH_3	889	68	29
$(C_2H_5)_3N$	876	94	42

[a] The band origin of the aniline monomer is 34 029 cm^{-1}. The reliability of the experimental value is ±4 cm^{-1}. [b] Definitions of the red shifts are given in the text. $\Delta\nu_S$ and $\Delta\nu_A$ are the shifts from the NH_2 symmetric and antisymmetric stretching vibrations of the aniline monomer. The NH_2 stretching vibrations of the aniline monomer are $\nu_{sym} = 3421$ and $\nu_{antisym} = 3508$ cm^{-1}. And the reliability is ±1 cm^{-1}.

A broad background was observed in the spectrum. It became stronger when a higher partial pressure of furan was used, and its origin seems to be an isomer complex or the fragment of the higher clusters.

The band origin of the aniline−furan complex is red-shifted from that of the aniline monomer (34 021 cm^{-1}) by 277 cm^{-1}. Table 1 compares the red shift of the band origin with those observed for the other aniline complexes. It is larger than that of the vdW complexes, except aniline−CO,[18] and significantly smaller than those observed in the aniline−amine complexes and NH-π type complexes.[9−15]

Infrared Depletion Spectrum of the Neutral Aniline−Furan Complex. Figure 2 shows the infrared depletion spectrum of the aniline−furan complex in the region of the NH_2 stretching vibrations. The wavelength of the UV laser was fixed to the 0−0 band (33 744 cm^{-1}) of the complex. There are two strong absorption bands observed at 3409 and 3497 cm^{-1}. The red shifts of these bands from the corresponding NH_2 stretching vibrations of aniline monomer are 12 and 11 cm^{-1} for the 3409 and 3497 cm^{-1} bands, respectively. They are compared with the red shifts of the related aniline complexes in Table 1. The frequency red shifts of these bands are larger than those of the

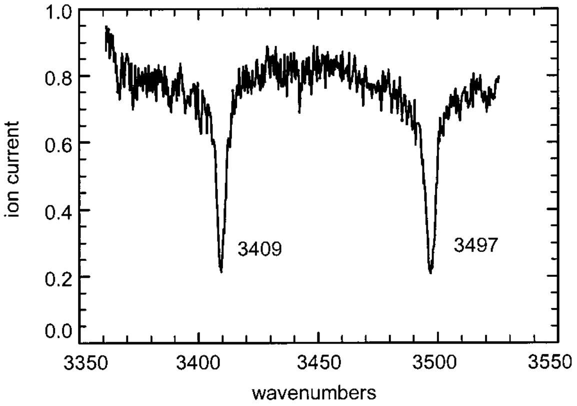

Figure 2. Infrared depletion spectrum of the aniline−furan complex measured using the resonance UV laser corresponding to the 0−0 band of the excitation spectrum.

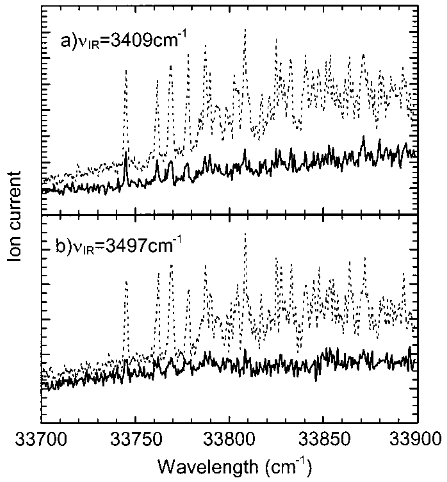

Figure 3. Infrared hole burning spectra of the aniline−furan complex. Spectra shown by the solid line and broken line were measured with and without an infrared laser, respectively. The wavelength of the infrared laser was fixed to (a) 3409 cm^{-1} and (b) 3497 cm^{-1}.

vdW clusters,[18] but smaller than those of the NH-σ type and NH-π type hydrogen bond complexes.[9−15]

When the infrared spectrum was measured, the partial pressure of furan was set to 400 Pa to get a good S/N ratio in the infrared spectrum. This made the background signal in the excitation spectrum stronger than that observed in Figure 1. The feature of the background of the excitation spectrum when the infrared spectrum was measured can be seen in Figure 3. The background signal was about one-third of the observed signal, and in this case, we should be careful whether the observed infrared spectrum is disturbed by the background signal or not. To clarify this, an infrared spectrum was measured with the UV laser frequency fixed to a wavelength that is different but close to the 0−0 band of the aniline−furan complex. It gave two infrared bands at exactly the same positions as were observed in Figure 2, although the intensity of these bands was weak and the bandwidth was wider than that measured using the 0−0 band. From this fact, it is concluded that the band positions of the infrared bands are not affected by the background signal.

Parts a and b of Figure 3 show the infrared hole burning spectra that were measured by irradiating the infrared laser whose wavelength was fixed to 3409 and 3497 cm^{-1}, respectively. It is apparent from the figure that the band structure of the excitation spectrum almost disappeared when the infrared laser was irradiated, and the intensity of the background also slightly decreased. From this result, the complex that gives the peaks or the band structure observed in the region of 295−296.5 nm has the infrared absorption bands at 3409 and 3497 cm^{-1}. This result suggests that the observed band structure in Figure 1 should be assigned to a single conformer of the complex.

There are two characteristic features in the red shift of the aniline−furan complex that differ from the other aniline complexes reported before as in Table 1:

(1) The frequency red shift is much smaller than those observed in the other hydrogen-bonded complexes, although they are larger than those observed for the vdW complexes.[18]

(2) The red shift $\Delta\nu_S$ is slightly larger than $\Delta\nu_A$. $\Delta\nu_S$ is much larger than $\Delta\nu_A$ in the case of a typical NH-σ type hydrogen-bonded complex, and much smaller in the case of NH-π hydrogen-bonded and vdW complexes.

When we compare the observed frequency shifts of $\Delta\nu_A$ and $\Delta\nu_S$ with the other complexes, aniline−furan seems to be classified to the NH-σ type hydrogen-bonded complex for the following reasons. In the case of the vdW complex, $\Delta\nu_A$ is usually larger than $\Delta\nu_S$, and also there is a linear correlation between $\Delta\nu_A$, $\Delta\nu_S$, and the shift of $\Delta\nu(S_1-S_0)$ in the UV excitation spectrum. The frequency shift of the aniline−furan complex does not satisfy either of them, and is also too large. In the case of the NH-π hydrogen bond complex, the magnitudes are much larger than that of the aniline−furan complex, and also $\Delta\nu_A$ is much larger than $\Delta\nu_S$. For these reasons, the aniline−furan complex cannot be classified into the vdW complex or the NH-π hydrogen bond complex. Since the oxygen atom of furan has two lone pairs, there might be the possibility that two NH bonds interact with two lone pairs symmetrically. However, if it is true, the angle of $\angle$HNH of the NH$_2$ group would become smaller by the interaction, and the splitting of sym and antisym stretching vibrations will decrease. As a result, the frequency shift of $\Delta\nu_A$ should be much larger than that of $\Delta\nu_S$ like the NH$_2$-π type interaction. This conflicts with the present observation.

The feature of the frequency shift of the NH$_2$ stretching vibrations of the aniline−furan complex can be explained by the way that the main interaction is the weak hydrogen bond between one of the NH bonds of aniline and the lone pair of the oxygen atom of furan. The shifts of the symmetric and antisymmetric vibrations can be explained as follows.

The Hamiltonian matrix of the two equivalent NH stretching vibrations can be approximately expressed as

$$\langle 1|H|1\rangle = \epsilon_0 \qquad \langle 2|H|2\rangle = \epsilon_0 \qquad \langle 1|H|2\rangle = W_0$$

where ϵ_0 is the original energy level of the NH stretching vibration with W_0 being the coupling term. The energy levels of the symmetric and the antisymmetric stretching vibrations are calculated to be $\epsilon_{\text{sym}} = \epsilon_0 - W_0$ and $\epsilon_{\text{antisym}} = \epsilon_0 + W_0$, respectively. By substituting the observed values of the aniline monomer, we obtain $\epsilon_0 \approx 3465$ cm^{-1} and $W_0 \approx 43$ cm^{-1}.

If one of the NH bonds ($|2\rangle$ state) interacts with an acceptor, the Hamiltonian will be modified as

$$\langle 1|H|1\rangle = \nu_0 - \Delta E_1 \qquad \langle 2|H|2\rangle = \nu_0 - \Delta E_2$$
$$\langle 1|H|2\rangle = W_1$$

where ΔE_2 is the energy shift by the hydrogen bond and ΔE_1

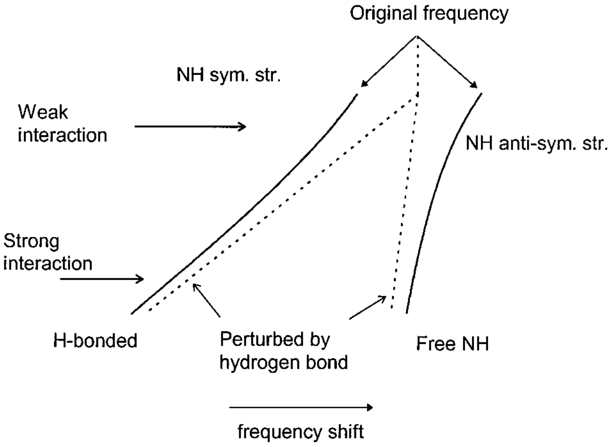

Figure 4. Schematic diagram of the perturbation of the NH_2 stretching vibration by a hydrogen bond through one of the NH bond.

is the indirect effect of the interaction. Assuming that $\Delta E_1 \ll \Delta E_2 \ll W_0 = W_1 = W$, we obtain the perturbed energy levels,

$$\nu_{\mathrm{sym}} = \nu_0 - W - \frac{\Delta E_2}{2} - \frac{\Delta E_2^{\,2}}{8W}$$

$$\nu_{\mathrm{antisym}} = \nu_0 + W - \frac{\Delta E_2}{2} + \frac{\Delta E_2^{\,2}}{8W}$$

and the frequency red shifts,

$$\Delta\nu_{\mathrm{S}} = \frac{\Delta E_2}{2} + \frac{\Delta E_2^{\,2}}{8W'} \qquad \text{and} \qquad \Delta\nu_{\mathrm{A}} = \frac{\Delta E_2}{2} - \frac{\Delta E_2^{\,2}}{8W}$$

This is the reason $\Delta\nu_{\mathrm{H-bond}}$ is slightly larger than $\Delta\nu_{\mathrm{H-free}}$ when the interaction is weak. Although the second condition, $\Delta E_2 \ll W$, is not well satisfied in the present case, we can easily solve the secular equation directly. The red shifts of 10 and 13 cm^{-1} were obtained for ν_{sym} and ν_{antisym}, respectively, when the parameters $\Delta E_2 = 23$ cm^{-1} and $W = 43$ cm^{-1} were used. Figure 4 shows the correlation of the NH_2 stretching vibrations of aniline on the formation of the hydrogen bond. In this case, the energy was calculated by solving the secular equation. The specific spectral feature of the aniline−furan complex seems to be the result of the weak interaction through one of the NH bonds.

The above conclusion was also confirmed by the MO calculation. The frequency shifts of the NH_2 stretching modes of the NH-σ and the NH-π type aniline−furan complexes have been calculated by the Gaussian 94 calculation program. In the calculation, the basis set of MP2/6-31G** was used to obtain the optimized structures and the vibrational frequencies of the NH_2 stretching modes. This basis set is known to give a good estimate of the frequency shifts of the NH_2 stretching vibrations of the other aniline complexes. However, since the reliability of the relative energy of the calculation is not good enough, we will discuss only the features of the red shifts of the NH_2 stretching frequencies because it reflects the information about the local structure around the NH_2 group of the complex.

Figure 5 and Table 2 summarize the calculated red shifts of the NH_2 stretching vibrations of the aniline−furan complexes for several isomers. There are two kinds of stable isomers for the aniline−furan complex. One is the NH-σ type complex (structure 1) and the other is the NH_2-π type complexes (structures 2 and 3). As seen in the table, only the NH_2-σ type complex (structure 1) gives a good estimate of the frequency shift of the NH_2 stretching vibrations. The calculated value of $\Delta\nu_{\mathrm{S}}$ is slightly larger than that of $\Delta\nu_{\mathrm{A}}$, and the magnitudes are also close to the experimental value. On the other hand, the calculated shifts for the NH_2-π type complexes do not agree with the experiment at all. $\Delta\nu_{\mathrm{A}}$ is calculated to be 2 times larger than $\Delta\nu_{\mathrm{S}}$, and the magnitude of the shifts are too large compared with the experiment. These results support the investigation of the experimental results that the aniline−furan complex should be an NH-σ type hydrogen-bonded complex.

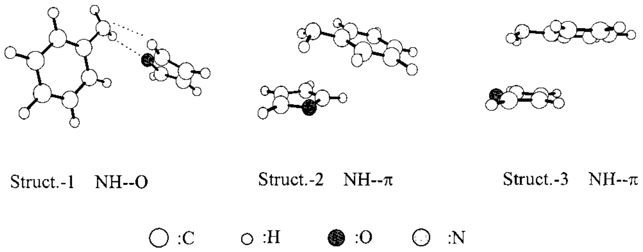

Figure 5. Several calculated structures of aniline−furan complexes. The basis set of MP2/6-31G** was used in the calculation. Structure 1 gives the best estimation of the frequency shift of NH_2 stretching vibrations.

TABLE 2: Observed and Calculated Red Shifts of the NH_2 Stretching Vibrations of the Neutral Aniline−Furan Complex[a]

	obsd		calcd frequency shift[b]		
			NH−O Figure 5, struct 1	NH_2-π Figure 5, struct 2	NH_2-π Figure 5, struct 3
	ν	$\Delta\nu$			
ΔE[c]			2010	1680	1870
$\Delta\nu_{\mathrm{A}}$[d]	3409	12	10.8	14.2	12.0
$\Delta\nu_{\mathrm{S}}$[d]	3497	11	8.7	22.1	20.1

[a] Unit is cm^{-1}. [b] MP2/6-31G** basis set was used. No correction was done for the calculated frequency shifts. [c] $\Delta E = E_{\mathrm{aniline}} + E_{\mathrm{furan}} - E_{\mathrm{complex}}$. No correction for the calculated interaction energy was made. [d] See text for the definition of the red shifts of $\Delta\nu_{\mathrm{A}}$ and $\Delta\nu_{\mathrm{B}}$.

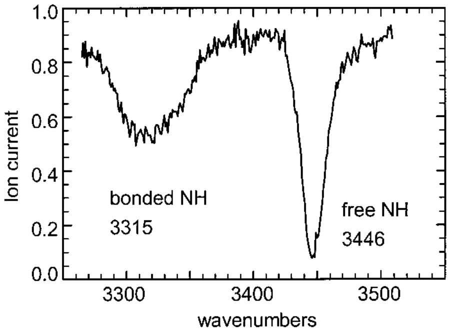

Figure 6. Infrared depletion spectrum of the aniline−furan complex cation.

The main interaction of the aniline−furan complex has been determined to be the NH-σ type hydrogen bond, as discussed above. This result is different from that of the aniline−pyrrole complex. In the case of the aniline−pyrrole complex, the atomic orbital of the nitrogen atom is an sp^2 type and is delocalized in the π orbital of the aromatic ring, and no basicity can be expected for the lone pair of the nitrogen atom. In the case of furan, since the atomic orbital of the oxygen atom should be an sp^3 type, and the lone pair of the oxygen atom only partially interacts with the π-orbital of the ring, it can act as an acceptor for the H atom of NH bond.

Infrared Depletion Spectrum of the Aniline−Furan Complex Cation. Figure 6 shows the infrared depletion spectrum of the aniline−furan complex cation. There are two absorption bands at 3315 and 3446 cm^{-1}, which can be assigned to the

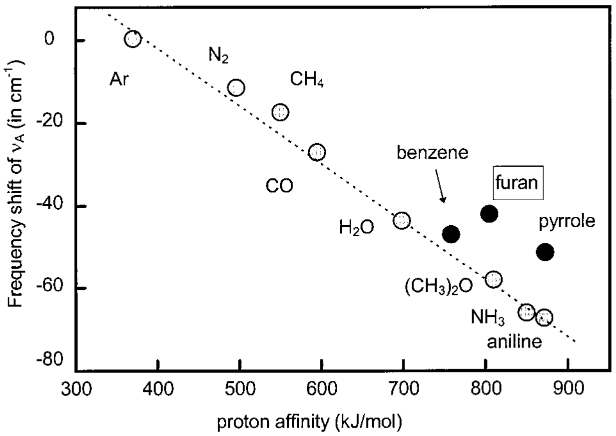

Figure 7. Plot of the frequency shifts $\Delta\nu_A$ of the aniline cation clusters. See text for the definition of $\Delta\nu_A$. References: Ar, N_2, CH_4, CO;[18] H_2O;[10] $(CH_3)_2O$;[19] NH_3;[9] aniline, benzene;[12] pyrrole.[15]

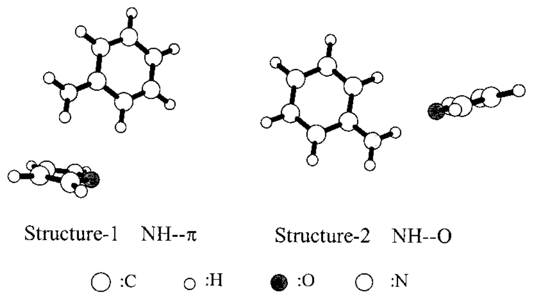

Figure 8. Calculated structure of the aniline−furan cation cluster. The basis set of UHF/6-31G** was used in the calculation.

NH stretching vibrations of aniline. A small spike found in the 3446 cm^{-1} band is an artifact due to the absorption by the water vapor in the air. The frequency red shift of these bands from those of the corresponding bands of aniline cation monomer are 81 and 42 cm^{-1} for the 3315 and 3446 cm^{-1} bands, respectively. The spectral feature resembles those of the aniline−benzene complex cation[12] and the aniline−pyrrole complex cation.[15] In the case of the NH-σ type complex cation, the red shift, $\Delta\nu_S$, became so large that the stretching mode of the interacting NH bond was unable to be observed by the authors' experimental setup. This fact strongly suggests that the aniline−furan complex cation should also be a member of the NH-π type hydrogen-bonded complex.

Figure 7 shows a plot of the proton affinity and $\Delta\nu_A$ of the related aniline complex cations. As seen in the figure, a good correlation between the proton affinity and the red shift was obtained for the NH-σ type complex cations. On the other hand, the red shifts of the NH-π type complex cations deviated from the correlation curve obtained for the NH-σ type ones. The red shift of the aniline−furan complex apparently deviated from this correlation curve and is close to that of the NH-π type aniline complex cation. This fact also suggests that the aniline−furan complex cation should be an NH-π type complex.

The frequency shifts were estimated using the Gaussian 94 calculation program. The frequency shifts of the two stable isomers, NH-π type and NH-σ type hydrogen-bonded complex cations, were calculated with the UHF/6-31G** basis set. This basis set gave a relatively good estimate for the red shifts of the NH_2 stretching vibrations of the aniline complex cations, although the energy is unreliable. Figure 8 and Table 3 summarize the results of the calculation. It is apparent that the calculation assuming the NH-π type complex reproduces the experimental vibrational frequencies much better than that for the NH-σ type one.

TABLE 3: Observed and Calculated Frequency Shifts of the NH_2 Stretching Vibrations of the Aniline−Furan Complex Cation[a]

	obsd		calcd frequency shifts[b]	
			NH-π	NH−O
	ν	$\Delta\nu$	Figure 4a	Figure 4b
ΔE^c			2960	3860
$\Delta\nu_A{}^d$	3446	42	33.7	44.3
$\Delta\nu_S{}^d$	3315	81	75.8	157.9

[a] Unit is cm^{-1}. [b] UHF/6-31G** basis set was used. No correction was done for the calculated frequency shifts. [c] $\Delta E = E_{\text{aniline−cation}} + E_{\text{furan}} - E_{\text{cluster}}$. No correction for the calculated interaction energy was made. [d] See text for the definition of the red shifts of $\Delta\nu_A$ and $\Delta\nu_B$.

The bandwidth of the 3315 cm^{-1} band was found to be as large as 50 cm^{-1}. Since the cation complex is not as cold as the neutral complex, due to the excess energy on ionization, the bandwidth tends to be larger than that of the neutral complex. This can be estimated from the bandwidth of the 3446 cm^{-1} band, and the original bandwidth may be about 30 cm^{-1}. This is comparable to that observed in the bandwidth of the NH stretching band of the interacting NH bond of the neutral aniline−NH_3 and aniline−triethylamine complexes whose red shifts are also 68 and 94 cm^{-1}.

Different Interaction Types of the Neutral and Cation Complexes. The main interaction in the neutral aniline−furan complex has been found to be the NH-σ type hydrogen bond, while that of the complex cation is of the NH-π type. Furan has two acceptor sites, the lone pair of the oxygen atom and the aromatic ring. In the case of the neutral complex, the weaker interaction between the CH bond of furan and the lone pair of the N atom of aniline seem to determine the structure. On the other hand, the interaction between the CH bond of aniline and the lone pair of the oxygen atom of furan determine the stable structure of the complex cation. From these facts, the stabilization energy of the NH-σ type and NH-π type interactions seem to be about the same, and a relatively weak interaction determines the structure of the complex.

It is interesting to note that this complex shows the opposite tendency to that of the aniline dimer.[13] In the case of the aniline dimer, the NH-π type and the NH-σ type hydrogen bond were observed for the neutral and cation complexes, respectively. The difference between these two systems is due to the number of hydrogen bonds available for the complex formation. There are two NH_2-π type hydrogen bonds in the neutral dimer, and the sum of the interaction energy exceeds the interaction energy of a single NH-σ type hydrogen bond. In the case of the dimer cation, only the aniline cation acts as the proton donor because the aniline cation is planer and its acidity is much stronger than that of neutral aniline. In this case the interaction energy of the NH-σ type interaction seems to be larger than that of the NH-π type interaction from the experimental fact.

Red Shift of NH Stretching Modes of the NH-π Type Complexes. The aniline−furan complex cation has been found to be the third example of the NH-π type hydrogen-bonded complex. It is interesting that all of the complex cations of this class (aniline−furan, aniline−pyrrole, and aniline−benzene) give the same frequency red shift of $\Delta\nu_S \sim 80$ cm^{-1} and $\Delta\nu_A \sim 40$ cm^{-1}. In the case of the NH-σ type complex cation, the frequency shift of $\Delta\nu_A$ shows a linear correlation with the proton affinity of the acceptor molecule (Figure 7). Since the proton affinity of furan is different from that of benzene and pyrrole, there should be a significant difference in the frequency shifts if a similar rule is expected for the NH-π type complex cations. The nature of the NH-π type complexes seems to be quite different from that of the NH-σ type complexes as far as the frequency shift of the NH stretching mode is concerned.

A similar tendency was also found in the neutral NH-π type complexes and seems to be a general tendency of the NH-π type complexes, or the aniline complex with a molecule with an aromatic ring. The reason for the constant frequency shift is not well understood yet. To clarify this, more experimental results about the NH-π type complexes with weaker interaction seem to be necessary.

Conclusions

The structures of the aniline−furan complex and the aniline−furan complex cation have been investigated using the vibrational spectra of the NH_2 stretching vibrations observed by the infrared depletion spectroscopy.

The main interaction in the neutral complex has been found to be the NH-σ type hydrogen bond interaction, while that of the complex cation is of the NH-π type interaction.

The frequency shift of the neutral complex was as small as 12 cm^{-1}, which suggests that the basicity of furan is weak. The frequency shifts of the NH stretching modes of the aniline−furan cation is about the same as that of the aniline−pyrrole or the aniline−benzene cation. The feature of the frequency shift of the NH-π type complex cation is significantly different from that of the NH-σ type complex.

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