IR Spectroscopy of Hydrogen-Bonded 2-Fluoropyridine−Methanol Clusters

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The electronic and infrared spectra of 2-fluoropyridine−methanol clusters were observed in a supersonic free jet. The structure of hydrogen-bonded clusters of 2-fluoropyridine with methanol was studied on the basis of the molecular orbital calculations. The IR spectra of 2-fluoropyridine−$(CH_3OH)_n$(n = 1−3) clusters were observed with a fluorescence-detected infrared depletion (FDIR) technique in the OH and CH stretching vibrational regions. The structures of the clusters are similar to those observed for 2-fluoropyridine−$(H_2O)_n$(n = 1−3) clusters. The existence of weak hydrogen bond interaction through aromatic hydrogen was observed in the IR spectra. The theoretical calculation also supports the result. The vibrational frequencies of CH bonds in CH_3 group are affected by hydrogen bond formation although these bonds do not directly relate to the hydrogen bond interaction. The B3LYP/6-311++G(d,p) calculations reproduce well the vibrational frequency of the hydrogen-bonded OH stretching vibrations. However, the calculated frequency of CH stretching vibration could not reproduce the IR spectra because of anharmonic interaction with closely lying overtone or combination bands for ν_3 and ν_9 vibrations. The vibrational shift of ν_2 vibration is reproduced well with molecular orbital calculations. The calculation also shows that the frequency shift of ν_2 vibration is closely related to the CH bond length at the trans position against the OH bond in hydrogen-bonded methanol.

Introduction

To understand the molecular interaction between molecules is a key to clarify chemical phenomena. Especially, a hydrogen bond is one of the most important intermolecular interactions to control chemical phenomena. Hydrogen bond also controls the structure of flexible molecule such as biological molecules. Pyridine is one of basic aza-aromatic molecules, and its derivatives exist widely in the biological systems. Therefore, it is very important to understand the nature of hydrogen bond interaction of pyridine derivatives to clarify the role of hydrogen bond interaction in the chemical systems. It is very important to understand the nature of pyridine molecule, however, the quantum yield of pyridine is too small to observe with laser-induced fluorescence (LIF) spectroscopy. As shown in previous papers, we have found that the pyridines substituted by fluorine atom fluoresce in the gas phase.[1,2] We also showed the electronic[1] and IR[2] spectra of 2-fluoropyridine (2-FP) clusters with water molecule. As the pyridine derivatives has hydrogen bond interaction through the nonbonding orbital of the ring, it is interesting to study the hydrogen-bonded cluster of 2-FP to understand the nature of hydrogen bond interaction through the nonbonding orbital. The present paper shows a study of 2-FP−$(CH_3OH)_n$ clusters. We focus not only on the OH bond that is directly related to hydrogen bond interaction but also on CH bonds in methyl group under hydrogen bond interaction.

For methanol clusters, Zwier and co-workers studied the IR spectra of benzene−$(CH_3OH)_n$ clusters and analyzed with molecular orbital calculations.[3,4] They showed that the frequencies of CH stretching vibrations in the methyl group sensitively shift as the circumstances around the methyl group under hydrogen bond interaction change. The hydrogen bond interaction of benzene−methanol is relatively weak because a methanol molecule interacts with π cloud of the benzene ring, which is considered to behave as a weak proton acceptor.

Halonen[5] analyzed the normal vibration of methanol molecule precisely and showed that the ν_3 and ν_9 vibrations are strongly mixed with lower lying vibrations through anharmonic coupling. However, the ν_2 vibration could be considered as a pure CH stretching vibration. In the present study, the electronic and IR spectra of hydrogen-bonded 2-FP are observed and analyzed on the basis of the molecular orbital calculations. The hydrogen bond effect on the OH and CH stretching vibrations of methanol is also discussed. Because methanol is one of the simplest aliphatic molecules, it is very interesting to understand CH stretching vibrations in methyl group, which is not related to the hydrogen bond interaction, with hydrogen bond formation.

Experiment and Molecular Orbital Calculation. The experimental setup for the observation of fluorescence excitation spectrum in a supersonic jet is the same as reported elsewhere[6] and is mentioned briefly. 2-FP stored in the nozzle housing was expanded into the vacuum chamber with 4 atm of He gas. The vacuum chamber was evacuated with a 6-in. oil diffusion pump, which is backed up by a rotary pump. A tunable UV laser radiation was obtained with a frequency doubled dye laser (Spectra Physics PDL-II), which was excited by a frequency tripled Nd:YAG laser (Spectra Physics INDI-50). The UV laser radiation was introduced into the vacuum chamber and was focused with a lens of 50-cm focal length. The UV laser radiation was focused 10 mm downstream from the nozzle exit, and the induced fluorescence was detected with a photomultiplier (R-928, Hamamatsu Photonics). A tunable IR laser pulse was generated with a differential harmonic generation (DFG) between the fundamental light of a Nd:YAG laser (Spectra Physics GCR-130) and the output of a dye laser (LAS, FL2005) that is simultaneously excited by the frequency doubled Nd:

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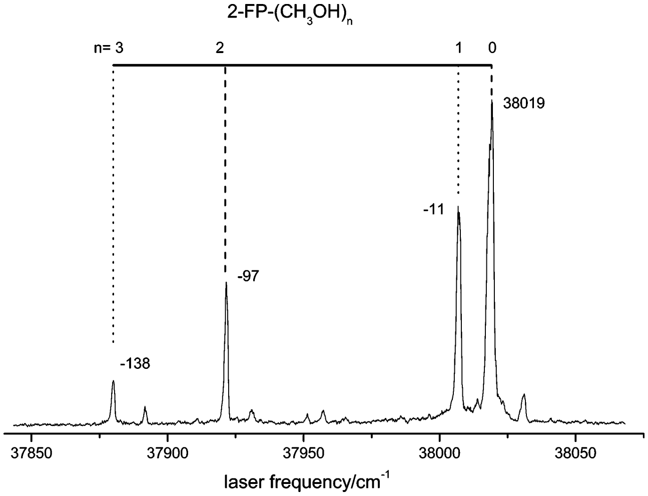

Figure 1. Fluorescence excitation spectrum of 2-fluoropyridine in a supersonic free jet expanded with methanol vapor seeded in 4 atm of He gas. The band at 38019 cm^{-1} is assigned to the band origin of bare 2-fluoropyridine.

YAG laser in LiNbO$_3$ crystals (Inrad, Autotracker III). The tunable IR radiation was introduced from the counter propagating direction against the UV laser. The IR laser radiation was introduced into the vacuum chamber 50 ns prior to the UV laser radiation. The IR spectrum of a cluster was detected as the decrease of LIF intensity because of the vibrational transition induced by the tunable IR laser radiation. Fluorescence intensity was accumulated with a boxcar integrator and was analyzed with a computer.

Molecular orbital calculations were carried out with Gaussian 98[7] and Gaussian 03[8] program packages at the computer centers of Fukuoka University and Kyushu University, respectively. The optimized structures and scaled vibrational frequencies of 2-FP−(CH$_3$OH)$_n$ ($n = 1-3$) clusters were obtained through the density functional theory with B3LYP functional. The 6-311++G(d,p) basis set was used for these calculations. The scaling factor of 0.9567 was determined to reproduce the experimental value of the OH stretching frequency of bare methanol. The stabilization energies to form the clusters were corrected with zero-point vibration and the basis set superposition error (BSSE) corrections with the counterpoise method.[9]

Results and Discussion

LIF Spectrum of 2FP−Methanol Clusters. Figure 1 shows the fluorescence excitation spectrum of 2-FP expanded with methanol vapor. The band origin of bare 2-FP molecule is observed at 38019 cm^{-1}. As reported in the previous paper, this band origin is the only one observed[1] without hydrogen bond forming molecules such as water or methanol. Therefore, the bands observed in the lower frequency side from the band origin are assigned to the band due to hydrogen-bonded clusters of 2-FP with methanol. In case of water molecule, the band origins of 2-FP-(H$_2$O)$_n$ ($n = 1-3$) clusters were observed at −4, −74, and −120 cm^{-1} from the band origin of bare molecule, respectively. In the 2-FP−methanol clusters, the bands at −11, −97, and −138 cm^{-1} are assigned to be due to 2-FP−(CH$_3$OH)$_n$ ($n = 1-3$) clusters, respectively, because the methanol molecule behaves as a proton donor as in the case of water clusters. The validity of the assignment will be ensured by the results of IR spectra of the clusters. The values of red shifts of these band origins of 2-FP−methanol clusters are larger than those of corresponding 2-FP−water clusters. This fact clearly indicates that the hydrogen-bonded cluster with methanol is stabilized in the electronically excited state in comparison with 2-FP−water cluster.

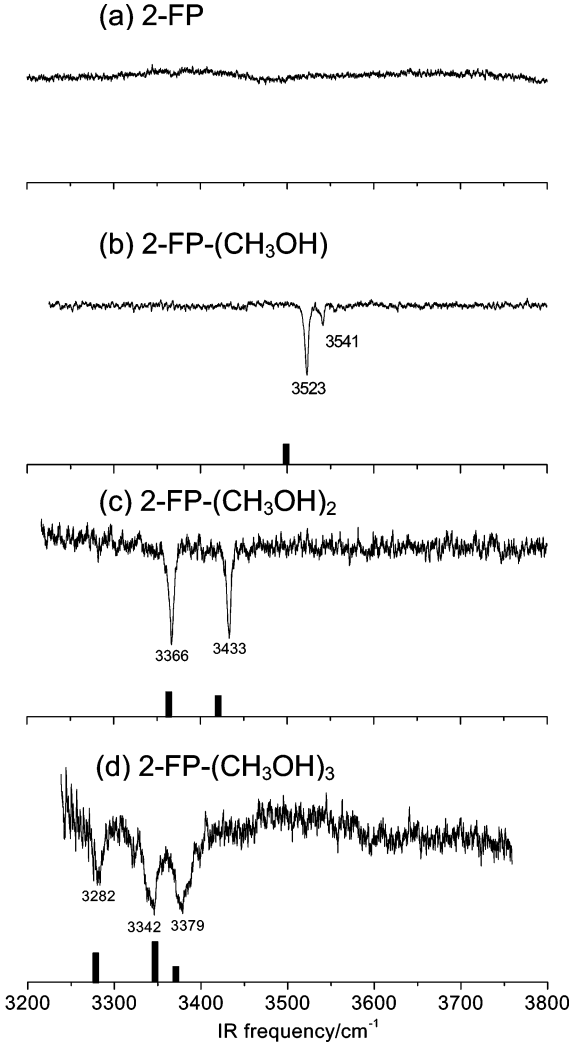

Figure 2. IR spectra of bare and hydrogen-bonded 2-fluoropyridine with fluorescence-detected IR depletion spectroscopy. (a) The band origin of bare 2-fluorpyridine is probed. The bands at (b) −11 cm^{-1}, (c) −97 cm^{-1}, and (d) −138 cm^{-1} from the band origin of bare 2-fluoropyridine were probed.

OH Stretching Vibrations. Figure 2 shows the IR spectra of 2-FP−methanol clusters in the OH stretching region probed at the three bands strongly observed in the LIF spectrum in Figure 1. Figure 2a shows the IR spectrum for bare 2-FP for comparison. No band is observed as expected from the molecular structure. In Figure 2b, the band at −11 cm^{-1} from the band origin of bare molecule, which is assigned to the band origin of 2-FP−(CH$_3$OH) cluster, is probed, and a very strong peak at 3523 cm^{-1} is clearly observed. The band observed weakly in the higher frequency side with 18 cm^{-1} from the strong peak might be assigned to a combination band of OH stretching and an intermolecular vibration or to a band induced with Fermi resonance with the OH stretching vibration. In the LIF spectrum, shown in Figure 1, a weak band is observed at the higher frequency side of band origin of bare 2-FP. The band is assigned to intermolecular vibration of 2FP−(CH$_3$OH) from the UV−UV hole burning spectroscopy probed with the band at −11 cm^{-1} from the band origin of bare 2-FP. The frequency of the intermolecular vibration is 23 cm^{-1} in the electronic excited state. The small red shift of the band origin from bare 2-FP and the strong intensity in band origin for the electronic transition of 2-FP−(CH$_3$OH) cluster anticipate that the structure

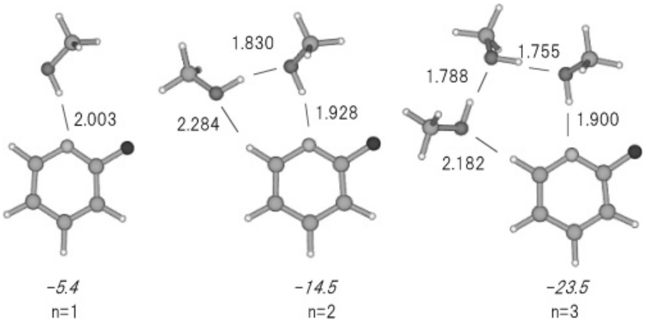

Figure 3. Calculated structure of 2-fluoropyridine−methanol clusters with B3LYP/6-311++G(d,p) level. The stabilization energies of the clusters were corrected with zero-vibration and basis set superposition error and are shown in kcal/mol. The bond distances are shown in Å unit.

and vibrational frequency are similar both in the electronic ground and excited states. Therefore, the band at 3541 cm^{-1} could be assigned to a combination band of the OH stretching and an intermolecular vibrations.

The OH stretching vibration of bare methanol[5] is 3681.5 cm^{-1} in the vapor phase, and the frequency decrease with hydrogen bond to 2-FP is 158.5 cm^{-1}. The red shift of the frequency is much larger than that of benzene−methanol[3,4] of 42 cm^{-1}, where a methanol molecule bonds to π electron cloud on the benzene ring. If the methanol molecule in the 2-FP−methanol cluster bonds to the π cloud of the pyridine ring, the frequency shift might be similar to that of benzene−methanol cluster. The larger frequency shift in 2-FP−methanol cluster means the existence of stronger interaction than that in benzene−methanol cluster. Figure 3 shows the optimized structure of 2-FP−methanol clusters obtained with the B3LYP/6-311++G(d,p) calculations. The stabilization energies with basis set superposition error (BSSE) and zero-point energy corrections are also given. For 2-FP−(CH$_3$OH)$_1$, the structure where the OH bonds to F atom is also obtained as a stable structure. However, the stabilization energy for the F-bonded cluster, 1.44 kcal/mol with zero-point and BSSE correction, is smaller than that of the one shown in Figure 3. Furthermore, the vibrational frequency calculation for the F-bonded cluster gives a very small red shift, less than 1 cm^{-1}, for the OH-stretching vibration, and does not reproduce the experimental result. Therefore, the methanol molecule bonds to the nitrogen atom of the pyridine ring for the 2-FP−(CH$_3$OH)$_1$ cluster. For the higher clusters, methanol molecules bond to the 2-FP−(CH$_3$OH)$_1$ cluster, consecutively.

Figure 2c shows that the spectrum probed the band at −97 cm^{-1} from the band origin of bare 2-FP. Two strong absorption bands are clearly observed at 3366 and 3433 cm^{-1}. This fact clearly indicates that the bands at −97 cm^{-1} from the band origin of bare 2-FP in the electronic spectrum is due to 2-FP−(CH$_3$OH)$_2$ because the structure has two hydrogen-bonded OH groups whose stretching frequencies are considerably lower than that of bare one. From the B3LYP/6-311++G(d,p) calculation for 2-FP−(CH$_3$OH)$_2$, the lower vibrational mode is mainly due to the OH bond of the first methanol (refer to methanol(I) hereafter) that directly bonds to the nitrogen atom of the pyridine ring and the higher one to the second methanol (refer to methanol(II) hereafter) that bonds to the oxygen atom of methanol(I). Huisken et al.[10] and Provencal et al.[11] measured the OH stretching frequencies of pure methanol dimer and reported 3684 and 3574 cm^{-1} for OH stretching vibrations for hydrogen bond acceptor and donor, respectively. In case of methanol dimer, the OH bond that behaves as proton acceptor is free from direct hydrogen bond interaction. In 2FP−(CH$_3$OH)$_2$, the OH stretching vibration of the methanol(II) corresponds to the donor OH stretching vibration in pure methanol dimer. The frequency of OH stretching of the second methanol, 3433 cm^{-1}, is much lower than that of the pure dimer, 3574 cm^{-1}. This OH stretching frequency difference between 2FP−(CH$_3$OH)$_2$ and (CH$_3$OH)$_2$ indicates that the second methanol reorganizes the existence of the hydrogen bond of the first methanol. The donor OH stretching frequencies of methanol(II) in X−(CH$_3$OH)$_2$ cluster are in the range between 3486 and 3506 cm^{-1} for X = benzene,[3,4] fluorobenzene,[12,13] and *p*-difluorobenzene,[13] where the first methanol molecules bond to π electrons or fluorine atoms. As seen from Figure 2c, the OH stretching vibrational frequency of methanol(II) is 3433 cm^{-1}. This fact clearly shows that the oxygen atom of a methanol molecule becomes a stronger proton acceptor when the OH bond has stronger hydrogen bond interaction as a proton donor.

Figure 2d shows the IR spectrum of 2-FP−(CH$_3$OH)$_3$ cluster. As expected from the structure of the cluster, three strong bands are clearly observed at 3282, 3342, and 3379 cm^{-1}. The vibrational mode calculation of the cluster shows that the highest frequency is mainly due to the edge methanol (refer to methanol(III) hereafter) of the cluster. The frequency shifts of the OH stretching vibrations for methanol(I), (II), and (III) of 2-FP−(CH$_3$OH)$_{1,2,3}$, from the bare one are −159, −248, and −302, cm^{-1}, respectively, if the highest frequency vibrations originate purely from methanol molecules at the edge. As the values of red shifts for these OH stretching frequencies reflect the hydrogen bond interaction of methanol, the larger shift indicates the stronger hydrogen bond interaction. The vibrational calculations indicate that the vibrational mode at highest frequency mainly originates from the methanol molecule at the edge in the clusters. Therefore, the OH stretching vibrations of edge methanol in 2-FP−(CH$_3$OH)$_{3,2,1}$ reflect the proton affinity of 2-FP−(CH$_3$OH)$_{2,1,0}$ clusters, respectively. This fact clearly shows that the increase of methanol molecules in the clusters enlarges the microscopic proton affinity of the oxygen atom in the clusters.

The red shifts of lowest OH stretching vibrations of 2-FP−(CH$_3$OH)$_n$ from bare CH$_3$OH are −159, −316, and −400 cm^{-1} for 1:1, 1:2, and 1:3 clusters, respectively. For benzene−(CH$_3$OH)$_n$ clusters,[3,4] the shifts of the lowest frequencies of benzene−(CH$_3$OH)$_n$ clusters are −42, −175, −292, −477, −510, and −504 cm^{-1} for $n = 1-6$, respectively. Pribble et al.[3] showed that the IR bandwidth of benzene−(CH$_3$OH)$_n$ ($n = 4-6$) considerably increases compared with those of $n = 1-3$. They claimed that the change of bandwidth is due to the strengthened hydrogen bond interaction as the structural change of clusters from chain structure for $n = 1-3$ to ringed structure for $n > 3$. As seen from Figure 2, the bandwidth of 2-FP−(CH$_3$OH)$_3$ considerably increases compared with those of 2-FP−(CH$_3$OH)$_1$ and 2-FP−(CH$_3$OH)$_2$. The hydrogen bond interaction between 2-FP and methanol is larger than that between benzene and methanol. Therefore, it is reasonable that the band broadening for 2-FP−methanol clusters occurs in smaller cluster size than that in benzene−methanol clusters. These broadenings of methanol-containing clusters are also observed for benzonitrile−methanol clusters[14] where the broad bands are observed for benzonitrile−(CH$_3$OH)$_3$ although the sharp band profile is observed for 1:1 and 1:2 clusters. As benzonitrile interacts with methanol more strongly than benzene does, it is concluded that stronger interaction gives band broadening in the smaller clusters.

The larger shifts of bonded OH stretching vibration of 2-FP−(CH$_3$OH)$_{2,3}$ than those of 2-FP−(H$_2$O)$_{2,3}$ are understood as a

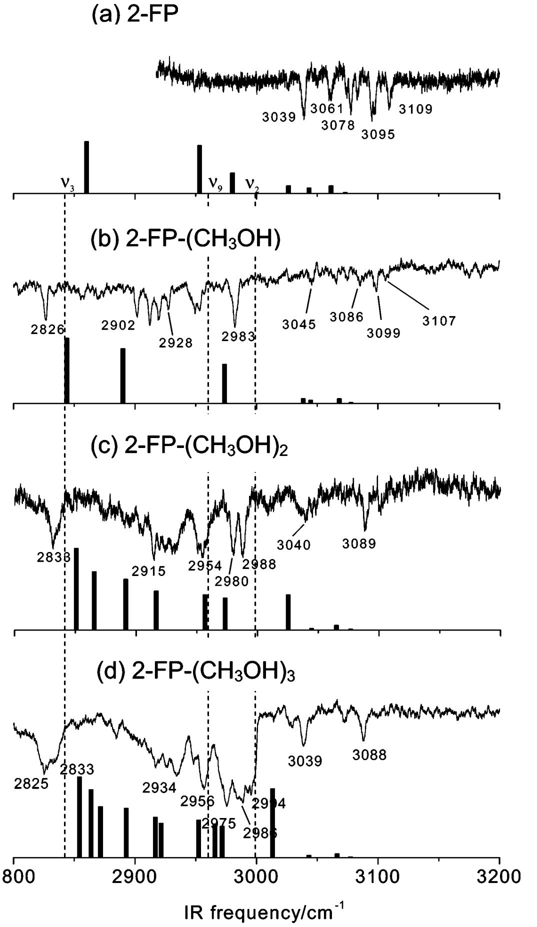

Figure 4. Observed and calculated IR spectra of 2-fluoropyridine−methanol clusters for CH stretching vibrational region. The CH stretching vibrations of pyridine ring and methyl group appear above and below 3000 cm^{-1}, respectively. (a) The band origin of bare 2-fluoropyridine is probed. The calculated intensity of bare methanol and bare 2-FP is shown. The bands at (b) −11 cm^{-1}, (c) −97 cm^{-1}, and (d) −138 cm^{-1} from the band origin of bare 2-fluoropyridine were probed. The observed frequencies for bare methanol ν_2, ν_3, and ν_9 are indicated with dotted lines. The length of the bars indicates the calculated absorption intensity in km/mol.

result of the larger proton affinity of CH$_3$OH than that of H$_2$O, which has been also an observed result of benzonitrile clusters with CH$_3$OH and H$_2$O.[14]

As can be seen from the figure, the calculated frequency and band intensity reproduce the observed spectra well. This result anticipates that the obtained structure and stabilization energies are reliable. This result also indicates that the molecular orbital calculation with B3LYP/6-311++G(d,p) level represents the hydrogen bond interaction between 2-FP and methanol.

CH Stretching Vibrations. Figure 4 shows the IR spectra of 2-FP−methanol clusters in the frequency region from 2800 to 3200 cm^{-1}, where CH stretching vibrations are expected. Figure 4a gives the IR spectra of bare 2-FP as a reference. The existence of four CH bonds for bare 2-FP might give four vibrational transitions in this region. However, the anharmonic coupling of CH stretching vibrations with overtone or combination bands causes an excess number of bands in this region as expected. In the frequency region higher than 3000 cm^{-1}, the band structure of 2-FP−(CH$_3$OH)$_1$ resembles that of bare 2-FP. However, the band structures of 2-FP−(CH$_3$OH)$_{2,3}$ are different from those of bare 2-FP and 2-FP−(CH$_3$OH)$_1$. As shown in Figure 3, the molecular orbital calculations of the methanol clusters predict the short distance of CH···O in 2-FP−(CH$_3$OH)$_{2,3}$ clusters. This fact anticipates the interaction between a CH and an O in the clusters. Actually, the calculations also show that the CH stretching vibration at the sixth position increases in infrared intensity with cluster formation for 2-FP−(CH$_3$OH)$_{2,3}$.(Table 1) This type of interaction was also observed in 2-FP−(H$_2$O)$_{2,3}$ clusters.[2] In the hydrated clusters, the vibrational structure of 2-FP−(H$_2$O)$_1$ is similar to that of bare 2-FP. However, the vibrational structures of 2-FP−(H$_2$O)$_{2,3}$ are different from those of bare 2-FP and 2-FP−(H$_2$O) and the vibrational structures of 2-FP−(H$_2$O)$_{2,3}$ resemble each other. These results support the calculated structures of 2-FP−(CH$_3$OH)$_{2,3}$ clusters, where an oxygen atom of methanol interacts with aromatic hydrogen at the sixth position in the pyridine ring. Several workers have observed the hydrogen bond interaction between an aromatic CH and a water molecule previously.[15−19] This means that the molecule that includes OH bond such as water or methanol has a possibility of hydrogen bond interaction with aromatic hydrogen. Although the interaction is weak, however, it might play an important role to determine the molecular structure of flexible molecule such as biomolecules. Our molecular orbital calculations of pyridine−water clusters, which have been carried out with B3LYP/6-31G(d,p) level, also indicate the existence of this type of interaction. Therefore, the weak hydrogen bond interaction between the O atom and CH in aromatic ring probably occurs for pyridine and pyridine derivatives even in the condensed phase.

The bands observed lower than 3000 cm^{-1} are assigned to CH stretching vibrations of methyl groups. The observed frequencies of bare methanol assigned by Halonen[5] are shown in Figure 4 with dotted lines. The band at 2983 cm^{-1} is assigned to ν_2 vibration of 2-FP−(CH$_3$OH)$_1$ (Figure 4b). The frequency shift from bare methanol is −16 cm^{-1}, which is slightly larger than that of benzene−(CH$_3$OH)$_1$ cluster, −12 cm^{-1}. One of the bands observed at 2949 and 2953 cm^{-1} could be assigned to ν_9, which has not been observed for benzene−(CH$_3$OH)$_1$ cluster. The ν_2 vibrations of 2-FP−(CH$_3$OH)$_{2,3}$ split into two and three bands depending on the number of methanol molecules in the clusters. These splittings of ν_2 vibrations are also supported with the molecular orbital calculations as shown in Table 1. However, the calculation of ν_3 and ν_9 does not reproduce the spectral frequency shift properly. For ν_3 and ν_9 vibrations, the calculation anticipates the similar splitting as ν_2 vibration. However, for 2-FP−(CH$_3$OH)$_{2,3}$, as seen from Figure 4c and d, the splitting is unclear because of the relatively broader band structure in the ν_3 region for 2FP−methanol clusters. The disagreement between the experimental results and calculations for ν_3 and ν_9 vibrations could be ascribed to anharmonic coupling of the vibrations with other vibrational levels in methanol.[5] As the vibrational calculations for the clusters have been carried out under harmonic oscillator approximation, it is not adequate to discuss about the relatively small frequency shift for ν_3 and ν_9 with hydrogen bond formation.

For ν_2, these anharmonic perturbations are relatively small and the mode could be treated as pure CH stretching vibration.[5] Therefore, the hydrogen bond effect on the CH stretching vibrations could be discussed for the ν_2 vibration of the clusters on the basis of molecular orbital calculations. The vibrational mode of ν_2 concentrates mainly on the CH bond stretching at the trans position against the OH bond in methanol. For 2-FP−(CH$_3$OH)$_{2,3}$ clusters, the vibrational calculations show that the ν_2 vibrations localize on each methyl group. As shown in Table 1, the vibrational mode of the highest frequency of ν_2 localized only on the methyl group of the methanol that directly bonds to the pyridine ring. Gruenloh et al.[4] also reported a similar

TABLE 1: Observed and Calculated Vibrational Frequencies of 2-Fluoropyridine−$(CH_3OH)_n$ Clusters for OH and CH Stretching Vibrational Region (cm^{-1})

	$n = 0^a$		$n = 1$		$n = 2$		$n = 3$	
assignment	observed[b]	calculated[c]	observed	calculated[c]	observed	calculated[c]	observed	calculated[c]
OH stretching	3682	3682 (30)	3541		3433	3420 (766) II−I	3349	3369 (565) III
			3523	3499 (728)	3366	3364 (902) I+II	3342	3345 (1407) I−II
							3282	3283 (1052) II+I
CH stretching (aromatic)	3109	3072 (1)	3107	3075 (1)	3101	3075 (1)	3088	3075 (1)
	3097	3062 (10)	3099	3067 (6)	3089	3065 (6)	3073	3066 (5)
	3095	3042 (7)	3086	3046 (4)	3045	3044 (2)	3039	3043 (3)
	3083	3028 (10)	3075	3039 (2)	3040	3022 (47)	3028	3012 (92)
	3078		3066					
	3074		3045					
	3061							
	3050							
	3039							
	3026							
CH stretching (methyl group)	2999	2978 (27) ν_2	2983	2957 (52) ν_2	2988	2970 (43) ν_2I	2994	2971 (42) ν_2I
			2953	2886 (73) ν_9	2980	2956 (47) ν_2II	2986	2966 (44) ν_2II
			2949		2954		2975	2952 (50) ν_2III
	2959	2905 (64) ν_9	2928		2932	2916 (52) ν_9I	2956	2923 (46) ν_9I
			2920		2924	2892 (68) ν_9II	2934	2915 (54) ν_9II
			2912		2919		2926	2893 (66) ν_9III
	2843	2861 (69) ν_3	2902		2915	2866 (78) ν_3I	2917	2871 (68) ν_3I
			2826	2846 (87) ν_3	2833	2851 (109) ν_3II	2884	2866 (99) ν_3II
							2833	2852 (108) ν_3III
							2825	

[a] Values for bare CH_3OH and 2-fluoropyridine. [b] Taken from ref. 5 for bare methanol. [c] Calculated with B3LYP/6-311++G(d,p). The numbers in parentheses give absorption intensity in km/mol unit. I, II, III refer to the methanol from the pyridine side in order. + and − represent relative phase of the OH steretching vibrations.

TABLE 2: Structural and Frequency Changes of Methyl Group in 2-FP−$(\text{Methanol})_n$ Clusters

cluster	methanol position[a]	type of CH bond[b]	$r_{CH}{}^c$	$\Delta r_{CH}{}^c$	$\nu_2{}^{\text{calcd } d}$	$\Delta\nu_2{}^{\text{calcd } d}$	$\nu_2{}^{\text{obsd } d}$	$\Delta\nu_2{}^{\text{obsd}}$
$n = 0$		$\mathrm{r_t}$	1.0902	0.0000	2978	0	2999	0
		$\mathrm{r_g}$	1.0969	0.0000				
		$\mathrm{r_g}$	1.0969	0.0000				
$n = 1$	I	$\mathrm{r_t}$	1.0917	0.0015	2957	−21	2983	−16
		$\mathrm{r_g}$	1.0985	0.0016				
		$\mathrm{r_g}$	1.0982	0.0013				
$n = 2$	I	$\mathrm{r_t}$	1.0909	0.0008	2970	−8	2988	−11
		$\mathrm{r_g}$	1.0967	−0.0002				
		$\mathrm{r_g}$	1.0966	−0.0003				
	II	$\mathrm{r_t}$	1.0919	0.0017	2956	−22	2980	−19
		$\mathrm{r_g}$	1.0979	0.0010				
		$\mathrm{r_g}$	1.0978	0.0009				
$n = 3$	I	$\mathrm{r_t}$	1.0909	0.0007	2971	−7	2994	−5
		$\mathrm{r_g}$	1.0963	−0.0006				
		$\mathrm{r_g}$	1.0951	−0.0018				
	II	$\mathrm{r_t}$	1.0913	0.0011	2966	−12	2986	−13
		$\mathrm{r_g}$	1.0960	−0.0009				
		$\mathrm{r_g}$	1.0963	−0.0006				
	III	$\mathrm{r_t}$	1.0922	0.0021	2952	−26	2975	−24
		$\mathrm{r_g}$	1.0978	0.0009				
		$\mathrm{r_g}$	1.0977	0.0008				

[a] I, II, and III represent the methanol from the one that bonds directly to the ring, in order. [b] $\mathrm{r_t}$ and $\mathrm{r_g}$ represent the trans and gauche positions in methyl group against the OH bond, respectively. [c] r_{CH} (bare) − r_{CH} (cluster) in Å. [d] $\Delta\nu = \nu_2$ (bare) − ν_2 (cluster). Calculated with B3LYP/6-311++G(d,p).

result for benzene−methanol clusters where the first methanol bonds to π electron cloud of benzene ring. They have shown that the ν_2 shifts depending on the characteristic of hydrogen bonding. Proton donating and accepting interactions of OH group in methanol cause the red and blue shifts of ν_2 bands, respectively. The degree of frequency shifts of 2-FP−$(CH_3OH)_n$ is slightly larger than those of corresponding benzene−$(CH_3OH)_n$ clusters.

Table 2 shows that the change of the calculated CH bond length of the methyl group correlates well with the vibrational frequency shifts with the cluster formation. The molecular structure of methyl group indicates that one of the CH bonds locates at the trans position against the OH bond and two CH bonds locate at gauche positions. As a result, a methanol molecule has one trans CH and two gauche CH bonds against the OH bond. The stable structure of methanol shows that the CH bond length at the trans position is slightly shorter than that of the gauche one with B3LYP/6-311++G(d,p) level, which was also shown by Gruenloh et al.[4] with the B3LYP/6-31+(d) level. This means that the force constant of the trans CH bond is larger than that of the gauche one. The vibrational mode calculation also shows that the vibrational motion of ν_2, whose frequency is the highest among the three CH stretching vibrations of methyl group, is mainly contributed by the stretching motion of the trans CH bond. As seen from Table 2, the changes of the trans CH bond length correlate very well with calculated and observed frequencies. That is, the degree of calculated bond distance correlates very well with the degree of observed and calculated frequency change of ν_2 vibrations. It can be concluded that the hydrogen bond formation changes the CH bond length at the trans position against the OH bond and the vibrational frequency of ν_2 with the small change of electronic distribution. Because the interaction between methanol and nonbonding electrons of 2-FP is stronger than that between methanol and π electrons of benzene, the 2-FP-methanol gives larger frequency shift.

Conclusion

The IR spectra of 2-fluoropyridine and methanol clusters were observed in a supersonic free jet. The comparison between the molecular orbital calculations and the experimental results indicates that the methanol molecule bonds to nitrogen atom of the ring for 2-fluoropyridine−$(CH_3OH)_1$ cluster as observed for its water clusters. For larger clusters, methanol molecules bond consecutively. The molecular orbital calculations for 2-fluoropyridine−$(CH_3OH)_n$ clusters reproduce the vibrational intensity well with B3LYP/6-311++G(d,p) level.

From the band structure of aromatic CH stretching vibrations, the oxygen atom of methanol interacts with aromatic hydrogen at the sixth position of the ring for 2-fluoropyridine−$(CH_3OH)_n$ clusters as observed for water clusters.

For CH stretching vibrations of methanol in the clusters, the frequency shifts of ν_2 vibrations are reproduced well with the B3LYP/6-311++G(d,p) calculations. However, the frequency shifts of ν_3 and ν_9 could not be reproduced properly. This might be due to the anharmonic coupling of ν_2 and ν_9 with combination or overtone vibrations, because these couplings are not taken into account in the calculations.

For 2-fluoropyridine−$(CH_3OH)_{2,3}$, the vibrational mode analyses indicate that each CH stretching vibration of methyl group localized only on the specific methanol molecule. The calculated frequencies of the ν_2 vibrations in the clusters show that the methyl groups belonging to the methanol molecule bonded directly to the pyridine ring have the highest frequencies. The ν_2 vibrations of edge methanol give the lowest frequency in 2-fluoropyridine−$(CH_3OH)_{2,3}$ clusters. This tendency well corresponds to that of benzene−methanol clusters. The vibrational shift of ν_2 and the change of bond length of trans CH bond in the methyl group could be induced with the small change of electron distribution with hydrogen bond formation.

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