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LETTERS

Photofragment-Detected IR Spectroscopy (PFDIRS) for the OH Stretching Vibration of the Hydrogen-Bonded Clusters in the S_1 State−Application to 2-Naphthol-B (B = H_2O and CH_3OH) Clusters

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IR spectra of the OH stretching vibrations of 2-naphthol-B (B = H_2O and CH_3OH) clusters in S_1 have been measured by photofragment detected IR spectroscopy (PFDIRS). In this spectroscopy, a tunable IR light pulse excites the OH stretching vibration of the electronically excited 2-naphthol-B, which is prepared by a UV light pulse. The vibrationally excited cluster immediately predissociates to generate a 2-naphthol fragment in S_1. By monitoring the emission only from the 0^0_0 band of the fragment with a monochromator while scanning the IR frequency, a background free IR spectrum of the OH stretching vibration of the cluster in S_1 has been successfully obtained. By comparing the IR spectra of the cluster in S_1 with those of in S_0, the effect of the electronic excitation on the frequency change of the OH stretching vibration in the cluster is discussed.

Introduction

Since the pioneering work on the observation of the CH stretching vibrations of benzene by Page et al.,[1] IR−UV double resonance technique have been extensively applied to isolated molecules and their clusters generated in a supersonic expansion. In particular, hydrogen-bonded clusters of aromatic molecules with solvent molecules have been widely investigated by observing their OH and NH stretching vibrations.[2−13] The IR spectroscopy of the OH and NH stretching vibrations may be the most powerful technique for the analysis of hydrogen-bonded structures, because the OH and NH stretching frequencies are easily perturbed by their environment. However, up to now, most of the works have been concerned with structures and vibrations of the clusters only in the electronically ground state (S_0), and the corresponding works for the electronically excited state (S_1) are still less performed.

For the measurement of the OH stretching vibrations in S_1, Ebata et al. applied UV−IR double resonance spectroscopy to the phenol−$(H_2O)_n$ clusters.[3] In the spectroscopy, the population of the zero point level of S_1 was monitored through its fluorescence intensity, and the population reduction induced by IR laser pumping was observed as a decrease of the total fluorescence. Since this spectroscopy utilizes the difference in fluorescence quantum yield between the zero point level and the vibrationally excited level, the application of this method is limited to the cluster whose fluorescence quantum yield changes upon the vibrational excitation.

In the present work, we report an advanced technique of the IR spectroscopy of cluster in S_1, which is applied to the 2-naphthol (2NpOH)-B (B= H_2O and CH_3OH) hydrogen-bonded clusters. We refer to this spectroscopy as "Photofragment-detected IR Spectroscopy (PFDIRS)". In this technique, we measure the dispersed fluorescence of the fragment generated by IR-induced vibrational predissociation. By using a monochromator, only the emission of the 2NpOH fragment was detected, resulting in the background free IR spectrum of the clusters in S_1. The advantage of this spectroscopy and the

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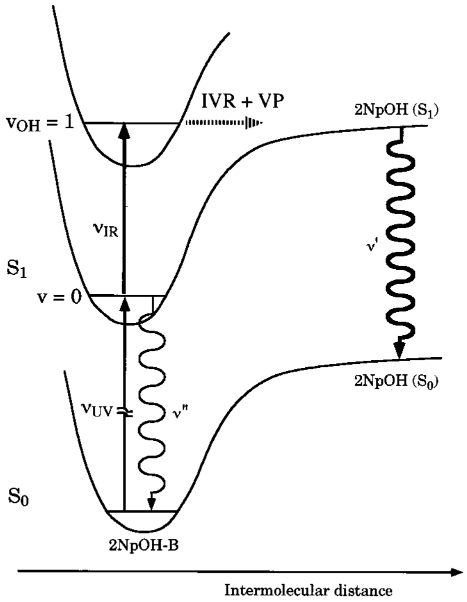

Figure 1. Schematic potential curves and the excitation scheme of the photofragment-detected IR spectroscopy (PFDIRS).

comparison of the OH stretching vibration between S_1 and S_0 will be discussed.

Experiment

Figure 1 shows the excitation scheme of PFDIRS. In this technique, 2NpOH−B, where B represents H_2O or CH_3OH in a supersonic jet, was prepared to the zero-point level (0^0) of S_1 by a UV pulse (ν_{UV}). Following the electronic excitation, a tunable IR pulse (ν_{IR}) was introduced to excite the cluster to the OH stretching vibration, where no delay time between the two pulses was applied. In general, the OH stretching frequency is larger in energy than that of the hydrogen bond, and the vibrationally excited cluster in S_1 dissociates into 2NpOH in S_1 and B. Following the dissociation, the 2NpOH fragment in S_1 emits the fluorescence mainly from the zero point level. Thus, the IR spectrum of the electronically excited cluster is obtained by scanning ν_{IR} while detecting the only $0^0{}_0$ fluorescence of the 2NpOH fragment by using a monochromator.

The second harmonic of an Nd:YAG laser pumped dye laser (Spectra-Physiks INDI-50-10/Lumonics HD-500) was used for the UV light. The IR light was generated by difference frequency mixing between the second harmonics of an Nd:YAG laser (Spectra-Physiks GCR-230) and the output of the Nd:YAG laser pumped dye laser (Continuum ND-6000), by using a $LiNbO_3$ crystal. The UV and IR beams were coaxially introduced into a vacuum chamber with a counterpropagating manner, and were focused by lenses ($f = 500$ mm for UV, $f = 250$ mm for IR) on a supersonic free jet at 15 mm downstream from a nozzle.

2NpOH−H_2O or −CH_3OH cluster was generated by a supersonic expansion of 2NpOH vapor seeded in a 5% gaseous mixture of H_2O (or CH_3OH)/He at a total pressure of 3 atm. 2NpOH was heated at 370 K to obtain a sufficient vapor pressure. The mixture was expanded into vacuum through a pulsed nozzle having a 800 μm aperture. Fluorescence was focused on a slit of a monochromator (Nikon G250, $f = 0.25$ m) by a lens and was detected by a photomultiplier tube (Hamamatsu Photonics 1P28). The slit of the monochromator was set to 500 μm, corresponding to a spectral resolution of $\approx$200 cm^{-1}. The photocurrent from the photomultiplier tube was integrated by a boxcar integrator (Par Model 4420) connected with a microcomputer.

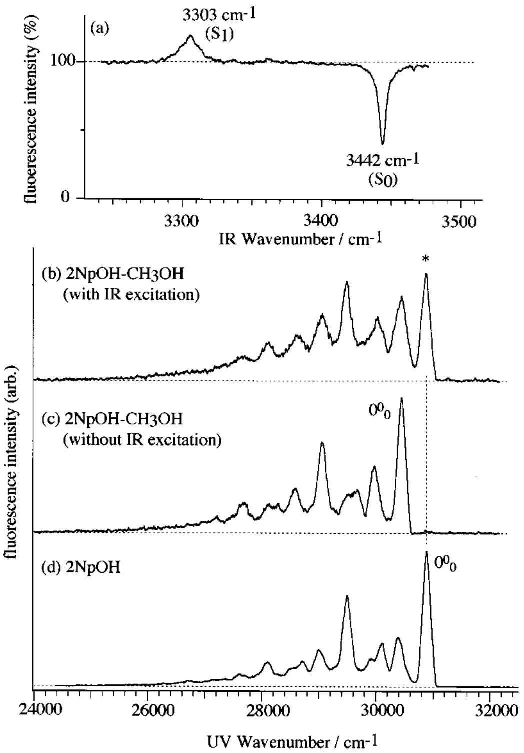

Figure 2. (a) Fluorescence-detected IR spectra of 2NpOH−CH_3OH, measured by setting the delay time between ν_{UV} and ν_{IR} to be 0 ns. (b) and (c) Dispersed fluorescence spectra of 2NpOH−CH_3OH with and without the IR excitation to the OH stretching vibration at 3303 cm^{-1}, respectively. (d) Dispersed fluorescence spectrum of bare 2NpOH observed by the $0^0{}_0$ band excitation.

As is well-known, there are two isomers in 2NpOH, cis and trans, depending on the orientation of the OH group with respect to the naphthalene ring.[5,14] Since cis-isomer is a major species in a supersonic free jet, only cis-isomer was investigated in this work. The S_1−S_0 $0^0{}_0$ transitions of *cis*-2NpOH, *cis*-2NpOH−H_2O, and *cis*-2NpOH−CH_3OH were observed at 30903, 30533, and 30481 cm^{-1}, respectively.

Results and Discussion

Figure 2a shows the fluorescence detected IR spectra of 2NpOH−CH_3OH. In the spectrum, no delay time between ν_{UV} and ν_{IR} was applied. As seen in the spectrum, two bands are observed, one is a depletion at 3442 cm^{-1} and the other is an enhancement at 3303 cm^{-1}. The former band is assigned to the hydrogen-bonded OH stretching vibration of the 2NpOH site, ν_{OH}(2NpOH), in S_0. The latter band is assigned to the ν_{OH}(2NpOH) in S_1, since this band disappears when ν_{IR} is introduced prior to ν_{UV}. Two possibilities are conceivable for the enhancement of the total fluorescence signal for the band at 3303 cm^{-1}. First is that the fluorescence quantum yield (FQY) at the OH stretching vibrational level is larger than that at the zero-point level for 2NpOH−CH_3OH. Second is that 2NpOH−CH_3OH predissociates after the IR excitation to its OH stretch band and the FQY of bare 2NpOH is larger than that of the cluster.

To examine the two possibilities above, we observed the dispersed fluorescence spectrum of 2NpOH−CH_3OH after the IR excitation to its OH stretching vibration in S_1. Figure 2 also shows the dispersed fluorescence spectra of 2NpOH−CH_3OH (b) with and (c) without the IR excitation to the ν_{OH}(2NpOH) at 3303 cm^{-1}, where ν_{UV} is tuned to the $0^0{}_0$ band of 2NpOH−CH_3OH. Figure 2d shows the dispersed fluorescence spectrum

TABLE 1: Frequencies (cm^{-1}) of the Observed OH Stretching Vibrations of 2NpOH, 2NpOH−H_2O, and 2NpOH−CH_3OH in S_0 and S_1

	S_0			S_0		
	frequency	assignment	$\Delta\nu_{OH}$[a]	frequency	assignment	$\Delta\nu_{OH}$[a]
2NpOH	3652	ν_{OH}(2NpOH)		3609	ν_{OH}(2NpOH)	
2NpOH−H_2O	3509	ν_{OH}(2NpOH)	−143	3408	ν_{OH}(2NpOH)	−201
	3651	ν_1		3650	ν_1	
	3746	ν_3		3746	ν_3	
2NpOH−CH_3OH	3442	ν_{OH}(2NpOH)	−210	3303	ν_{OH}(2NpOH)	−306
	3679	ν_{OH}(CH_3OH)		3679	ν_{OH}(CH_3OH)	

[a] Red shift from the OH stretching vibration of bare *cis*-2NpOH in each electronic state.

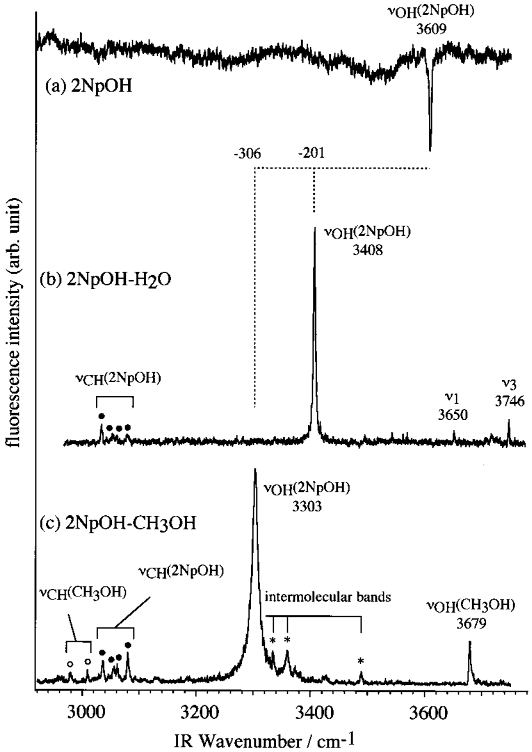

Figure 3. (a) Fluorescence-detected IR (FDIR) spectrum of bare 2NpOH in S_1. (b) and (c) PFDIR spectra of 2NpOH−H_2O and −CH_3OH in S_1 measured by monitoring the 0^0_0 band of the 2NpOH fragment while scanning the IR frequency.

of bare 2NpOH observed after the excitation to the 0^0_0 band. As seen in Figure 2b, a new band appears at the high-frequency side of the 0^0_0 band of 2NpOH−CH_3OH, which is not seen in Figure 2c. In addition, the spectral feature of Figure 2b is very similar to the spectrum obtained by the 0^0_0 band excitation for bare 2NpOH in Figure 2d. Thus, it is concluded that after the OH excitation, 2NpOH−CH_3OH predissociates to generate the 2NpOH fragment, which is mostly populated in the zero-point level in S_1. We fixed the wavelength of the monochromator to the 0^0_0 band of bare 2NpOH and scanned the IR frequency. By this method, the background free IR spectra of 2NpOH−CH_3OH and −H_2O in S_1 were successfully obtained. This method is called “photofragment-detected IR spectroscopy (PFDIRS)”.

Figure 3 shows the PFDIR spectra of (b) 2NpOH−H_2O and (c) −CH_3OH in S_1, and (a) represents the IR spectrum of bare 2NpOH in S_1 obtained by UV−IR double resonance spectroscopy. The frequencies of the observed bands and the corresponding frequencies in S_0 are listed in Table 1. Because of an efficient improvement of the signal-to-noise ratio, not only the ν_{OH}(2NpOH), but also other weak bands such as the OH stretching vibrations of the solvent sites and the CH stretching vibrations are unambiguously observed. In the spectra, the intense bands at 3408 and 3303 cm^{-1} are assigned to ν_{OH}(2NpOH) for 2NpOH−H_2O and −CH_3OH, respectively. As seen in Figure 3a−c, ν_{OH}(2NpOH) shows a shift to lower frequency by 201 cm^{-1} for 2NpOH−H_2O, and by 306 cm^{-1} for 2NpOH−CH_3OH from that of bare 2NpOH. As listed in Table 1, the shifts of the ν_{OH}(2NpOH) in S_0 are 143 and 210 cm^{-1} for 2NpOH−H_2O and −CH_3OH, respectively. Therefore, the shifts in S_1 are about 1.5 times larger than those in S_0. These larger shifts in S_1 correspond to the increase of the acidity of 2NpOH in S_1; $pK_a = 3.0$ in the S_1 state while $pK_a = 9.45$ in the S_0 state.[15,16] Thus, OH bond strength is more weakened in S_1 by the stronger hydrogen bond than in S_0.

As described above, in addition to the intense ν_{OH}(2NpOH), several weak bands are also observed. The bands at 3650 and 3746 cm^{-1} in 2NpOH−H_2O are assigned to ν_1 and ν_3 vibrations of the H_2O site, respectively. The band at 3679 cm^{-1} in 2NpOH−CH_3OH is assigned to the free OH stretching vibration of the CH_3OH site (ν_{OH}(CH_3OH)). As seen in Table 1, the frequencies of the OH stretching vibrations of the solvent site in S_1 are the same with those in S_0, which indicates that these hydrogen-bond free vibrations are not affected upon electronic excitation. Around 3400 cm^{-1} of the spectrum of 2NpOH−CH_3OH, three weak bands are observed at 3334, 3360, and 3489 cm^{-1}. The relative frequencies of these bands with respect to the ν_{OH}(2NpOH) at 3303 cm^{-1} are +31, +57, and +186 cm^{-1}, respectively. These bands may be assigned as combination bands between the OH stretching and intermolecular vibrations. Kleinermanns and co-workers reported the analysis of the intermolecular vibrations of phenol−CH_3OH[17] and of catechol−CH_3OH[18] in S_0 and S_1. On the basis of their assignment, we tentatively assigned the bands at +31, +57, and +186 cm^{-1} to the combination bands with torsion, wagging, and stretch vibrations, respectively.

Finally, four bands at 3036, 3056, 3061, and 3080 cm^{-1}, which are commonly observed for 2NpOH−H_2O, and −CH_3OH, are assigned to the CH stretching vibrations of the 2NpOH site (ν_{CH}(2NpOH)), and the bands at 2979 and 3010 cm^{-1} are assigned to the CH stretching vibrations of the CH_3OH site (ν_{CH}(CH_3OH)) of 2NpOH−CH_3OH. Since PFDIR spectroscopy involves the vibrational predissociation of the cluster, the band observed at the lowest frequency represents an upper limit of the dissociation energy of the cluster in S_1. The lowest frequency bands at 3036 cm^{-1} for 2NpOH−H_2O, and 2979 cm^{-1} for 2NpOH−CH_3OH represent the upper limit of their hydrogen-bond energies. Since 2NpOH−H_2O has no CH vibration of methyl group at ~2900 cm^{-1}, we obtained somewhat larger value for its hydrogen-bond energy than that of 2NpOH−CH_3OH. The obtained upper limit in S_1 also provides us with the upper limit of the dissociation energies in S_0 by combining the S_1−S_0 electronic transition energies. The obtained values are 2666 and 2557 cm^{-1} for 2NpOH−H_2O and for −CH_3OH, respectively. These values can be compared with the dissociation energies of 1NpOH−H_2O and −CH_3OH reported by Leutwyler and co-workers. From the SEP-R2PI spectroscopy, they obtained the dissociation energies for 1NpOH−H_2O and −CH_3OH to be 2035 ± 69 and 2645 ± 136 cm^{-1}, respectively.[19] These values are very close to those obtained in the present work and our obtained values may represent reasonable dissociation energies of the clusters.

In summary, the background free IR spectrum of 2NpOH−CH_3OH in S_1 has been successfully measured by the photofragment-detected IR spectroscopy. This technique will make contribution to the vibrational spectroscopy of the electronically excited hydrogen-bonded clusters.

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