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IR−UV Double-Resonance Spectroscopic Study of 2-Hydroxypyridine and Its Hydrogen-Bonded Clusters in Supersonic Jets

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Infrared spectra of 2-hydroxypyridine (2HP) and its hydrogen-bonded clusters with water and methanol have been observed by IR−UV double-resonance spectroscopy. The OH stretching vibrations of the 2-HP site as well as either the water or methanol site were observed. The spectra were compared with those of the corresponding clusters of 2-pyridone (2PY), which have been reported in *J. Chem. Phys.* **1999**, *110*, 8397. The OH stretching vibration of bare 2HP was observed at 3600 cm^{-1}, representing a clear difference from the NH stretching vibration of 2PY (3441 cm^{-1}). On the other hand, the IR spectra of the 2HP−water and −methanol clusters were found to be very similar to those of the corresponding clusters of 2PY, indicating a solvation-mediated tautomerization between 2HP and 2PY. The cluster structures were examined using ab initio molecular orbital calculations.

I. Introduction

2-Hydroxypyridine (2HP) exhibits two stable tautomeric forms, the enol form (Figure 1a) and the keto form, called 2-pyridone (2PY; Figure 1b). The keto−enol tautomerization between 2PY and 2HP has been extensively studied experimentally in various phases,[1−16] in matrixes,[17,18] and also theoretically[19−35] as one of the simplest systems of the intramolecular proton-transfer reaction. A variety of measurements such as UV, IR, microwave, X-ray, and UV photoelectron spectroscopies have been performed for keto−enol tautomerization. From those experiments, it is concluded that the enthalpy change between 2HP and 2PY is 2−3 kJ/mol in favor of the former form with a barrier height larger than 46 kcal/mol. On the other hand, the latter form is known to predominate in polar solvents. The tautomerization reaction in a protic solvent is of special interest, because the reaction is thought to be mediated by hydrogen (H) bonds with solvent molecules, which might lead to a drastic reduction of the barrier height compared to the case of a monomer. Thus, the intermolecular binding characteristics of the H-bonded clusters of 2HP and 2PY are a clue in the microscopic investigation of the tautomerization of 2HP in protic solvents.

The electronic spectra of 2HP, 2PY, and their clusters in supersonic jets have been studied by several workers.[36−42] Bernstein's group[37] examined the S_1−S_0 electronic transition of jet-cooled 2HP/2PY in detail. They measured fluorescence spectra and mass-resolved resonance-enhanced multiphoton ionization spectra (REMPI) of bare molecules and their H-bonded clusters. Three electronic origins were observed: 29832 and 29935 cm^{-1} for 2PY and 36316 cm^{-1} for 2HP. Later, Pratt's group observed rotationally resolved laser-induced fluorescence (LIF) spectra of 2PY, 2PY−water, and $(2PY)_2$ to determine their structures.[38−41] Though those studies based on electronic spectroscopy are sensitive enough to detect low-density clusters in supersonic jets, they have difficulty observing the key vibration for the tautomerization, such as NH or OH vibration. This is because the vibronic bands involving those vibrations are generally inactive in the electronic transition due to very small Franck−Condon factors.

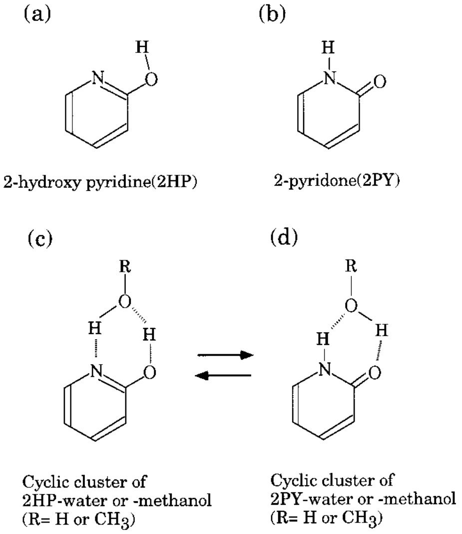

Figure 1. Schematic representation of the stable structures of (a) 2HP, (b) 2PY, (c) 2HP−water (methanol), and (d) 2PY−water (methanol).

To overcome the above difficulty, we have applied double-resonance vibrational spectroscopy,[43−48] in which we measure IR and stimulated Raman spectra of 2PY and its clusters in supersonic jets. In our previous works,[47,48] we observed the C═O and NH stretching vibrations for 2PY, and also the OH stretching vibration of its H-bonded clusters with water, methanol, etc. By use of ab initio molecular orbital calculations, we determined geometrical structures of various clusters of 2PY, and found a clear correlation between the H-bonded structure and the lower-frequency shift of the NH stretching vibration. We also measured the vibrations for the electronically excited 2PY and its clusters to investigate the effect of the electronic excitation on the acidity of 2PY.[48]

In the present study, we observed vibrational spectra of 2HP and its H-bonded clusters with water or methanol. Though the clusters of 2PY have been studied in detail experimentally and theoretically, the corresponding structures of the 2HP clusters

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have been less studied. In the IR spectrum in an Ar matrix,[17,18] 2HP exhibits the OH stretching vibration at 3574 cm^{-1}, while 2PY exhibits the NH stretching vibration at 3438 cm^{-1}. In addition, 2HP and 2PY exhibit different electronic transition energies.[37] This is a good system to apply double-resonance vibrational spectroscopy, because we can discriminate individual species in the jet and measure its vibrational spectrum. Figure 1c,d shows schematic structures of 2HP−water (methanol) and 2PY−water (methanol). It can be seen that all the clusters have a cyclic form and the two tautomers are interchanged by exchanging protons with the solvent molecules. It would be very interesting to examine the difference in the IR spectra between the clusters of the two tautomers. So, the aim of this work is first to discriminate the two tautomers, 2HP and 2PY, in their hydrogen-bonded forms with protic solvents by the measurement of the OH and NH stretching vibrational spectra, and then to investigate how the tautomerization is reflected in their vibrational spectra. By using the difference in the electronic transition energies, we discriminated the two tautomers of bare molecules and also of their H-bonded clusters, and measured their vibrational spectra in the OH and NH stretching vibrational region by IR−UV double-resonance spectroscopy. Very interestingly, we found that the IR spectra are very similar between 2HP−water and 2PY−water and also between 2HP−methanol and 2PY−methanol. The results suggest the importance of the use of the clusters for investigation of the tautomerism of 2HP ↔ 2PY in protic solvents.

II. Experimental Section

The experimental setup of IR−UV double-resonance spectroscopy with fluorescence detection, the so-called fluorescence-detected IR (FDIR) spectroscopy, was described in detail elsewhere.[43−48] In this spectroscopy, we measure the IR spectrum of the selected species in a supersonic jet as the fluorescence-dip spectrum. The selection of the particular species is carried out by LIF. Frequency of a pulsed tunable UV laser is fixed to the transition of a specific species in the jet, and its fluorescence intensity is monitored as a measure of the population in S$_0$. Under this condition, a pulsed tunable IR light is introduced prior to the UV pulse. When the IR frequency is resonant with the vibrational transition of the species selected by the UV light, a depletion of the fluorescence signal occurs due to the reduction of the ground-state population caused by the IR absorption. Thus, the IR spectrum is obtained as the fluorescence-dip spectrum by monitoring the fluorescence intensity while scanning the IR frequency.

The tunable IR beam was generated by a difference frequency generation (DFG) with a LiNbO$_3$ crystal. For DFG, a second harmonic of a Nd:YAG laser (Quanta-Ray GCR/230) and the output of a Nd:YAG laser pumped dye laser (Continuum ND 6000 with DCM dye) were used. The UV light source was a second harmonic of a XeCl excimer laser pumped dye laser (Lambda Physik LPX100/FL3002). The IR and the UV beams were introduced into the vacuum chamber in a counterpropagated manner and crossed the supersonic jet at 20 mm downstream of the pulsed nozzle. The fluorescence of 2HP or 2PY and its clusters were monitored by a photomultiplier tube (Hamamatsu photonics 1P28) after being passed through a band-pass filter (Corning 7-54). The photocurrent was integrated by a boxcar integrator (Par model 4400/4420) connected with a personal computer.

A gaseous mixture of 2HP/water or methanol was seeded in He carrier gas at a total pressure of 3 atm, and was expanded supersonically into a vacuum through a pulsed nozzle having a 0.8 mm diameter. To obtain sufficient pressure, a sample housing of 2HP was heated at 370 K. 2HP (97%) was purchased from Wako Chemical Industries, Ltd. and was used without further purification. Methanol-d_4 (CD$_3$OD, 99.8 atom %) was purchased from Aldrich.

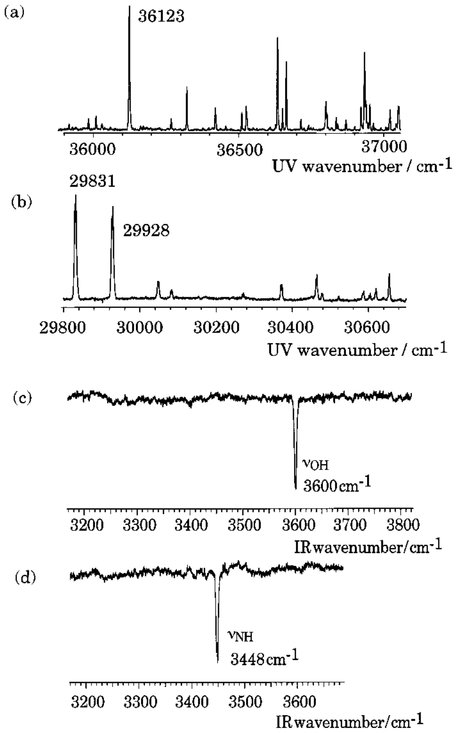

Figure 2. LIF excitation spectra of (a) 2HP and (b) 2PY and FDIR spectra of (c) 2HP and (d) 2PY.

Ab initio molecular orbital calculations have been carried out by using the GAUSSIAN 94 program[49] with the HF/6-31G basis set. Obtained vibrational frequencies were scaled by a factor of 0.896.

III. Results and Discussion

III.1. Electronic and IR Spectra of Bare 2HP and 2PY.

The coexistence of 2HP and 2PY in the supersonic jet was demonstrated by Nimlos et al.[37] Figure 2 shows the LIF spectra of the S$_1$−S$_0$ ($\pi\pi^*$) transition of (a) 2HP and (b) 2PY. For 2PY, there are two intense bands at 29831 and 29928 cm^{-1}. From the analysis of the high-resolution LIF spectrum[38] and by double-resonant vibrational spectroscopic study,[47,48] the two bands were assigned to the origins of the different electronic states, whose upper state structures are slightly different with respect to the NH group. For 2HP, the S$_1$−S$_0$ origin band occurs at 36123 cm^{-1}.

We first measured the FDIR spectrum of the OH stretching vibration of bare 2HP by fixing the UV frequency at 36123 cm^{-1}. Figure 2c shows the FDIR spectrum of bare 2HP, which is compared with the NH stretching vibration of 2PY (Figure 2d) observed in our previous work.[47] As seen in the figures, the OH stretching vibration of 2HP appears at 3600 cm^{-1}, which is well separated from the NH stretching vibration of 2PY at 3448 cm^{-1}. The obtained vibrational frequencies are in good agreement with those obtained in an Ar matrix,[17,18] except that the frequencies in the Ar matrix are 10−26 cm^{-1} lower than those observed in supersonic jets. The result is a clear demonstration of the IR−UV double-resonant spectroscopy, in which one can discriminate the two tautomers and measure their IR spectra independently.

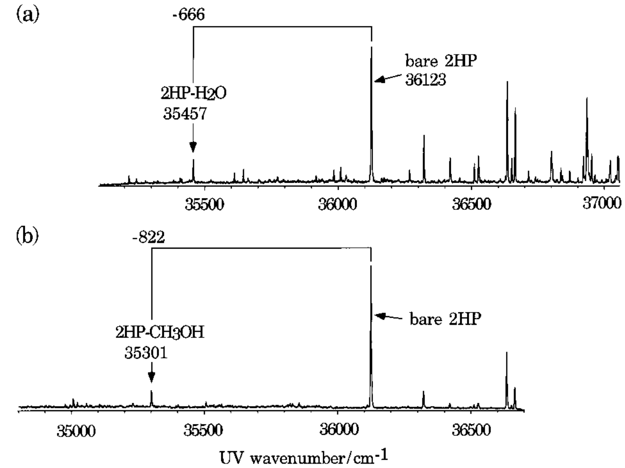

Figure 3. LIF excitation spectra of (a) 2HP–water, and (b) 2PY–methanol in supersonic jets.

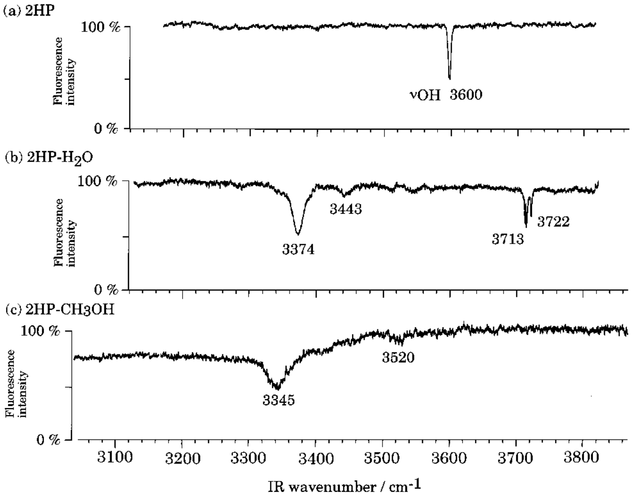

Figure 4. FDIR spectra of (a) 2HP, (b) 2HP–water, and (c) 2HP–methanol in supersonic jets.

III.2. 2HP–Water and –Methanol.

Figure 3 shows the LIF spectra of the 2HP clusters obtained by expanding the gaseous mixtures of (a) 2HP/water and (b) 2HP/methanol, respectively. The peak at 35457 cm^{-1} was found to gain its intensity with increasing water vapor pressure. Similarly, the intensity of the peak at 35301 cm^{-1} increased with an increase of methanol vapor pressure. Earlier, Nimlos et al. assigned the band at 35457 cm^{-1} to the origin of the 2HP–water (1:1) cluster by measuring the mass-resolved REMPI spectrum.[37] From the similarity of the solvent vapor pressure dependence to that of 2HP–water, the band at 35301 cm^{-1} is assigned to the origin of the 2HP–methanol (1:1) cluster. The red shift of the origin band is 666 cm^{-1} for 2HP–water and 822 cm^{-1} for 2HP–methanol. Thus, the cluster is highly stabilized in S_1 and the similar red-shifts for 2HP-water and 2HP-methanol suggest the two clusters have the similar H-bonded structures.

Figure 4 shows the FDIR spectra of (a) 2HP, (b) 2HP–water, and (c) 2HP–methanol. In the FDIR spectrum of 2HP–water, an intense dip is observed at 3374 cm^{-1} and a very weak dip is seen at 3443 cm^{-1}. At higher frequency, two peaks are observed at 3713 and 3722 cm^{-1}. The splitting of the band at 3713 cm^{-1}, however, is associated with the reduction of the IR light intensity due to ambient water vapor absorption in this region, and the band expected in this region is readily assigned to the antisymmetric vibration (ν_3) of the water site. The H-bonded OH stretching vibrations of 2HP and H_2O sites correspond to the bands at either 3374 and 3443 cm^{-1} or vice versa, respectively. Although the observed spectrum suggests a cyclic form as shown in Figure 1c, there is difficulty in the assignments of the observed vibrational bands in the IR spectra. That is, in such a cyclic form, two H-bonded OH stretching vibrations are usually expected to be intense in the IR spectrum, while only one of them is intense in the spectrum of Figure 4b.

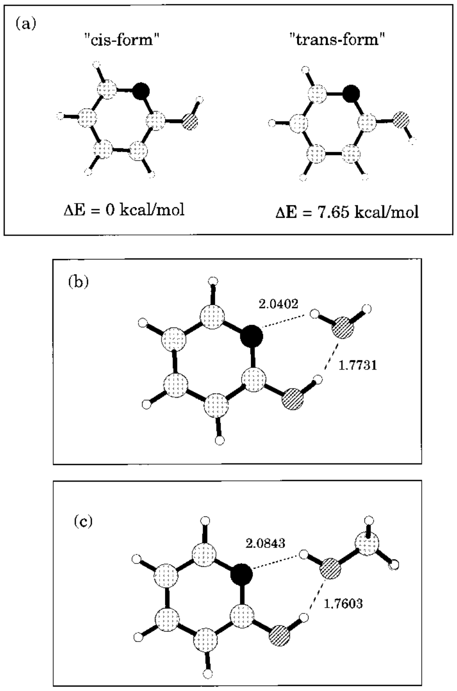

Figure 5. Energy-optimized structure of (a) 2HP, (b) 2HP–water, and (c) 2HP–methanol obtained by ab initio calculation with HF/6-31G. The distances are in angstroms. See the text.

To solve the above problem, we observed the FDIR spectrum of 2HP–methanol. As shown in Figure 4c, two dips are observed: an intense dip at 3345 cm^{-1} and a very weak dip at 3520 cm^{-1}. These two bands would be assigned to the H-bonded OH stretch vibrations of either the 2HP or methanol site. Surprisingly, the spectral feature is very similar with that of 2HP–water. That is, the spectrum exhibits one intense band and one weak band in the H-bonded OH stretching region. Since no free OH band is observed at ~3680 cm^{-1} in the IR spectrum of 2HP–methanol, the two OH groups of both molecules are involved in the H-bonding, supporting the cyclic form.

To assign the observed vibrational bands, we then carried out ab initio molecular orbital calculations. Figure 5 shows the energy-optimized structures of 2HP, 2HP–water, and 2HP–methanol obtained by ab initio calculations with the HF/6-31G basis set. For bare 2HP, two forms were obtained: one is the cis-form and the other is the trans-form, in which the former is 7.65 kcal/mol more stable than the latter. The larger stabilization energy of the cis-form is due to a large attractive interaction between the OH hydrogen and the lone pair electron of the N atom. Thus, we focused on the cluster structures only for the cis-form 2HP. Figure 5b,c shows energy-optimized cyclic forms for 2HP–water and 2HP–methanol, both of which are thought to be the most probable structures. In Figure 6 is shown a comparison between the observed and the calculated IR spectra for 2HP–water and –methanol. As was argued previously, two H-bonded OH stretching vibrations are seen with intensities comparable with the HF/6-31G level calculations, which do not provide good agreement with the observed spectra. A possible

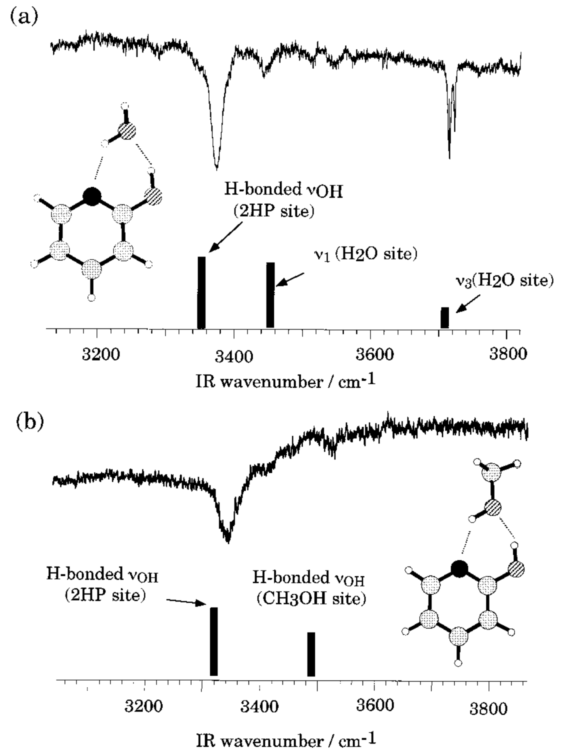

Figure 6. Comparison between the observed spectra and the calculated spectra with the HF/6-31G basis set: (a) 2HP−water, (b) 2HP−methanol. Calculated spectra are shown by stick diagrams.

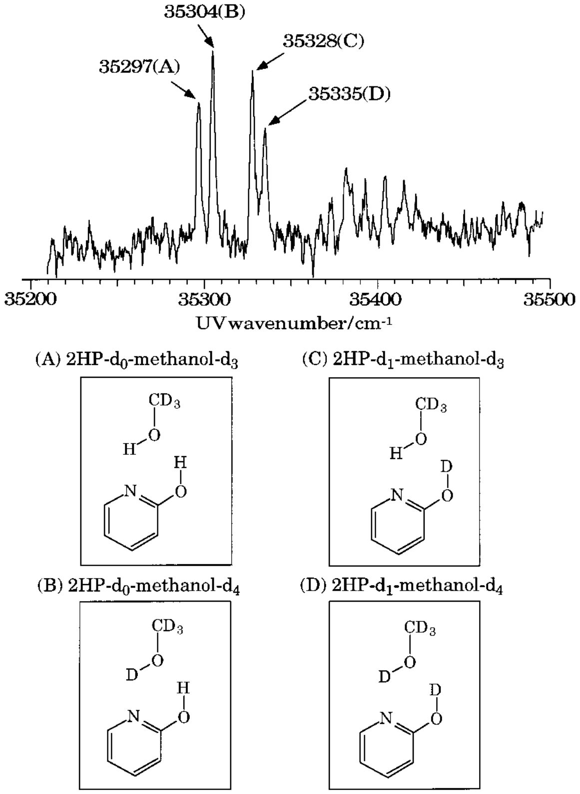

Figure 7. (Top) LIF spectrum obtained by expanding the gaseous mixture of 2HP/methanol-d_4. (Bottom) Schematic representations of the deuterium-substituted 2HP−methanol cluster. See the text.

reason for the appearance of only one H-bonded OH stretching band in the clusters is either the two OH vibrations are overlapped within the one band or one of the OH stretching bands is very weak compared to the other.

III.3. Deuterium-Substituted 2HP−Methanol Cluster. To answer the above-mentioned question from an experimental point of view, we observed the OH stretching vibrations of 2HP−methanol in more detail by using deuterated methanol, that is, methanol-d_4. In methanol-d_4, the OD deuterium is easily exchanged with hydrogen. Thus, four isotopomers of 2HP−methanol coexist in the free jet as shown in the lower part of Figure 7. Figure 7 shows the LIF spectrum of the 2HP/methanol-d_4 mixture, which shows four bands as expected. In the figure, the lowest frequency band A is due to 2HP-d_0−methanol-d_3. Since the deuterium substitution of the OH group of the 2HP site may lead to a large change in the electronic transition energy compared to that of the OH group of methanol, bands C and D are thought to belong to the species having the 2HP-d_1 isotope. The correspondence between the LIF bands and the isotope-substituted clusters is given in Figure 7, which is finally supported by the results of the IR spectroscopic measurements.

Figure 8 shows the FDIR spectra measured by fixing the UV frequencies to bands A and B in Figure 7. In the IR spectrum of 2HP-d_0−methanol-d_3 (Figure 8a), obtained by tuning the UV frequency to band A, two bands are observed: an intense band at 3345 cm^{-1} and a weak band at 3516 cm^{-1}. The spectrum is very similar to that of 2HP-d_0−methanol-d_0 shown in Figure 4c, except the band at 3516 cm^{-1} is more prominent in Figure 8a. The IR spectrum of 2HP-d_0−methanol-d_4, obtained by monitoring band B, exhibits a band at 3195 cm^{-1}, which is due to the OH stretching vibration of 2HP site. In the IR spectrum of 2HP-d_1−methanol-d_3, obtained by monitoring band C, an intense band is observed at 3331 cm^{-1}, which is due to the OH stretching vibration of methanol-d_3. Finally, in the spectrum of 2HP-d_1−methanol-d_4, obtained by monitoring band D, no OH band is observed. From the IR spectra of Figure 8b,c, we can conclude that the frequency of the H-bonded OH stretching vibration of the 2HP site is lower than that of the methanol site. Thus, in the IR spectrum of 2HP-d_0−methanol-d_3 in Figure 8a, the intense band at 3345 cm^{-1} is assigned to the H-bonded OH stretch vibration of the 2HP site and the band at 3516 cm^{-1} to that of the methanol site.

On the basis of the IR spectra of the isotope-substituted 2HP−methanol, we carried out the assignments of the vibrations of 2HP−methanol as well as 2HP−water. Since a very small effect is expected for the OH stretching vibration upon the deuterium substitution of the methyl group of methanol, the IR spectra of the OH stretching vibration of 2HP-d_0−methanol-d_3 exhibit a feature very similar to that of 2HP-d_0−methanol-d_0 as shown in Figures 8a and 4c. Here, the band at 3345 cm^{-1} is very intense and the other band is observed very weakly at 3516 or 3520 cm^{-1}. It was also found that the frequency of the OH stretching vibration of the 2HP site is lower than that of the methanol site. This is in good agreement with the results of the ab initio calculation. Thus, these results strongly suggest that the intense band at 3345 cm^{-1} is due to the OH stretch of 2HP, and a very weak band at 3520 cm^{-1} to that of methanol. In a similar manner, the intense band at 3374 cm^{-1} in the IR spectrum of 2HP−water (Figure 4b) is assigned to the H-bonded OH stretch of the 2HP site, and that at 3443 cm^{-1} to the symmetric stretching vibration of the water site.

The disagreement between the calculated relative intensities of the two OH stretching vibrations and the observed ones might be solved by using higher basis sets or density functional calculations. A possible explanation of the observed unusual intensity pattern for the two bands is that each vibration might not be localized in each site but the modes are strongly coupled through anharmonic coupling since their vibrational frequencies are very close. In such a case, the vibrations can

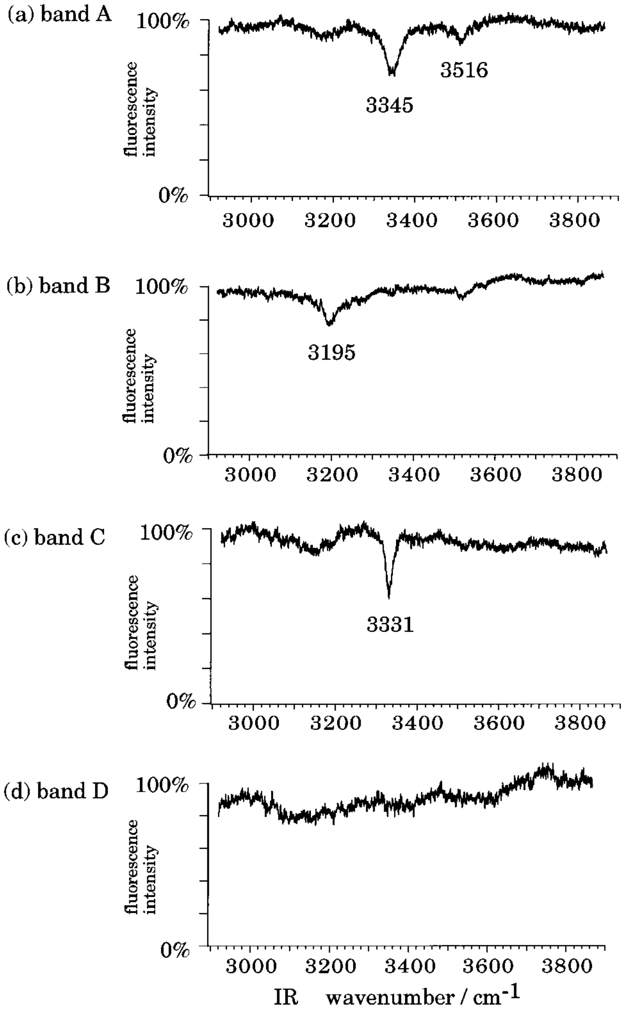

Figure 8. FDIR spectra of the deuterium-substituted 2HP−methanol cluster obtained by monitoring the bands in Figure 7.

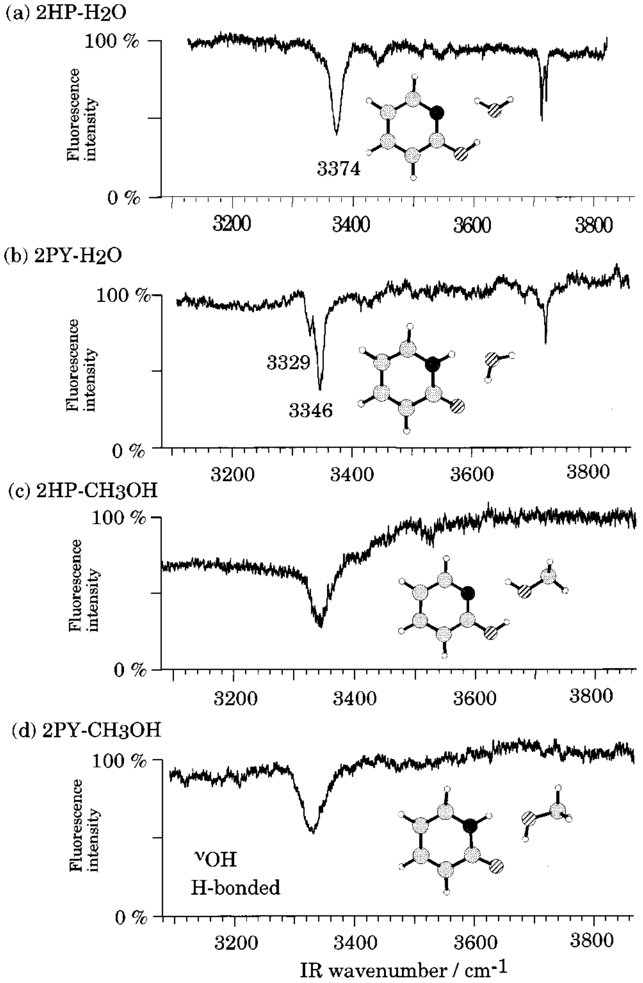

Figure 9. Comparisons of the FDIR spectra between (a) 2HP−water and (b) 2PY−water and between (c) 2HP−methanol and (d) 2PY−methanol.

be expressed by a linear combination of those modes. One is IR active, which was strongly observed in the present work, and the other will be Raman active. Though we tried to observe the Raman spectrum for the two vibrations to confirm the above hypothesis by fluorescence-detected stimulated Raman spectroscopy, we failed to observe them due to experimental difficulties. So, we cannot provide definitive evidence at this moment.

Finally, we comment on the comparison of the IR spectra of the clusters of 2HP with those of 2PY which were reported in our previous work.[47] As was discussed above, both 2HP−water and −methanol have a cyclic structure and also 2PY−water and −methanol have a cyclic structure. They are interchanged with each other by an exchange reaction of two protons (or hydrogen atoms), and the tautomerization reaction can be identified from the difference in the vibrational spectra. However, it was found that the two tautomers exhibit very similar vibrational spectra. Parts a and b of Figure 9 show a comparison of the IR spectra of 2HP−water with that of 2PY−water,[47] and parts c and d of Figure 9 show the IR spectra of 2HP−methanol and 2PY−methanol.[47] As seen in the figure, the IR spectra are surprisingly similar to each other. That is, each spectrum exhibits an intense broad band in the H-bonded OH or NH stretching vibrational region and their frequencies are very close.

The similarity in frequency, in intensity, and in bandwidth of the OH stretching vibration of the clusters suggests that the potential energy surfaces (PESs) along the OH stretching coordinate are similar between the cyclic form clusters of the tautomers. If the intermolecular H bond becomes more prominent, the PESs of the clusters of the two tautomers will be unified to have a single local minimum, and as a result the hydrogen atom (or a proton) associated with the H bond will be located in the middle of the tautomerization coordinate. In this respect, it is noticed in Figure 9 that the similarity of the IR spectra of the clusters with methanol for 2HP and 2PY is more pronounced than that of clusters with water. Since the proton-accepting ability of methanol oxygen is larger than that of water oxygen, it is expected that the potential energy minima of the clusters with methanol will be much closer than in the case of the clusters with water.

It should, however, be noted that the frequency in the hydrogen-bonded OH stretching region of the 2HP form is slightly (18 cm^{-1}) higher than that of the 2PY form, indicating that the two PESs are not still unified even in the clusters with methanol. The results indicate that the solvation-mediated tautomerization of the cyclic form H-bonded clusters is not accomplished in a 1:1 cluster with either methanol or water, though the IR spectra give a spectroscopic sign of this reaction. Although we could not identify the larger size clusters, it is necessary to investigate the IR spectra of the larger size clusters for the details of the microscopic study of the solvation-mediated keto−enol tautomerization occurring in protic solvents.

IV. Conclusion

In the present work, we compared the IR spectra of 2HP and 2PY and their hydrogen-bonded clusters with water and methanol. It was shown that both tautomers form cyclic hydrogen-bonded structures with the protic solvent molecules. It was found that their vibrational spectra exhibit very similar features in the OH and NH stretching region, and such a similarity has been revealed for the first time by the IR−UV double-resonance spectroscopic study of the size-selected clusters. For future work, it will be very interesting to examine the OH stretching vibration of the electronically excited 2HP−water and −methanol clusters, since 2HP → 2PY is a highly exothermic reaction in S_1 and the excitation to its OH stretching vibration may promote the tautomerization.

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