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Electronic Spectra of Hydrogen-Bonded 2-Fluoropyridine Clusters with Water in a Supersonic Free Jet

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Fluorescence excitation, multiphoton ionization, and dispersed fluorescence spectra of bare and hydrogen-bonded 2-fluoropyridine with water were measured in a supersonic free jet. For bare 2-fluoropyridine, fluorescence quantum yield decrease in the higher vibronic levels was observed even under collision-free conditions. The intersystem crossing channel was probed experimentally by two color R2PI and found to be negligible. The nonradiative relaxation process of 2-fluoropyridine is mainly governed by the relaxation to the electronic ground state. Electronic spectra of 2-fluoropyridine−(water)$_n$ ($n = 1\sim3$) were also obtained. The hydrogen bond formation with water increases the quantum yield in the higher vibronic levels. Rather low frequency vibrations were observed in the hole burning spectrum of bare 2-fluoropyridine; however, these vibronic bands disappeared with the hydrogen bond formation with water. The appearance of low frequency vibronic bands observed for bare 2-fluoropyridine is ascribed to the existence of closely lying (n,π*) state.

1. Introduction

Pyridine derivatives exist widely in biological systems. The type of hydrogen bond in pyridine, where the ring nitrogen behaves as a proton acceptor, plays an important role in biological systems and observed, for example, in the double helix structure of DNA. Therefore, a study of the structure for hydrogen-bonded pyridine gives important information to discuss the structure of biological molecules under the influence of hydrogen bond interactions.

From the photochemical aspect of biological molecules, a molecule exposed to UV or visible light leads to a dangerous situation because the electronically excited molecule is chemically unstable. In the real biological system, an electronically excited molecule deactivates through fast electronic relaxation to prevent damage from light. From the point of view of the deactivation efficiency, pyridine is one of the more favorable constructive molecules for the biological system because the molecule has very fast relaxation processes from the electronic excited state.[1] Because of the situation mentioned above, studies of relaxation processes and the structure of hydrogen-bonded pyridine give important information toward understanding the role of the hydrogen bond effect on biological systems. However, pyridine is nonfluorescent, and therefore, only a few spectroscopic studies have been made under jet conditions.[2,3] Difluorine-substituted pyridine, 2,6-difluoropyridine, does fluoresce from the excited state, and fluorescence excitation and dispersed fluorescence spectra have been observed in a supersonic free jet. [4] The electronic spectrum of hydrogen-bonded 2,6-difluoropyridine with water has been also observed.[4] The reason the substitution with fluorine makes pyridine fluorescent has been explained as follows. Bondybye et al. have claimed that the fluorine substitution stabilizes the energy level of nonbonding orbital by increasing of fluorine atoms.[5] Fluorine substitution causes the raising of the energy level of the S_1(n,π*) state that corresponds to the nonfluorescent state in pyridine, and results in a (π,π*) state being S_1 in 2,6-difluoropyridine.

For a study on the electronic transition of 2-fluoropyridine (2-FP), Stephenson has observed solvent effects on the electronic transition and concluded that the (n,π*) transition of 2-FP is hiding under the strong (π,π*) transition.[6] Mhedi and Mhedi also observed the absorption spectrum of 2-FP in the vapor phase.[7] They have assigned the band at 38047 cm^{-1} to the origin of the lowest singlet (π,π*) state. For 3-fluoropyridine, the band origin of the S_1(n,π*) state was clearly observed at 35066 cm^{-1} in the vapor phase,[8] however, the band due to the (n,π*) state has not been observed for 2-FP. These observation shows that the lowest singlet state is the (π,π*) state and the (n,π*) state lies closely above the (π,π*) state in 2-FP.

In the present study, the electronic transition of bare 2-FP is observed with laser-induced fluorescence(LIF), hole burning and two color multiphoton ionization spectra in a supersonic free jet. From the spectra obtained in a jet, a sudden quantum yield drop, which has not been obtained in the absorption spectrum in the vapor phase,[7] is discussed. The electronic spectra of hydrogen-bonded 2-FP with water is also reported, and the hydrogen bond effect on the electronic transition of 2-FP is discussed together with the results of molecular orbital calculations for the clusters.

2 Experimental and Theoretical Calculations

2-FP−water clusters were formed and cooled in a pulsed supersonic free jet expansion using 4 atm of He. The detail of the apparatus and the outline of the experimental setup have been shown elsewhere[9] and are mentioned briefly. Water and 2-FP were premixed in a nozzle housing and expanded into vacuum chamber through the pulsed nozzle with a hole of 400 μm in diameter. To observe the fluorescence excitation,

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dispersed fluorescence, multiphoton ionization, and hole-burning spectra, two dye lasers were used, a PDL-II (Spectra Physics) pumped by the third harmonic of a Nd:YAG laser, DCR-11 (Spectra Physics) and/or a FL2005 (Laser Analytic Systems) pumped by the third harmonic of a Nd:YAG laser, GCR-130 (Spectra Physics). For the observation of two color multiphoton ionization spectra, the ionization frequency of 51200 cm^{-1} was obtained with the eighth anti-Stokes line of the stimulated Raman band of hydrogen gas exciting with the second harmonic of the Nd:YAG laser (GCR130). The pulse width of dye lasers used in these experiments was estimated to be about 4−5 ns. Signals were integrated with a boxcar integrator (SRS-250) and recorded with a chart recorder. The time interval between the two lasers was controlled by a digital delay generator, DG535 (SRS). Laser-induced fluorescence was dispersed with the SPEX 1702 spectrometer equipped with a photomultiplier tube or the ICCD detector (Princeton, ITE-1024M).

Molecular orbital calculations were carried out with Gaussian 98[10] and Gaussian 03[11] program packages at the computer center of Fukuoka University and Kyushu University, respectively. Optimized structures and vibrational frequencies of 2-FP(H_2O)$_n$ ($n = 1-3$) clusters were obtained through the density functional theory with B3LYP functional and MP2 methods. The 6-311++G(d,p) basis set was used for the calculations. Stabilization energies obtained were corrected with zero point vibration and with basis set superposition error (BSSE) by counterpoise method.[12]

To calculate the vibrational frequency of 1:3 cluster with the method of MP2/6-311++G(d,p) has been beyond the capability of our computer system. Therefore, only the optimized structure was determined for 1:3 cluster with this method.

3. Results and Discussion

3A. Electronic Spectrum of Bare 2-Fluoropyridine. Figure 1a shows the fluorescence excitation spectrum of bare 2-FP in a supersonic free jet. The output intensity of the dye laser in the region was kept constant. As seen from the figure, only a single peak is observed at 38019 cm^{-1}. The band is assigned to the band origin of the electronic transition for bare 2-FP. The band also corresponds to that observed in the vapor phase at 38048 cm^{-1} by Mhedi.[7] There is a discrepancy between the band origin frequencies in the vapor phase and in jet. The reasons for the discrepancy are ascribed to the broad bandwidth, which is about 50 cm^{-1}, and the use of vacuum uncorrected frequency in the vapor phase spectrum.[7] In the higher frequency region from the band origin, none of band is observed in the LIF spectrum although a number of vibronic bands are observed in the absorption spectrum in the gas phase.[7] This phenomenon is ascribed to the sudden decrease of quantum yield just above the band origin. Figure 1b shows the dispersed fluorescence spectrum from the band origin. The vibronic bands appearing in the spectrum are summarized in Table 1 together with the assignment based on the molecular orbital calculations. The observed bands are assigned to the fundamental vibrations in the ground state because the observed frequencies coincide well with the bands observed in the Raman and infrared spectra of 2-FP.[13] The correspondence between the dispersed fluorescence and the vibrational spectra confirms that the observed fluorescence is originated from bare 2-FP. The vibrations appeared in the dispersed fluorescence spectrum are assigned to the totally symmetric in-plane vibrations based on the normal coordinate analysis by the B3LYP/6-311++G(d,p) calculation.

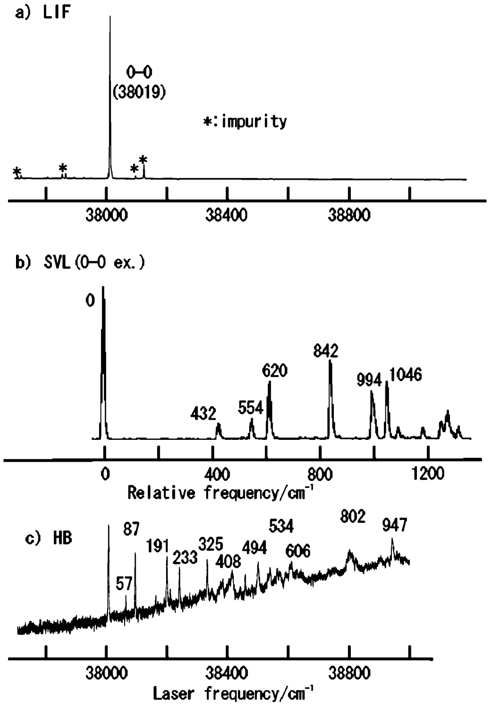


Figure 1. (a) Fluorescence excitation spectrum of bare 2-fluoropyridine in a supersonic free jet. The bands marked with an asterisk are assigned to the bands due to impurities. (b) Dispersed fluorescence spectrum of bare 2-fluoropyridine exciting to the band origin. (c) UV−UV hole-burning spectrum of bare 2-fluoropyridine, where the band origin is probed.

Figure 1c shows the hole-burning spectrum of bare 2-FP, where the band origin was probed. A hole burning spectrum generally well reproduces the absorption spectrum because the band intensity reflects the degree of population transfer by the absorption of laser light, which is proportional to transition probability. In the spectrum of Figure 1c, many vibronic bands are observed in the higher frequency side from the band origin, and these bands correspond well with the bands observed in the absorption spectrum in the vapor phase.[7] Low-frequency bands at 87, 188, 229, and 325 cm^{-1}, which were assigned as hot bands in the vapor phase spectrum,[7] should be ascribed to cold bands and correspond to 87, 191, 233, and 325 cm^{-1}, respectively, in the jet spectrum. Vibrational frequencies usually become lower with a electronic excitation because the electron is excited from a bonding orbital to an unstable antibonding orbital. By taking into account of this frequency decrease in the excited state, the vibrational correspondence is shown in Table 1. If this correspondence is correct, the mirror image relationship holds in bare 2-FP for the bands observed in the SVL spectrum. However, low frequency vibrations observed in the hole-burning spectrum of bare 2-FP have no corresponding bands in the SVL spectrum. Questions arise as to why these lower frequency vibrations appear in the hole-burning spectrum and why the quantum yield decreases in the higher vibronic level. These questions will be discussed later together with the hydrogen bond effect of water on the electronic transition of 2-FP. In addition to the appearance of low frequency vibrations in the hole-burning spectrum of bare 2-FP, it should be noted that the considerably complex vibrational structure is observed in the energy region around 400−600 cm^{-1} despite the relatively simple molecular structure. Contrary to the hole-burning spectrum, a simple vibrational structure is observed in the SVL spectrum of bare 2-FP.

The absence of vibronic band in the LIF spectrum of bare 2-FP ascribed to the fluorescence quantum yield decrease in the vibronic levels in the excited state. The parent molecule of 2-FP, pyridine is known as a nonfluorescent molecule because

TABLE 1: Vibrational Frequency Observed in the Electronic Transitions of Bare and Hydrogen-Bonded 2-FP

Intramolecular Vibration

bare					1:1 cluster			1:2 cluster			1:3 cluster			
S_0[a]	S_1[a]	S_1[b]	calcd[c]	Raman[d]	S_0[a]	S_1[a]	calcd[c]	S_0[a]	S_1[a]	calcd[c]	S_0[a]	S_1[a]	calcd[c,e]	calcd[c,f]
1046		1045	1062	1045	1045		1063	1049		1067	1049		1070	1063
994	947	944	1011	993	1004	935	1019	1007	942	1020	1008	945	1021	1018
842	802	800	847	826	842	800	848	844	801	846	843	802	845	849
620	624		635	621	624		639	626		640	627		642	639
554	534	526	559	553	556	533	562	555	540	561	554	542	561	563
432	408	392	433	432	438	416	441	438	422	442	438	421	435	438
	325													
	233													
220[g]	191			229[h]		207				213				213
	87													
	57													

Intermolecular Vibration[i]

	1:1 cluster			1:2 cluster			1:3 cluster			
assignment	S_0	S_1	calcd[c]	S_0	S_1	calcd[c]	S_0	S_1	calcd[c,e]	calcd[c,f]
OH rotation (out of plane)						191				193
hydrogen bond stretching										174[j]
	125	123	136	142	142	157	141	143	153	100[k]
out-of-plane bending			60			55			70	
	38	38	35	45	46	43			37	64
							18	18	28	26
in-plane bending			25			95			109	47
						62			66	18
									49	13

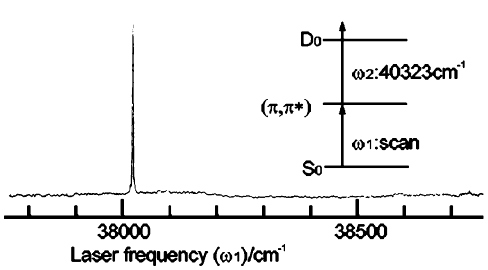
[a] This work. [b] Taken from ref 6. [c] Calculated for vibrational frequency in the ground state with B3LYP/6-311++G(d,p). [d] Taken from ref 13. [e] Calculated for bridged structure (see Figure 5, n = 3a). [f] Calculated for ring structure (see Figure 5, n = 3b). [g] This band is too weak (about 1/20 of the band at 432 cm^{-1}) to be observed in the Figure. [h] Assigned as out-of-plane fluorine bending vibration. [i] Vibrational frequencies lower than 200 cm^{-1} are shown. [j] Stretching vibration among ring forming water molecules. [k] Stretching vibration between 2-FP and water ring.

of fast nonradiative relaxation from the $S_1(n,\pi^*)$ state.[1] The main reason for the very low quantum yield of pyridine in the S_1 state has been attributed to the relaxation to the ground states, internal conversion, determined from the observation of absorption spectrum with high resolution.[3] The energy levels of $^3(n,\pi^*)$ states in aza-aromatic molecule lie lower than those of singlet states, and therefore, the relaxation to the triplet state might contribute to the relaxation process. For 2-FP, a question is which process, relaxation to either S_0 or T_n, governs the nonradiative decay. To clarify the relaxation process from the excited state, two-color ionization spectra were observed for bare 2-FP.

Figure 2a shows the (1 + 1′) ionization spectrum where the frequency of the ionization laser, ω_2, was fixed at 40323 cm^{-1} and the excitation laser, ω_1, was scanned. The frequency of 40323 cm^{-1} has enough energy to ionize the 2-FP from the band origin because the ionization potential of 2-FP was determined to be 9.401 eV (=75820 cm^{-1}) through our two color ionization experiment. The delay time of ω_2 with respect to ω_1 was scanned and the lifetime of the excited state was measured from the signal intensity of the ion. The decay time was too short to determine accurately with our laser system-(4−5ns pulse width) by using the wavelength of ω_2 mentioned above. Therefore, the decay time of the band origin is estimated to be shorter than a few ns.

Figure 2b shows the (1 + 1′) REMPI spectrum where the ionization laser, ω_2, was fixed at 51200 cm^{-1}. To observe the spectrum, the time interval between ω_1 and ω_2 was set at 40 ns. The decay time, which is determined with the time interval scan between ω_1 and ω_2 as mentioned above, was measured to be about 40 ns in the use of 51200 cm^{-1} as the ionization frequency. The obtained longer lifetime indicates that the ionization occurs not from excited (π,π^*) state but from the relaxed state. The candidate of the relaxed state is the S_0 or triplet states if a (π,π^*) state is the lowest excited singlet state as claimed by Stephanson.[6] The ionization from the S_0 state is difficult because the Franck−Condon overlap between relaxed S_0 and ionized state is considerably small if the potential surfaces are similar to each other. For the T_1 state, Mhedi and Mhedi

(a) Ionization from Singlet state(Δt=0)



(b) Ionization from Triplet state(Δt=40ns)

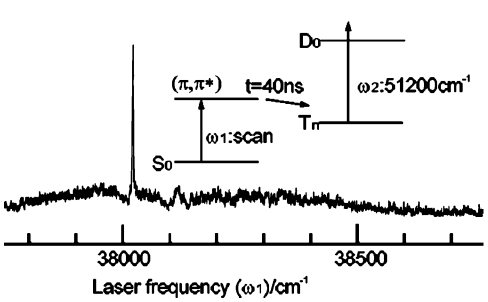


Figure 2. Two color ionization spectra of bare 2-fluoropyridine with the scanning of the ω_1 laser used for the electronic excitation. The ionization laser, ω_2, was fixed at (a) 40323 cm^{-1} in frequency with no delay with respect to ω_1 and (b) 51200 cm^{-1} in frequency with 40 ns delay with respect to ω_1.

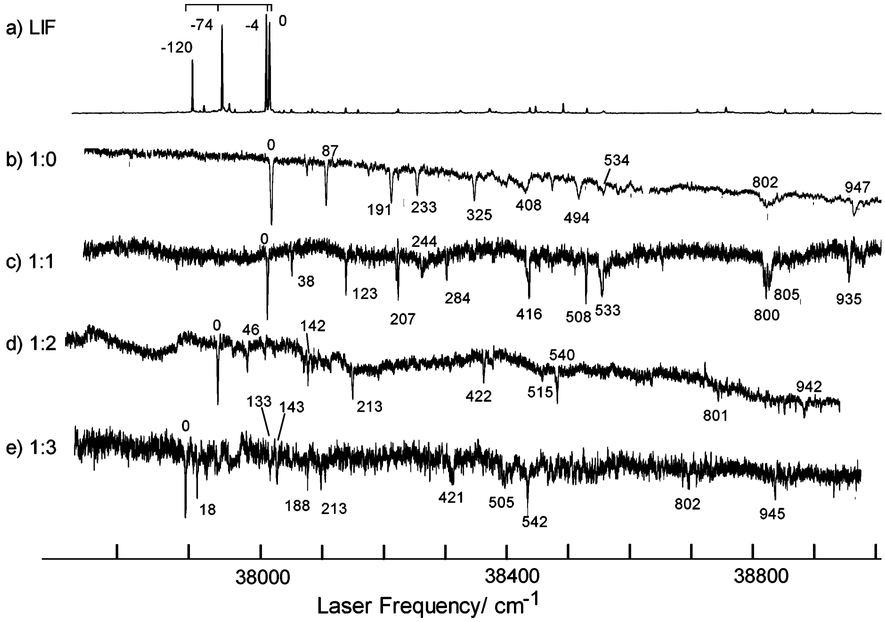


Figure 3. (a) Fluorescence excitation spectrum of 2-fluoropyridine expanded with water. UV−UV hole-burning spectra of (b) bare 2-fluoropyridine and (c) 1:1, (d) 1:2, and (e) 1:3 complexes, respectively.

observed phosphorescence spectrum of 2-FP in cyclohexane at 77 K.[7] The spectrum has shown a broad emission profile started from about 370 nm. This means that the T_1 state lies around 27000 cm^{-1} in energy. To make the discussion simpler, the potential surfaces are assumed to be the same among the electronic states under consideration. This means that the Franck−Condon overlap between the states has a nonzero value only between the same vibrational levels, which have the same frequency in both states under the assumption mentioned above. The excess energy between the band origin of the $^1(\pi,\pi^*)$ state and the triplet state is about $38019 - 27000 = 11019$ cm^{-1}. To ionize the lowest triplet state needs the energy of 86839 cm^{-1} ($=75820 + 11019$). The total ionization energy of 89219 cm^{-1} ($=38019(\omega_1) + 51200(\omega_2)$) used for the second experiment(Figure 2b) can ionize the molecule from the triplet state. This means that the ω_2 of 51200 cm^{-1} is able to ionize the molecule from the triplet state as shown in Figure 2b. Therefore, the lifetime of 40 ns reveals the lifetime of the triplet state, which is relaxed from the band origin through intersystem crossing. If the reason for the quantum yield decrease is due to the relaxation to the triplet state, the vibronic bands in the higher energy region become stronger as compared with the band origin. However, as shown in Figure 2b, no band is observed except for the band origin in the higher frequency region. This fact clearly shows that the relaxation passway to the triplet state is not the reason for the quantum yield decrease in the vibronic level of the (π,π^*) state. Therefore, if 2-FP has no another relaxation process such as photochemical reaction from vibronic level in the exited state, it is concluded that the main reason for the quantum yield decrease in the excited state is attributed to the relaxation to the ground state as the case of the $S_1(n,\pi^*)$ state in pyridine.[3]

3B. **Electronic Spectra of 2-Fluoropyridine—Water Clusters.** Figure 3a shows the fluorescence excitation spectrum of 2-FP with water under jet conditions. In the lower frequency side of the band origin of bare 2-FP, several vibronic bands appear along with an increase in the vapor pressure of water. Among these newly observed bands, three bands are extremely strong. The relative intensity of the three bands strongly depends on the concentration of the vapor pressure of water. Under the lower concentration of water, the 4 cm^{-1} red-shifted band is most intense. As the concentration of water increases, the 74 cm^{-1} red-shifted band becomes intense and the 120 cm^{-1} red-shifted band becomes most intense when the concentration of water and the pressure of He are relatively high. From the intensity behavior of these three bands, the 4, 74, and 120 cm^{-1} red shifted bands are assigned to the band origins of 1:1, 1:2, and 1:3 2-FP−water clusters, respectively. Besides these three band origins, several bands are observed in the higher frequency region and assigned to vibronic bands of 2-FP−water clusters. These bands are composed of inter- and intramolecular vibrations in the excited state of these clusters. The appearance of vibronic bands besides the band origins, which are not observed in the LIF spectrum of bare 2-FP, indicates that the cluster formation with water increases the fluorescence quantum yield in the vibronic levels in the excited state compared to that of bare 2-FP. However, the fluorescence quantum yield remains small for vibronic bands, despite there being a slight trend to increase.

Parts c−e of Figure 3 show the hole-burning spectra of hydrogen-bonded 2-FP with water together with that of bare one in convenience for comparison, which is the same as the one in Figure 1b. Parts c−e of Figure 3 give the depletion in the different wavelengths, and therefore, the three bands obviously originate from different cluster species.

For intramolecular vibrations of hydrogen-bonded 2-FP, the frequency change due to hydrogen-bond formation is expected to be small in the ground state as seen from Table 1. This means that the vibronic structures in the electronic spectra for bare and hydrogen-bonded 2-FP are also similar to each other except for the bands due to intermolecular vibrations. The bands assigned to intramolecualr vibrations of bare 2-FP well correspond to those of 2-FP−H_2O clusters. The vibrational correspondence is also observed in 2-FP−$(H_2O)_2$ and 2-FP−$(H_2O)_3$ clusters. As a result, the frequencies of intramolecular vibrations are similar among bare 2-FP and hydrogen-bonded 2-FP with water in the excited state.

SVL spectra from the band origins of hydrogen-bonded 2-FP with water are shown in Figure 4, and the results are summarized in Table 1. Vibronic structures in the spectra of these clusters are quite similar to that of bare one for intramolecular vibrational

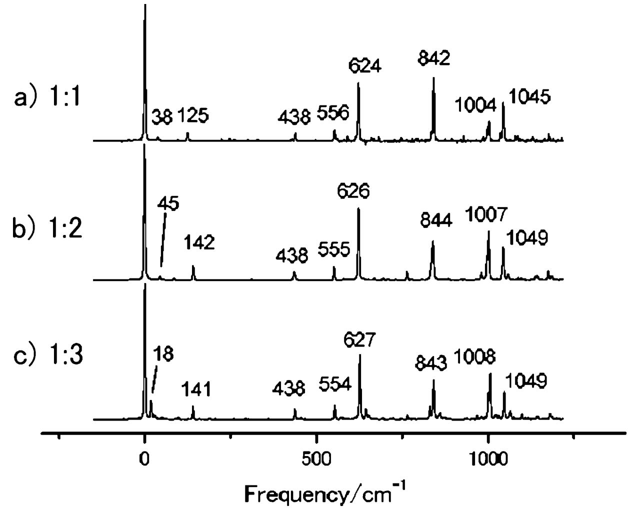


Figure 4. Dispersed fluorescence spectra of hydrogen-bonded 2-fluoropyridine with water. These spectra were obtained with exciting to the band origins of (a) 1:1, (b) 1:2, and (c) 1:3 clusters, respectively.

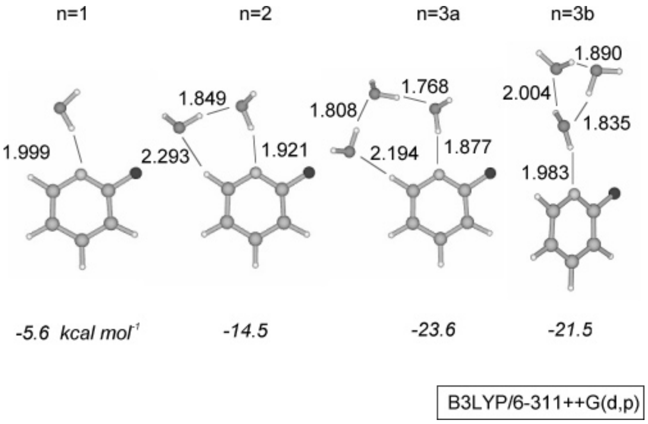


Figure 5. Optimized structures and stabilization energies of hydrogen-bonded 2-fluoropyridine-$(H_2O)_n$ ($n = 1-3$) obtained with B3LYP/6-311++G(d,p), with BSSE corrections.[12] Atomic distance and stabilization energy are shown in angstroms and kilocalories per mole, respectively.

region. Low-frequency bands observed in the SVL spectra of these clusters are assigned to the bands due to intermolecular vibrations.

The optimized structures of hydrogen-bonded clusters with water are shown in Figure 5, and vibrational frequencies are also shown in Table 1. As shown in Figure 5, the first water molecule bonds to the nitrogen atom and water molecules bond to the first water molecule one by one. The fluorine atom is also a candidate as a proton accepting site because fluorine is relatively electron negative. Our calculation also gives this type of 1:1 cluster with B3LYP/6-311++G(d,p) level. However, since the stabilization energy of the structure of F atom bonded cluster is 2.0 kcal/mol less than that shown in Figure 5, it is expected that the N atom bonded cluster is dominant species in our jet condition. The structures obtained with MP2/6-311++G-(d,p) level are quite similar to those shown in Figure 5. For the 1:3 cluster, two structural isomers are obtained, as shown in the figure. One structure has a bridged form, where the third water molecule interacts with the hydrogen atom at the 6-th position. Another structure has the ringed form, where three water molecules form a ring structure and the ring bonds to the nitrogen atom on the pyridine ring. The observed bands at 125, 142, and 141 cm^{-1} are well reproduced by the calculated values of 136 (139), 157 (153), and 153 cm^{-1} by B3LYP/6-311++G-(d,p) (MP2/6-311++G(d,p)) calculations for 1:1, 1:2, and 1:3 (bridged form) clusters, respectively. For the 1:3 cluster, the MP2 calculation has not been carried out. The vibrational mode calculations for the clusters reproduce well for the observed stretching vibration between pyridine ring and water molecule. The intermolecular vibrational frequencies of the ringed form in the 1:3 cluster cannot reproduce the vibronic frequency in the spectrum. Furthermore, the stabilization energy of the bridged form is 2.1 kcal/mol larger than that of the ringed form. These facts suggest that the structure of the 1:3 cluster appearing in the LIF spectrum has the bridged form. For lower frequency vibrations less than 50 cm^{-1} observed in the spectra could be assigned as in-plane or out-of-plane intermolecular vibrations. If the frequency calculation reproduces the intermolecular vibrations of these clusters, these bands observed in the low-frequency region could be assigned to the out-of-plane bending vibration. However, since it is very difficult to reproduce these loose potential surfaces along the intermolecular vibrations precisely, this assignment is not definitive.

The intermolecular stretching frequency of the 1:2 cluster increases by 17 cm^{-1} as compared with that of the 1:1 cluster, however, the frequency of the 1:3 cluster is close to that of the 1:2 cluster. A comparison of these stretching frequencies among the clusters shows that the second water molecules in 1:2 and 1:3 clusters increase the hydrogen-bond interaction between the first water molecule and the nitrogen. However, the coordination of a third water molecule in the 1:3 cluster has a weak influence on the frequency of the hydrogen bond stretching vibration between the first water molecule and the nitrogen atom. If the frequency of the intermolecular stretching vibration directly represents the interaction of the hydrogen bond, it is expected that the third water molecule has weak influence on the hydrogen bond interaction between the first water molecule and nonbonding electrons at the pyridine ring. From the calculated structures of the clusters shown in Figure 5, the bond distances between the hydrogen atom of water and the nitrogen atom decreases 0.078 and 0.044 Å from 1:1 to 1:2 and from 1:2 to 1:3, respectively. This means that the hydrogen bond interaction changes larger from 1:1 to 1:2 than that from 1:2 to 1:3. The calculated frquencies for the stretching vibrations agree well with the result. These calculations with B3LYP and MP2 also well reproduce the frequency increase of 1:2 cluster compared with 1:1 cluster. This fact indicates that this level of the calculation well reproduces the cluster structure. The intermolecular vibrations in the electronic excited state of hydrogen-bonded 2-FP with water well corresponds to the bands observed in the SVL spectra (Table 1). Small frequency changes with the electronic excitation well correspond to the relatively small red shift of the band origin, which represents the degree of stabilization energy in the excited state compared with the ground state. These facts show that the hydrogen bond interaction through nonbonding electrons is similar both for electronic ground and excited (π,π*) states in 2-FP. For the phenol−water 1:1 cluster, where phenol acts as proton donor, the red shift of the band origin is 355 cm^{-1} from that of the bare one.[14] The change of hydrogen bond interaction with the electronic excitation to the (π,π*) state of 2-FP is considerably smaller compared with that of phenol−water cluster although the hydrogen bond interacts directly to the nonbonding orbital on the ring forming nitrogen atom for 2-FP. The fact shows that the proton affinity of 2-FP in the (π,π*) excited state might be similar to that in the ground state.

A comparison of SVL and hole-burning spectra of 2-FP−water clusters indicates that the vibrational correspondence between the absorption and emission spectra holds for both the inter- and intramolecular vibrations. For intramolecular vibrations with higher frequencies, the vibronic structure of the clusters resembles that of the bare one. However, the low-frequency vibrations appeared in the hole-burning spectrum of bare 2-FP do not appear in the SVL spectrum. This fact means that the break down of the vibrational correspondence takes place in bare 2-FP for the low-frequency vibronic bands observed in the hole burning spectrum. As seen from the hole burning spectra, the hydrogen bond formation removes the low-frequency vibronic bands observed in bare 2-FP.

In the present study, none of vibronic bands due to (n,π*) state could be observed in the lower frequency region than 38019 cm^{-1}, which is the band origin of the (π,π*) transition in bare 2-FP. No (n,π*) transition has also been observed in the absorption spectrum of 2-FP in the vapor phase.[7] For 3-fluoropyridine, which is a structural isomer of 2-FP, the band origin of the (n,π*) transition has been observed at 35066 cm^{-1} in the vapor phase.[8] If the transition energy to the lowest (n,π*) state of bare 2-FP is similar to that of 3-fluoropyridine, the energy of the (n,π*) state of 2-FP is expected to be much lower than that of (π,π*) state. Even if the energy of (n,π*) state of 2-FP increases by a few thousand wavenumbers compared to that of 3-fluoropyridine, an (n,π*) state of 2-FP is expected to lie closely to the (π,π*) state under consideration.

Parts c−e of Figure 3 show the hole burning spectra of 1:1, 1:2, and 1:3 clusters, respectively. The lower frequency vibronic bands that are observed at lower than about 150 cm^{-1} could be assigned as intermolecular vibrations between 2-FP and water. From the comparison of Figure 3b and Figure 3c−e, the hydrogen bond formation with water considerably changes the vibronic structure of lower frequency bands observed in bare 2-FP.

It can be found out that the spectra of 1:1, 1:2, and 1:3 clusters have similar vibronic structure in the higher intramolecular vibrational region (Table 1). These facts mean that the intramolecular vibronic structure of bare 2-FP is different from those of hydrogen-bonded ones; however, the vibronic structures of these clusters resemble each other. This result shows that the first hydrogen bond formation with water mainly governs the hydrogen bond effect on the electronic excited state of 2-FP. The origin of the lower frequency vibronic bands observed in the bare 2-FP could be due to the existence of a closely lying (n,π*) state because the hydrogen-bond formation considerably increases the transition energy of the (n,π*) state. In the case of isoquinoline,[16] the band origin of S_2(π,π*) state splits into three bands due to the interaction with the vibronic levels belonging to the lower lying S_1(n,π*) state. The three bands in bare isoquinoline become single peak with the hydrogen bond formation because the hydrogen bond increases the energy of the lower lying (n,π*) state[16] and removes the interaction between the (n,π*) and (π,π*) states. The SVL spectrum from the band origin of hydrogen-bonded isoquinoline is similar to that of bare one in the intramolecular vibrational region. The removal of low-frequency vibronic bands with hydrogen bond formation and the resemblance of SVL spectra in the intramolecular vibrational region between bare and clustered 2-FP correspond well to the results observed in hydrogen-bonded isoquinoline.

Another possibility for the appearance of the lower vibronic bands in bare 2-FP in the excited state might be explained as the interaction with the electronic state that exists in the higher energy than the (π,π*) state. If the perturbing electronic state is an (n,π*) state, the interaction with the (π,π*) state cannot lead to gain transition intensity. However, the potential surface of the (π,π*) state is distorted through the interaction and the vibrational frequency related to the interaction decreases, as observed for the S_1(n,π*) state of pyrazine.[17] In the case of pyrazine, the potential surface of the lowest singlet state is severely distorted along the vibrational mode that induces the interaction and the overtone of the mode appears in the SVL spectra because the vibronic level of overtone belongs to totally symmetric and becomes Franck−Condon active. Therefore, the removal of the vibronic interaction might change the potential surface in the excited state. If this case were applicable for 2-FP, the vibronic structure of hydrogen-bonded 2-FP might be different from that of bare one in the intramolecular vibrational region in the SVL spectra. It should be noted that the vibronic structure of SVL spectra is similar to that of bare 2-FP for intramolecular vibrations.

If the appearance of low-frequency vibronic bands in bare 2-FP originates from the direct interaction between (n,π*) and (π,π*) states as observed in isoquinoline,[15,16] the band origin of (n,π*) state exists just above the band origin of (π,π*) state. Since an (n,π*) state lies higher than the (π,π*) state in energy, estimated from the result of Stephanson,[6] the low-frequency vibronic bands originate from the result of the interaction between vibronic level belonging to (π,π*) state and the band origin of (n,π*) state. This assumption might well explains the relatively complex vibrational structure in the 400−600 cm^{-1} in the hole burning spectrum of bare 2-FP. Our experiment could not clarify the origin of the lower frequency vibronic bands in bare 2-FP in the hole burning spectrum. However, it should be noted that this phenomenon is induced by the existence of nearly lying (n,π*) state.

Taking into account the higher relaxation character of (n,π*) states, the sudden quantum yield decrease just above the band origin could be also explained if the (n,π*) state exists just above the (π,π*) state. The strong interaction between the (π,π*) and (n,π*) states considerably distorts the potential surface in S_1 state. Because the distorted potential surface increases the Franck−Condon overlap between S_1 and higher vibronic levels belonging to S_0, the internal conversion to S_0 from S_1 states is accelerated with the vibronic interaction and decelerated with hydrogen bond interaction.

4. Conclusion

The electronic spectra of bare and hydrogen-bonded 2-fluoropyridine were observed in a supersonic free jet. Sudden quantum yield decrease is observed in bare 2-fluoropyridine from the region just above the band origin of fluorescent (π,π*) state. The vibronic levels relaxed mainly to the S_0 state because no enhancement was observed in the ionization spectrum via triplet state that is populated with the relaxation from the S_1 state. The appearance of extremely low-frequency bands in the spectrum of bare 2-fluoropyridine is ascribed to the interaction between (π,π*) and (n,π*) states because the low-frequency intramoleucular vibronic bands disappear with the hydrogen bond formation with water. The hydrogen bond formation with water increases the quantum yield in the vibronic levels of the (π,π*) state. The molecular orbital calculations with B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels well represent the hydrogen bond stretching frequencies between 2-fluoropyridine and water.

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