

# Infrared Spectroscopy of Hydrogen-Bonded 2-Fluoropyridine–Water Clusters in Supersonic Jets

Yoshinori Nibu,\* Ryosuke Marui, and Hiroko Shimada

Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma 8-19-1, Jyonann-ku, Fukuoka 814-0180, Japan

Received: March 28, 2006; In Final Form: June 7, 2006

The hydrogen-bonded clusters of 2-fluoropyridine with water were studied experimentally in a supersonic free jet and analyzed with molecular orbital calculations. The IR spectra of 2-fluoropyridine–(H<sub>2</sub>O)<sub>n</sub> (*n* = 1 to 3) clusters were observed with a fluorescence detected infrared depletion (FDIR) technique in the OH and CH stretching vibrational regions. The frequencies of OH stretching vibrations show that water molecules bond to the nitrogen atom of 2-fluoropyridine in the clusters. The hydrogen-bond formation between aromatic CH and O was evidenced in the 1:2 and 1:3 clusters from the experimental and calculated results. The overtone vibrations of the OH bending mode in hydrogen-bonded water molecules appear in the IR spectra, and these frequencies become higher with the increase of the number of water molecules in the clusters. The band structure of the IR spectra in the CH stretching region changes depending on the number of coordinating water molecules.

## Introduction

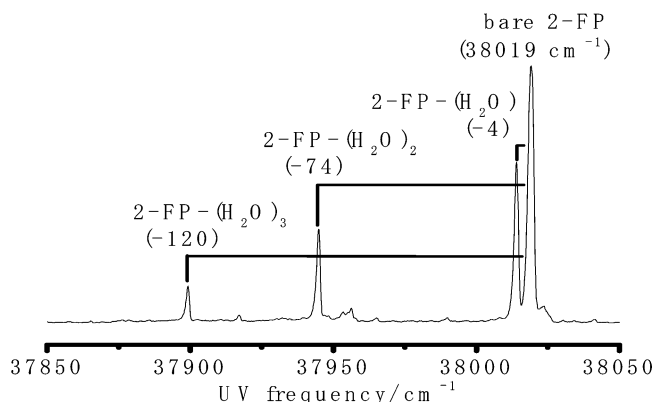
Pyridine is one of the most basic biological molecules, and its derivatives exist widely in biological systems. As pyridine is also one of the simplest aza-aromatic molecules, it is very interesting to study the nature of the pyridine molecule.<sup>1</sup> The pyridine molecule has lone pair electrons on the nitrogen atom in the ring and can behave as a proton acceptor. In real biological systems, hydrogen-bond interactions play a key role in determining the structure of biological molecules. Therefore, it is very interesting to study the cluster structure and electronic effect of hydrogen-bond interactions between pyridine and proton donating molecule, such as water. The study of these clusters under jet conditions clarifies the hydrogen-bond effect from a microscopic standpoint. However, pyridine is nonfluorescent, and therefore, little spectroscopic work has been done on the bare molecule,<sup>2,3</sup> and there are no reports on the electronic spectrum of hydrogen-bonded molecule. In our previous reports, the substitution of pyridine for a fluorine atom has increased the quantum yield, and the LIF spectra of fluorine derivatives of pyridine have been observed for 2-fluoropyridine (2-FP)<sup>4</sup> and 2,6-difluoropyridine<sup>5</sup> under jet conditions. For these molecules, the electronic spectra of hydrogen-bonded clusters with water have been also reported, and the structure of the clusters has been discussed based on the results of the electronic transition and molecular orbital calculations. In recent years, IR spectroscopy of hydrogen-bonded clusters with water<sup>6</sup> under jet conditions has been considerably developed and has provided important information on the cluster structure. Among the many works for hydrated clusters, the IR spectra of phenol–water clusters in jets, whose electronic spectrum was observed first by Abe et al. in jet conditions,<sup>7</sup> have been studied in detail.<sup>8–16</sup> In the phenol–water cluster, the water molecule behaves as a proton acceptor. As to the cluster where water behaves as a proton donor, Mitsui et al. have observed the IR spectra of

acridine–(water)<sub>n</sub> clusters.<sup>17</sup> They have concluded that the first water molecule bonds to the nitrogen atom in the pyridine ring and that the remaining water molecules bond consecutively to form a chain structure with an increasing cluster size. In the previous paper on 2-FP,<sup>4</sup> the molecular orbital calculations have shown the possibility of weak hydrogen-bond interactions between aromatic hydrogen and oxygen atoms from the calculated optimized structures. The hydrogen bonds containing aromatic hydrogen have been already reported in jet conditions by Mikami et al.<sup>18,19</sup> and Brutschy et al.<sup>20–23</sup> In this paper, the IR spectra of hydrogen-bonded 2-FP with water are shown, and the existence of these weak hydrogen-bond interactions is also discussed.

## Experimental and Molecular Orbital Calculations

The experimental setup for the observation of fluorescence excitation spectra in a supersonic jet is the same as reported elsewhere<sup>24</sup> and is mentioned briefly. 2-Fluoropyridine, which is 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 was backed up by a rotary pump. A pulsed nozzle was improved from a fuel injector valve of an automobile.<sup>25</sup> On the tip of the pulsed valve, a thin metal plate with a 0.4 mm hole was glued. 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 focused with a lens of 50 cm focal length. The UV laser radiation was focused at 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 was excited by the frequency doubled Nd:YAG laser, in LiNbO<sub>3</sub> crystals (Inrad, Autotracker III). The tunable

\* Corresponding author. Tel.: 81-92-8716631; fax: 81-92-8656030; e-mail: nibu@fukuoka-u.ac.jp.



**Figure 1.** Fluorescence excitation spectrum of 2-fluoropyridine expanded with water.

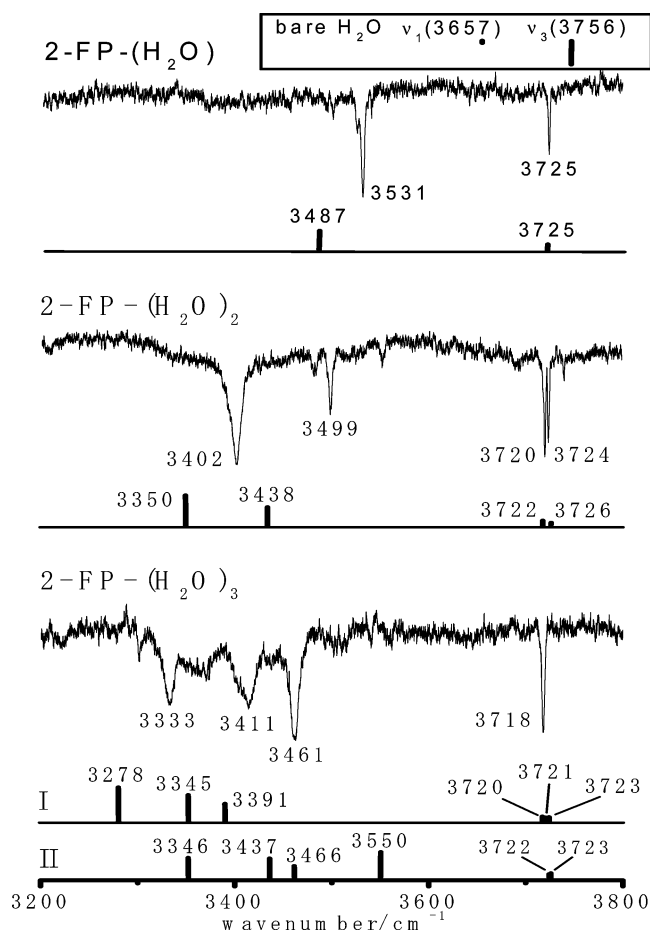
IR radiation was introduced from the counter propagating direction due to the UV laser. The IR laser radiation was introduced into the vacuum chamber 50 ns prior to the UV laser radiation. The IR spectrum of the cluster was detected as the decrease in LIF intensity due to the vibrational transition induced by the tunable IR laser radiation. The fluorescence intensity was accumulated with a boxcar integrator and analyzed with a computer.

Molecular orbital calculations have been carried out with the Gaussian 98<sup>26</sup> and Gaussian 03<sup>27</sup> program packages at the computer centers of Fukuoka University and Kyushu University, respectively. The optimized structures and vibrational frequencies of the 2-FP-(H<sub>2</sub>O)<sub>n</sub> (*n* = 1–3) clusters were obtained through density functional theory with B3LYP functional and MP2 calculations. The 6-311++G(d,p) basis set was used for these calculations. For the optimized structures of the clusters, the vibrational frequencies were also calculated except for the MP2/6-311++G(d,p) calculation of 2-FP-(H<sub>2</sub>O)<sub>3</sub> because the calculation was too heavy to be carried out with our system. The stabilization energies to form the clusters were corrected with zero-point vibration, and the basis set superposition error (BSSE) corrections were fixed with the counterpoise method.<sup>28</sup> A portion of the calculated results and a detailed discussion of the cluster structures were reported in the previous paper.<sup>4</sup>

## Results and Discussion

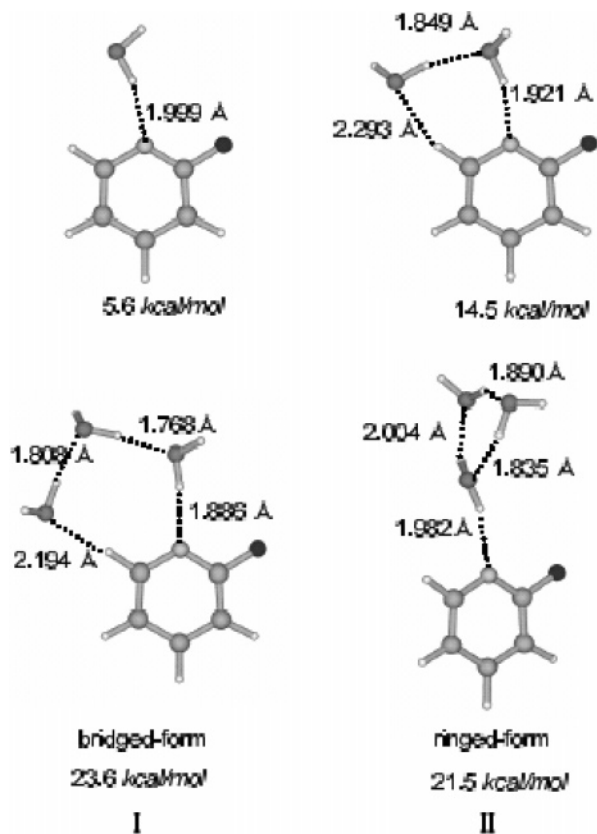
**Fluorescence Excitation Spectrum.** Figure 1 shows the fluorescence excitation spectrum when 2-FP was expanded into the vacuum chamber together with water vapor. All bands other than 38 019 cm<sup>-1</sup> are gone in the absence of water.<sup>4</sup> Therefore, the bands observed in the lower frequency side are assigned to the bands due to the hydrogen-bonded 2-FP clusters with water. The assignment of the clusters has been done based on the band intensity dependence on the concentration of water.<sup>4</sup> These three strong bands were probed to observe the FDIR spectra of these clusters.

**IR Spectra for OH Stretching Vibrational Regions.** Figure 2 shows the IR spectra of hydrogen-bonded clusters in a OH stretching vibrational region together with the calculated result of the B3LYP/6-311++G(d,p) level. The calculated structures of the clusters with the B3LYP/6-311++G(d,p) level are shown in Figure 3. The MP2/6-311++G(d,p) calculations also give similar structures for the clusters. Calculated frequencies have been corrected with a scaling factor of 0.9577 and are shown as bars with the results of experiments. The length of a bar indicates the absorption intensity. The value of the scaling factor is determined to reproduce the frequencies of symmetric and anti-symmetric OH stretching vibrations of bare water observed



**Figure 2.** Fluorescence detected IR dip spectra of 2-fluoropyridene-(H<sub>2</sub>O)<sub>n</sub> clusters (a) *n* = 1, (b) *n* = 2, and (c) *n* = 3 in the OH stretching vibrational region. I and II in the 2-FP-(H<sub>2</sub>O)<sub>3</sub> cluster correspond to the calculated spectra of bridged and ringed forms, respectively. The bars at upper side of panel a express the experimental band positions due to bare water molecules.

in the vapor phase.<sup>29</sup> The IR laser intensity lower than 3300 cm<sup>-1</sup> decreased gradually because of the intensity drop of the dye laser used to obtain the IR radiation. The IR intensity around 3500 cm<sup>-1</sup> was also very weak because of the absorption due to an OH group existing in the LiNbO<sub>3</sub> crystal. In Figure 2a, the IR spectrum of the 1:1 cluster is shown. Two strong bands are clearly observed at 3531 and 3725 cm<sup>-1</sup> and assigned to the OH stretching vibrations originating from the water molecule in the cluster because the IR spectrum of bare 2-FP has no absorption band in this region. For bare water, symmetric and anti-symmetric OH stretching vibrations were observed at 3657 and 3757 cm<sup>-1</sup> in the gas phase,<sup>29</sup> respectively, as shown in the upper side of Figure 2a. The band intensity of the anti-symmetric OH stretching vibration is stronger than that of the symmetric one in the IR spectrum of the bare water molecule. As shown from Figure 2a, the band in the lower frequency is stronger than that in the higher one. The band at 3531 cm<sup>-1</sup> in the 1:1 cluster is correlated to the band at 3657 cm<sup>-1</sup> that is assigned to the symmetric OH stretching vibration in a bare water molecule. The two OH bonds in the hydrogen-bonded water molecule are not equivalent any more, and therefore, they are better to be assigned to hydrogen-bonded and free OH stretching vibrations in the cluster. The red shift of 126 cm<sup>-1</sup> from the symmetric stretching vibration of the bare molecule clearly shows that the water molecule behaves as the proton donor in the cluster. The two OH stretching vibrations at lower and higher frequencies observed in Figure 2a can be assigned



**Figure 3.** Structures of the clusters optimized with the B3LYP/6-311++G(d,p) level. Stabilization energies with BSSE and zero-point energy corrections are given in kcal/mol. The hydrogen-bond lengths for the clusters are also shown in angstroms.

to the vibrations due to the hydrogen-bonded and free OH stretching vibrations, respectively. The vibrational mode calculation of the cluster also shows that the atomic motion for the lower frequency vibration is mainly from the hydrogen-bonded OH stretching. Mitsui et al. have observed the OH stretching vibrations at 3714 and 3404  $\text{cm}^{-1}$  in the hydrogen-bonded cluster of acridine with water.<sup>17</sup> The band due to the hydrogen-bonded OH stretching vibration of the acridine–water cluster is lower than that of the 2-FP–water cluster. This means that the hydrogen-bond energy of acridine–water is larger than that of 2-FP–water. The proton affinity of acridine and 2-FP is 972.6 and 930 kJ/mol, respectively.<sup>31</sup> In the case of phenol, the red shift of the phenolic OH stretching frequency by hydrogen-bond formation relates well to the proton affinity of the bonding partner in the cluster.<sup>32</sup> Proton affinity is considered to be directly related to the strength of the hydrogen-bond interaction. The degree of red shift of the OH stretching vibration of the water molecule under the hydrogen-bond formation corresponds well to the strength of the hydrogen bond between 2-FP and water, where the water molecule behaves as a proton donor.

Figure 2b shows the IR spectrum of the 2-FP–water 1:2 cluster. Four bands are observed at 3402, 3499, 3720, and 3724  $\text{cm}^{-1}$ . Two lower bands are assigned to the bands due to the hydrogen-bonded OH stretching vibration and the higher two bands to free OH ones, respectively. The band at 3499  $\text{cm}^{-1}$  is observed very weakly because the intensity of the IR laser radiation is very weak in this region. Therefore, the corrected intensity of this band is considerably stronger than that observed. The relatively strong two bands observed at 3402 and 3499  $\text{cm}^{-1}$  are assigned to stretching vibrations of hydrogen-bonded OH. The bands at 3720 and 3724  $\text{cm}^{-1}$  are due to the free OH

stretching vibrations. The frequencies of the free OH stretching vibrations are similar to that of the 1:1 cluster.

Figure 2c shows the IR spectrum of the 1:3 cluster. In the lower frequency side, three bands are observed at 333, 3411, and 3461  $\text{cm}^{-1}$ . In the higher frequency side, only a single peak is observed. This may be due to the fact that the free OH stretching vibrations are accidentally overlapped in this frequency. For the structure of the 1:3 cluster, two structural isomers were expected from the molecular orbital calculation as shown in Figure 3. The assignment of the structure was done based on the calculated optimization energy and intermolecular vibrational frequencies observed in the dispersed fluorescence spectrum.<sup>4</sup> The appearance of the three bands in the region of the hydrogen-bonded OH stretching vibration corresponds well with the assignment of the bridged form structure for the 1:3 cluster. The ringed form structure predicts four hydrogen-bonded OH stretching vibrations in the lower frequency region as shown in Figure 2c. As to the calculated frequencies of the hydrogen-bonded 2-FP with water, the frequency and intensity are shown in the figure together with the observed spectra.

The frequencies for the free OH stretching vibrations, around 3720  $\text{cm}^{-1}$ , are reproduced very well for the observed spectrum. However, the bands for the hydrogen-bonded OH stretching vibrations have calculated lower frequencies than those observed. This tendency is also observed for the three hydrogen-bonded clusters. These results show that the B3LYP/6-311++(d,p) calculation reproduces well the observed results for free OH stretching vibrations. However, for the hydrogen-bonded OH stretching vibrations, the calculated frequencies underestimated the observed results with the use of scaling factors optimized for the bare water molecule. The calculated hydrogen-bonded OH frequencies are 50 to  $\sim 70$   $\text{cm}^{-1}$  lower than that observed. However, the relative frequency shifts as the increasing water molecule reproduces the observed results very well. For example, for the lowest frequency OH stretching vibrations, the calculated red shifts of  $-137$  and  $-72$   $\text{cm}^{-1}$  reproduce well the observed  $-131$  and  $-67$   $\text{cm}^{-1}$  measurements from 1:1 to 1:2 and from 1:2 to 1:3, respectively. This fact means that the use of the scaling factor adjusted for hydrogen-bonded OH frequencies gives close values for the observed hydrogen-bonded OH stretching vibrations and different ones for the free OH stretching vibrations. The discrepancy could be ascribed to the use of the same scaling factor both for free and for hydrogen-bonded OH stretching frequencies and/or to the insufficiency of the B3LYP functional to reproduce the hydrogen bond properly. However, the MP2/6-311++G(d,p) calculations shown in Table 1, where the calculation for the 1:3 cluster has not been carried out, give closer values for the hydrogen-bonded OH frequency as compared with the results of the B3LYP/6-311++G(d,p) calculations. The fact seems that the MP2 calculation gives better results for the OH stretching vibration. The discussion for the reliability of these calculations needs more experimental and theoretical examples.

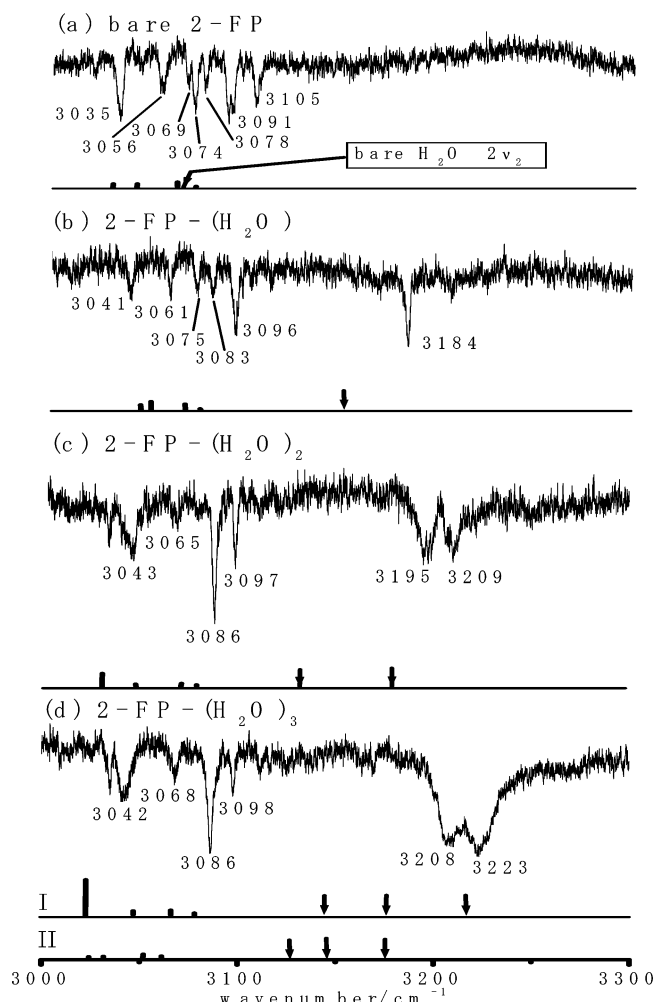
**CH Stretching Vibrations.** Figure 4 shows the FDIR spectra of bare and 2-FP–water clusters in the CH stretching vibrational region. For bare 2-FP (Figure 4a), four CH stretching vibrations might be expected at most from its molecular structure; however, more than four bands are clearly observed in this region. This means that the CH stretching vibrations interact with the overtone and/or combination bands, whose fundamental vibrations exist in the lower vibrational energy region, through anharmonic couplings. Figure 4b shows the IR spectrum of the 2-FP–H<sub>2</sub>O cluster. The vibrational structure around 3050  $\text{cm}^{-1}$  changes slightly from that of the bare one. This change is

**TABLE 1: Observed and Calculated Frequencies of 2-Fluoropyridine–Water Clusters ( $\text{cm}^{-1}$ )**

2-FP– (H <sub>2</sub> O) <sub>n</sub>	assignment	observed	calculated	
			B3LYP/ 6-311++G- (d,p) <sup>a</sup>	MP2/ 6-311++G- (d,p) <sup>b</sup>
<i>n</i> = 0	$\nu_3^c$	3756 <sup>d</sup>	3756	3763
	$\nu_1^e$	3657 <sup>d</sup>	3657	3651
	CH str.		3076	3056
	CH str.	3105, 3095, 3091	3066	3046
	CH str.	3078, 3074, 3069	3046	3025
	CH str.	3056, 3035, 3021	3031	3015
	$2^*\nu_2$	3151 <sup>f</sup>	3068 <sup>g</sup>	3060 <sup>g</sup>
<i>n</i> = 1	Free OH	3725	3725	3724
	H-bonded OH	3531	3487	3519
	CH str.		3078	3058
	CH str.	3096, 3083, 3075	3070	3050
	CH str.	3061, 3041	3050	3030
	CH str.		3043	3024
	$2^*\nu_2$	3184	3153 <sup>g</sup>	3120 <sup>g</sup>
<i>n</i> = 2	Free OH	3724	3726	3719
	Free OH	3720	3722	3712
	H-bonded OH	3499	3438	3481
	H-bonded OH	3402	3350	3397
	CH str.		3079	3058
	CH str.	3097, 3086, 3065	3069	3050
	CH str.	3043, 3032	3047	3029
	CH str.		3030	3022
	$2^*\nu_2$	3209	3180 <sup>g</sup>	3180 <sup>g</sup>
	$2^*\nu_2$	3195	3132 <sup>g</sup>	3135 <sup>g</sup>
<i>n</i> = 3	Free OH		3723	
	Free OH	3718	3721	
	Free OH		3720	
	H-bonded OH	3461	3391	
	H-bonded OH	3411	3345	
	H-bonded OH	3333	3278	
	CH str.		3079	
	CH str.	3098, 3086, 3068	3070	
	CH str.	3042, 3035	3048	
	CH str.		3024	
	$2^*\nu_2$	3223	3218 <sup>f</sup>	
	$2^*\nu_2$	3178	3178 <sup>f</sup>	
	$2^*\nu_2$	3208	3145 <sup>f</sup>	

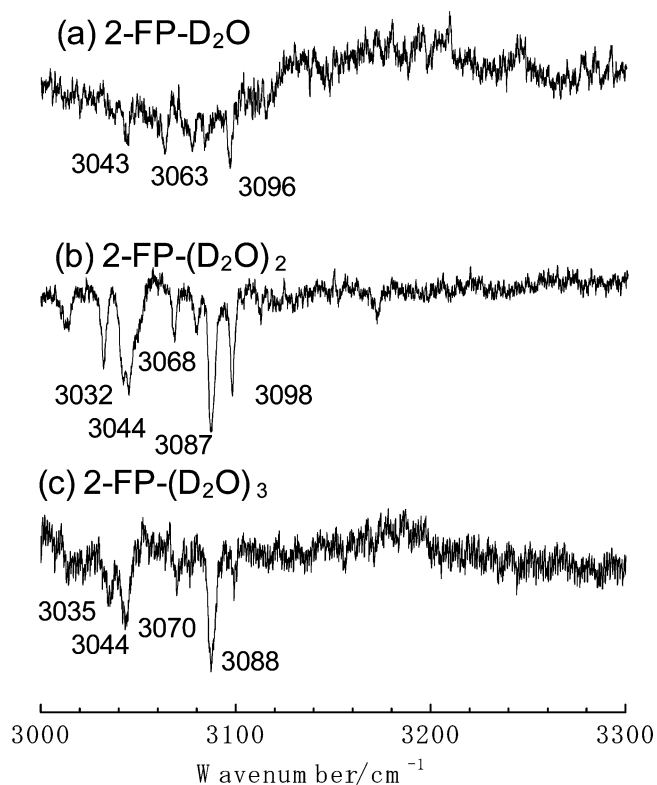
<sup>a</sup> Scaling factor of 0.9577 is multiplied. <sup>b</sup> Scaling factor of 0.9397 is multiplied. <sup>c</sup> Anti-symmetric OH stretching vibration. <sup>d</sup> Taken from ref 29. <sup>e</sup> Symmetric OH stretching vibration. <sup>f</sup> Taken from ref 30. <sup>g</sup> Double scaled-OH bending frequency.

reasonable because the hydrogen-bond formation with water affects the fundamental vibrations of 2-FP and the anharmonic interactions. In the spectrum of the 1:2 cluster shown in Figure 4c, the vibrational structure is different from those of the bare and 1:1 cluster. The band at 3043  $\text{cm}^{-1}$  has a broader band profile as compared with other bands observed in this region. The broader bandwidth is also observed at the 3042  $\text{cm}^{-1}$  band in the 1:3 cluster (see Figure 4d). The molecular orbital calculations for the 1:3 clusters show that the CH...O distance in the bridged form is considerably short, 2.194 and 2.198 Å with the B3LYP/6-311++G(d,p) (see Figure 3) and MP2/6-311++G(d,p) calculations, respectively. The stretching vibration under hydrogen-bond interactions usually gives a relatively broader band profile as observed for the hydrogen-bonded OH stretching vibrations of these clusters (see Figure 2). The broader bandwidth in the CH stretching vibrational region might originate from the hydrogen-bond interaction of the CH bond. The short distance between CH and O atoms is also obtained in the calculations at the MP2/6-31G(d,p) and MP2/6-31++G(d,p) levels. The band structure of the 1:3 cluster in this region also resembles to that of the 1:2 cluster. The resemblance of the vibrational structure between 1:2 and 1:3 clusters is explained as follows. The oxygen atoms of the second and third coordinating water molecules in the 1:2 and 1:3 clusters,



**Figure 4.** Fluorescence detected IR dip spectra of 2-fluoropyridine–(H<sub>2</sub>O)<sub>n</sub> clusters (a) *n* = 0, (b) *n* = 1, (c) *n* = 2, and (d) *n* = 3 in the CH stretching vibrational region.

respectively, interact with the aromatic hydrogen at the sixth position in the pyridine ring. The environment from the point of view of the 2-FP side is similar among the two clusters as expected from the cluster structure shown in Figure 3. This resemblance of the environment gives similar vibrational interactions between the clusters and results in a similar vibrational structure for the IR spectra. This fact also corresponds well to the assignment of the 1:3 cluster to the bridged form. Molecular orbital calculations also suggest the resemblance of the vibrational structure (see Figure 4c,d). This similar type of interaction also has been reported by Mikami et al.<sup>18,19</sup> and Brutschy et al.<sup>20–23</sup> This phenomenon is very interesting because the CH bond, which is considered to be nonactive for hydrogen-bond interactions, behaves as a weak proton donor. In addition to the bands assigned to the CH stretching vibrations, relatively stronger and broader bands are observed at 3184  $\text{cm}^{-1}$  in the 1:1 cluster, 3195 and 3209  $\text{cm}^{-1}$  in the 1:2 cluster, and 3208 and 3223  $\text{cm}^{-1}$  in the 1:3 cluster. These bands are assigned either to water originating bands or combination bands including intermolecular vibrations because these bands are observed along with cluster formation with water. To clarify the origin of these bands, the IR spectra of the 2-FP–(D<sub>2</sub>O)<sub>n</sub> (*n* = 1 to 3) clusters have been observed and are shown in Figure 5. As can be seen from the figure, the bands originating from the CH stretching vibrations give similar frequencies and band structures to those



**Figure 5.** IR dip spectra of 2-fluoropyridine–( $\text{D}_2\text{O}$ ) $_n$  clusters (a)  $n = 1$ , (b)  $n = 2$ , and (c)  $n = 3$  in the same region as in Figure 3.

of the corresponding 2-FP–( $\text{H}_2\text{O}$ ) $_n$  clusters. These experimental results clearly indicate that these bands other than the CH stretching vibrations originate from water itself. If these bands originated from the intermolecular vibrations between 2-FP and water, the band structure might be similar between the corresponding clusters, and the frequencies of 2-FP–( $\text{D}_2\text{O}$ ) $_n$  might be slightly lower than those of 2-FP–( $\text{H}_2\text{O}$ ) $_n$ . Therefore, these bands obviously originate from overtones or a combination band of intramolecular vibrations of the water molecule. Because the only intramolecular mode of water lower than  $3000\text{ cm}^{-1}$  is the OH bending vibration, the candidate for the band must be the overtone vibration of the symmetric OH bending mode that is observed at  $3151\text{ cm}^{-1}$  for bare water in the vapor phase.<sup>30</sup> The calculated overtone frequencies of OH bending vibrations are shown in Figure 4 with arrows and are given in Table 1. The calculated frequencies of the overtone vibrations shift the higher frequency side as the number of bonding water molecules increases in the clusters. These calculations reproduce well the tendency of the observed frequency shift in the experiment. Saykally et al. have also observed the bending vibration of pure water clusters with a cavity ring down technique and have shown the blue shift of the OH bending vibration with an increase of the cluster size.<sup>29</sup> It should also be noted that the band profiles of these bands became broader as the cluster size increased. These broader bandwidths are also observed for hydrogen-bonded OH stretching vibrations located in the higher frequency side. This phenomenon indicates that the hydrogen bond makes the vibrational band broader not only for OH stretching vibrations but also for OH bending overtone vibrations. These broader band profiles mean that the hydrogen bond considerably enhances the absorption intensity of these overtone vibrations because the intensity should be proportional to the integrated absorption profile. Kleinermanns et al.<sup>15</sup> also have observed the bands in this region for phenol–water clusters and suggested that an overtone vibration appears with a Fermi resonance with

nearly lying OH stretching vibrations. In the case of the 2-FP–water clusters, the explanation mentioned stated previously is not reasonable for the appearance of these overtone vibrations originating from the anharmonic coupling with an OH stretching vibration because the overtone vibration is also observed in the 1:1 cluster where the energy difference between the overtone and the OH stretching vibrations is considerably large. In the spectra of the hydrogen-bonded acridine–water clusters, several bands also have been observed between  $3200$  and  $3400\text{ cm}^{-1}$ , which have not been definitely assigned.<sup>17</sup> The overtone vibrations might be also observed in acridine–water clusters because these band positions are dependent on the cluster size, and the bandwidths are considerably broader than that of the band due to the CH stretching vibration. These facts indicate that the hydrogen-bond formation of water increases the intensity of the overtone vibration of the bending mode in some cases. Under the harmonic oscillator approximation for an OH bending vibration, the overtone vibration is infrared inactive. The anharmonic coupling with hydrogen-bonded OH stretching vibrations is not the reason for the appearance in the IR spectrum for the 2-AP–( $\text{H}_2\text{O}$ ) $_1$  cluster because the energy gap between the vibrational levels,  $347\text{ cm}^{-1}$  ( $3531$ – $3184$  from Figures 2a and 4b), is considerably large. The reason that infrared intensity for the overtone vibrations is gained might originate from the anharmonic character of the hydrogen-bonded OH bending vibration itself. However, for the 1:2 and 1:3 clusters, the coupling between the overtone and the OH stretching vibrations might not be discarded for the appearance of overtone vibrations in the IR spectra because the interval between the vibrational levels becomes smaller as the number of water molecule in the clusters increases. The mechanism of the appearance of the overtone vibrations could not be clarified from these experiments. Detailed theoretical analysis should be helpful for this issue.

## Conclusion

The IR spectra of the clusters confirm the structural assignment of the clusters, which has been performed based on electronic transitions and molecular orbital calculations.<sup>4</sup> 2-FP behaves as a proton acceptor in the clusters as expected. The hydrogen-bond interaction between 2-FP and water is weaker than that between acridine and water as expected from the proton affinity of these molecules. The CH stretching vibrations of bare 2-FP interact with a combination and/or overtone vibrations through anharmonic interactions, and a very complex band structure is observed as expected from the molecular structure. The aromatic hydrogen atom behaves as a proton donor in the 2-FP–(water) $_{2,3}$  clusters. The similarity in the environment for the pyridine ring between 1:2 and 1:3 clusters gives a similar vibronic structure in the CH stretching region. The calculated frequencies with B3LYP/6-311++G(d,p) reproduce well the observed frequencies of the free OH stretching vibrations in the clusters. However, as to the hydrogen-bonded OH stretching vibrations, the use of a scaling factor optimized for bare water molecules gives lower frequencies than those observed in the experiment. MP2/6-311++G(d,p) calculations have shown a closer frequency for the 1:1 and 1:2 clusters than that of the B3LYP/6-311++G(d,p) calculations, although the scaling factor is also optimized for bare molecules. The overtone vibrations of the OH bending vibration become higher in frequency and stronger in intensity in the IR spectrum as the cluster size increases. The phenomenon corresponds well to the result observed for the blue shift of the OH bending vibrations in pure water clusters.<sup>33</sup>

**Acknowledgment.** The present work was supported by a Grant-in-Aid (14540478) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

## References and Notes

- (1) Srinivasan, R.; Feenstra, J. S.; Park, S. T.; Xu, S.; Zewail, A. H. *Science* **2005**, *307*, 558.
- (2) Villa, E.; Amirav, A.; Lim, E. C. *J. Phys. Chem.* **1988**, *93*, 5393.
- (3) Becucci, M.; Lakin, N. M.; Pietraperzia, G.; Salvi, P. R.; Castellucci, E.; Kerstel, E. R. T. *J. Chem. Phys.* **1997**, *107*, 10399.
- (4) Nibu, Y.; Okabe, C.; Ohsaki, T.; Shimada, H. *J. Phys. Chem. A* **2006**, *110*, 6047.
- (5) Nibu, Y.; Okabe, C.; Shimada, H. *J. Phys. Chem. A* **2003**, *107*, 1945.
- (6) Zwier, T. S. *J. Phys. Chem. A* **2001**, *105*, 8827.
- (7) Abe, H.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1982**, *186*, 1768.
- (8) Tanabe, S.; Ebata, T.; Fujii, M.; Mikami, N. *Chem. Phys. Lett.* **1993**, *215*, 347.
- (9) Ebata, T.; Mizuochi, N.; Watanabe, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 546.
- (10) Watanabe, T.; Ebata, T.; Tanabe, S.; Mikami, N. *J. Chem. Phys.* **1996**, *105*, 408.
- (11) Sawamura, T.; Fujii, A.; Sato, S.; Ebata, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 8131.
- (12) Janzen, C.; Spangenberg, W.; Roth, D. *J. Chem. Phys.* **1999**, *110*, 9898.
- (13) Kleinerhmanns, K.; Janzen, C.; Spangenberg, D.; Gerhards, M. *J. Phys. Chem. A* **1999**, *103*, 5232.
- (14) Ebata, T.; Iwasaki, A.; Mikami, N. *J. Phys. Chem. A* **2000**, *104*, 7974.
- (15) Luchow, A.; Spangenberg, D.; Janzen, C.; Jansen, A.; Gerhards, M.; Kleinerhmanns, K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2771.
- (16) Gerhards, M.; Jansen, A.; Unterberg, C.; Kleinerhmanns, K. *Chem. Phys. Lett.* **2001**, *344*, 113.
- (17) Mitsui, M.; Ohshima, Y.; Ishiuchi, S.; Sakai, M.; Fujii, M. *Chem. Phys. Lett.* **2000**, *317*, 211.
- (18) Venkatesan, V.; Fujii, A.; Ebata, T.; Mikami, N. *Chem. Phys. Lett.* **2004**, *394*, 45.
- (19) Venkatesan, V.; Fujii, A.; Mikami, N. *Chem. Phys. Lett.* **2005**, *409*, 57.
- (20) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **1999**, *110*, 8501.
- (21) Riehn, C.; Buchhold, K.; Reimann, B.; Djafari, S.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 1170.
- (22) Buchhold, K.; Reimann, B.; Djafari, S.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 1844.
- (23) Riehn, C.; Reimann, B.; Buchhold, K.; Vaupel, S.; Barth, H.-D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2001**, *115*, 10045.
- (24) Nibu, Y.; Sakamoto, D.; Satoh, T.; Shimada, H. *Chem. Phys. Lett.* **1996**, *262*, 615.
- (25) Behlen, F. M.; Mikami, N.; Rice, S. A. *Chem. Phys. Lett.* **1979**, *60*, 364.
- (26) Frisch, M. J. et al. *Gaussian 98*, revision A.9; Gaussian Inc.: Pittsburgh, PA, 1998.
- (27) Frisch, M. J. et al. *Gaussian 03*, revision A.2; Gaussian Inc.: Pittsburgh, PA, 2003.
- (28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
- (29) <http://webbook.nist.gov/chemistry/>.
- (30) Hertzberg, G. *Molecular Spectra and Molecular structure II*; Van Nostrand Reinhold: New York, 1945; p 280.
- (31) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
- (32) Iwasaki, A.; Fujii, A.; Watanabe, T.; Ebata, T.; Mikami, N. *J. Phys. Chem.* **1996**, *100*, 16053.
- (33) Paul, J. B.; Provencal, R. A.; Chapo, C.; Roth, K.; Casaes, R.; Saykally, R. J. *J. Phys. Chem. A* **1999**, *103*, 2972.