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Characterizations of the hydrogen-bond structures of 2-naphthol-$(H_2O)_n$ ($n=0-3$ and 5) clusters by infrared-ultraviolet double-resonance spectroscopy

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OH stretching vibrations of 2-naphthol-$(H_2O)_n$ ($n=0-3$ and 5) hydrogen-bonded clusters in the S_0 state have been observed by infrared-ultraviolet (IR-UV) double-resonance spectroscopy. In bare 2-naphthol, *cis*- and *trans*-isomers were identified by the comparison of the observed OH frequencies with those obtained by *ab initio* calculations with the HF/6-31G basis set. The OH stretching vibrations (ν_{OH}) of hydrogen-bonded 2-naphthol-$(H_2O)_n$ show characteristic shifts depending on the cluster size. They are classified into hydrogen-bonded ν_{OH}, and ν_{OH} free from the hydrogen bond. The cluster structures were also examined by comparing the observed IR spectra with simulated ones. It was found that the clusters with $n=2$ and 3 form ring structures, while the cluster with $n=5$ exhibits an ice (I) structure. © *1998 American Institute of Physics.* [S0021-9606(98)00239-6]

I. INTRODUCTION

Hydrogen-bonded (H-bonded) clusters between aromatic acids and water molecules, generated in supersonic jets, have been of considerable interest for many years. Among them, phenol-$(H_2O)_n$, 1- and 2-naphthol-$(H_2O)_n$ clusters have been thought to give a basic idea for the structures and dynamics of the H-bonded system of aromatic molecules.[1–19] Most of the studies have been done so far by the use of electronic spectroscopy, such as resonance enhanced multiphoton ionization (REMPI) with mass-selection, laser induced fluorescence (LIF), dispersed fluorescence, and stimulated emission pumping techniques.[1–19] High resolution electronic spectroscopy and rotational coherence spectroscopy have been also applied to obtain their rotational constants.[20,21]

Recently, several vibrational spectroscopic studies using a double-resonance technique have been successfully applied to observe the OH stretching vibrations which provide the key feature of the H-bonds. The observation of the OH stretching vibration of a jet-cooled aromatic molecule and its clusters was first reported by Felker and co-workers, who applied stimulated Raman-UV double-resonance spectroscopy or ionization-detected stimulated Raman spectroscopy (IDSRS) to the H-bonded clusters of phenol.[22] In this spectroscopy, the population depletion of the ground vibrational level induced by stimulated Raman pumping is monitored by resonance enhanced multiphoton ionization (REMPI) with an ultraviolet (UV) laser. Our group applied a similar double-resonance method by using an infrared (IR) light source, IR-UV double-resonance spectroscopy, for the observation of the OH vibrational level. Here, a depletion of the ground state population by an effective vibrational excitation with the IR light is monitored by an electronic transition with the UV light. IR-UV double-resonance spectroscopy has been successfully applied by several groups to the H-bonded clusters, such as $(phenol)_n$,[23] phenol-$(H_2O)_n$,[24–26] phenol-amines,[27] and tropolone-$(H_2O)_n$ and tropolone-$(CH_3OH)_n$.[28–30] For phenol-$(H_2O)_{n=1-5}$, for example, the OH stretching vibrations of the phenol site as well as H_2O sites were observed and the cluster structures were determined by comparing the observed IR spectra with those obtained by *ab initio* calculations.[26,31]

In the present paper, we report the spectroscopic investigation of the OH stretching vibrations and the structures of the 2-naphthol-$(H_2O)_n$ clusters in the S_0 state. It is known that the acidity of 2-naphthol increases drastically upon electronic excitation, and the dynamics of the H-bonded clusters of electronically excited 2-naphthol, including the proton transfer reaction with polar solvents, has been studied by several groups. For the 2-naphthol-$(H_2O)_n$ clusters, the LIF and dispersed fluorescence spectra have been reported.[16,19] However, detailed information about the H-bonding structures of the 2-naphthol-$(H_2O)_n$ clusters could not be provided from the analyses of electronic spectroscopy alone. In this work, we characterize the H-bond structures of 2-naphthol-$(H_2O)_n$ clusters on the basis of the analysis of the observed IR spectra of the OH stretching vibrations with the help of *ab initio* calculations. For 2-naphthol-$(H_2O)_n$ clusters, there are several interesting points; the first is that there are two rotamers, *cis*- and *trans*-forms in 2-naphthol. It may be possible to distinguish two rotamers by the difference of their OH stretching vibrational frequencies. The second point is whether we can see any differences in cluster structures between *cis*- and *trans*-forms, and what would be a major reason for the difference, if any. The third point is the comparison of the IR spectra of 2-naphthol-$(H_2O)_n$ with those of phenol-$(H_2O)_n$. The pKa value of 2-naphthol in S_0 is 9.45,[32,33] which is slightly smaller than that of phenol (pKa $=9.82$); the difference in pKa will be expected to affect the hydrogen bond of the clusters.

II. EXPERIMENT

In the present experiment, we applied fluorescence detected infrared spectroscopy (FDIRS) for the observation of

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the vibrational spectrum of size-selected 2-naphthol-$(H_2O)_n$ clusters. The experimental setup for FDIRS was the same as that described elsewhere.[25] A brief description will be given in the following. The 2-naphthol-$(H_2O)_n$ clusters were generated by a supersonic expansion of a gaseous mixture of 2-naphthol and H_2O, which is seeded in He. 2-naphthol was heated at 350 K to obtain sufficient vapor pressure. The mixture was expanded into a vacuum chamber through a pulsed valve having an 800 μm orifice.

The tunable UV and IR laser beams were introduced coaxially in opposite directions into the vacuum chamber. They were focused on the supersonic free jet at 15 mm downstream of the nozzle by using lenses (an $f=500$ mm lens for UV and an $f=250$ mm CaF_2 lens for IR). The IR laser pulse was introduced 50 ns prior to the UV laser pulse, which was controlled with a digital delay generator (SRS DG535). The frequency of the UV laser light was fixed to the S_1-S_0 electronic transition, normally the 0-0 band, of a specific cluster, and its fluorescence intensity was monitored. When the IR laser frequency is resonant with the vibrational transition of the cluster, the ground state population is pumped to the vibrationally excited state, resulting in depletion of the fluorescence signal. Thus, FDIR spectra were obtained by scanning the IR laser frequency while monitoring the fluorescence signal.

The UV source was a second harmonic of a XeCl excimer laser pumped dye laser (Lambda Physik LPX100/FL2002). The pulse energy and the spectral resolution of the UV laser were 5 μJ and 0.2 cm^{-1}, respectively. Fluorescence was collected by a lens and detected by a photomultiplier tube (Hamamatsu Photonics 1P28). The photocurrent from the photomultiplier tube was integrated by a boxcar integrator (Par Model 4400/4402) connected with a microcomputer. Tunable IR laser pulse was generated by a difference-frequency mixing between a second harmonic of an injection seeded Nd:YAG laser (Quanta Ray GCR 230) and a Nd:YAG laser pumped dye laser (Continuum ND6000, DCM dye) with a $LiNbO_3$ crystal. The pulse energy and the spectral resolution of the IR laser were 0.4 mJ and 0.1 cm^{-1}, respectively. The lasers and the pulsed valve were operated with a repetition of 10 Hz.

In the present study, we also applied mass-selected REMPI spectroscopy to specify the size of each cluster in the electronic spectra. The experimental setup for this spectroscopy was described previously.[34] Briefly, the cluster ions generated by the REMPI were mass selected by a quadrapole mass filter and detected by an electron multiplier. The ion current was amplified by a current amplifier and averaged by a digital boxcar integrator system.

2-naphthol was purchased from Wako Chemical Industries, Ltd. and purified by vacuum sublimation before used.

To analyze the structures and the vibrational spectra of 2-naphthol-$(H_2O)_n$, *ab initio* molecular orbital calculations were performed. The energy-optimized structures and harmonic vibrational frequencies, as well as their IR intensities, were obtained at the HF/6-31G level. According to the calculation done by Watanabe and Iwata,[31] the calculation at the HF/6-31G level did not provide precise relative energies of isomers of the H-bonded clusters of phenol. However, they showed that for the calculation of the IR spectra in the ν_{OH} region, this level was enough to reproduce the observed spectra. Since we determine the structures of the clusters by the comparison of the vibrational spectra in the ν_{OH} region in the present work, the calculation with this level is thought to give reliable results. The calculated frequencies of the ν_{OH} vibrations were adjusted by multiplying a scaling factor of 0.9034. This scaling factor is determined so as to fit the calculated ν_{OH} frequency of *cis*-rotamer to the observed one, and this factor is also used for all the clusters. The program used was GAUSSIAN 92.[35]

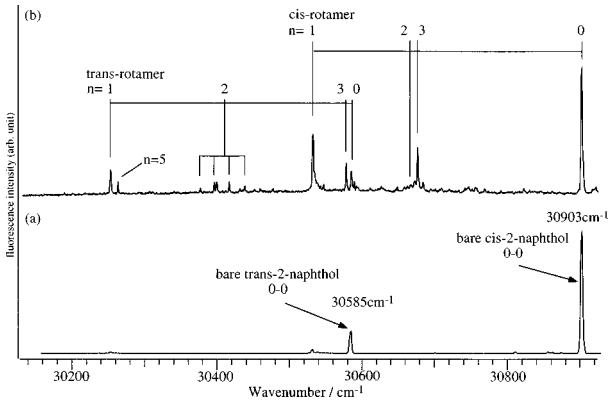

FIG. 1. Laser induced fluorescence (LIF) spectra of 2-naphthol and 2-naphthol-$(H_2O)_n$ clusters measured under (a) low concentration, and (b) high concentration of water vapor.

III. RESULTS AND DISCUSSION

A. S_1-S_0 electronic spectra of 2-naphthol and 2-naphthol-$(H_2O)_n$

Figure 1(a) shows the S_1-S_0 LIF spectrum of 2-naphthol measured under a condition of a low water vapor pressure. The spectrum is essentially the same as that reported by Oikawa and others, who emphasized the discrimination of the two rotamers in the electronic spectrum.[36] According to the recent assignment given by Johnson and coworkers, who observed the rotationally resolved LIF spectrum,[37] two prominent peaks at 30 903 and 30 585 cm^{-1} are assigned to the origin bands of *cis*- and *trans*-rotamers of bare 2-naphthol, respectively. In the present work, as will be discussed below, we confirmed their assignment for the two rotamers by comparing the IR spectra of the OH stretching vibrations with those obtained by *ab initio* calculations.

Figure 1(b) shows the S_1-S_0 LIF spectrum of 2-naphthol measured under a higher H_2O vapor pressure condition, so that many bands due to the clusters with H_2O were observed. The bands of each cluster were assigned from the results of the mass-selected REMPI spectra and the analysis of the IR spectra described later. Figures 2(b)–2(e) show the mass-selected REMPI spectra, which are compared with the LIF spectrum of Fig. 2(a). Since the S_1-S_0 transition energy of bare 2-naphthol is less than a half of the ionization potential (63 670 for *cis*-rotamer and 63 189 cm^{-1} for *trans*-rotamer),[38] its multiphoton ionization (MPI) spectrum [Fig. 2(b)] was measured by two-color $(1+1')$ REMPI with $h\nu_2=34\,000$ cm^{-1}. Figure 2(b) shows the REMPI spectrum

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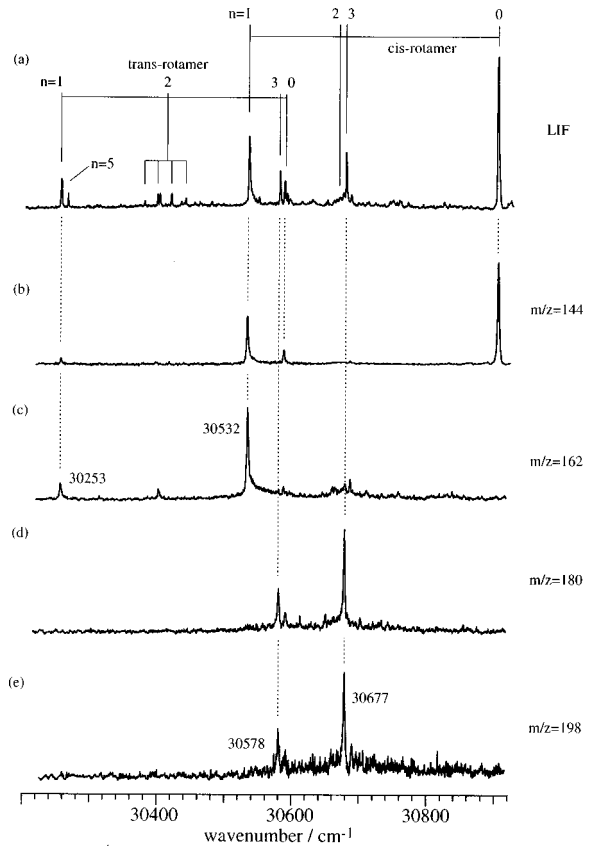

FIG. 2. (a) LIF spectrum of 2-naphthol-$(H_2O)_n$, same as Fig. 1(b). (b)–(e) mass-selected REMPI spectra of 2-naphthol-$(H_2O)_n$: the monitoring masses are (b) $m/z=144$, $[\text{naphthol}]^+$, (c) $m/z=162$, $[\text{naphthol-}H_2O]^+$, (d) $m/z=180$, $[\text{naphthol-}(H_2O)_2]^+$, (e) $m/z=198$, $[\text{naphthol-}(H_2O)_3]^+$, respectively. The spectrum (b) was measured by two-color $(1+1')$ REMPI with $h\nu_2=34\,000\ \text{cm}^{-1}$.

obtained by monitoring $[\text{naphthol}]^+$ $(m/z=144)$. In this spectrum, besides the bands of bare *cis*- and *trans*-2-naphthol, two bands are observed at 30 532 and 30 253 cm^{-1}. Since these bands are observed at the $m/z=162$ (corresponding to $[\text{naphthol-}H_2O]^+$), but not at the mass of $m/z=180$ (corresponding to $[\text{naphthol-}(H_2O)_2]^+$), they are assigned to the 0-0 bands of *cis*- and *trans*-2-naphthol-H_2O clusters, respectively. In a similar manner, we identified the cluster size by measuring the mass-selected REMPI spectrum. In general, two ion products were observed for each cluster, that is $[\text{naphthol-}(H_2O)_n]^+$ and $[\text{naphthol-}(H_2O)_{n-1}]^+$. Figures 2(d) and 2(e) show the one-color REMPI spectra obtained by monitoring $[\text{naphthol-}(H_2O)_2]^+$ and $[\text{naphthol-}(H_2O)_3]^+$ $(m/z=198)$, respectively. In these spectra, two bands are observed at 30 677 and 30 578 cm^{-1}. Since we did not observe the ion signal at the mass of $[\text{naphthol-}(H_2O)_4]^+$ $(m/z=216)$, we assigned the bands at 30 677 and 30 578 cm^{-1} to the 0-0 bands of the *cis*- and *trans*-2-naphthol-$(H_2O)_3$ clusters, respectively. For the 2-naphthol-$(H_2O)_2$ and 2-naphthol-$(H_2O)_5$ clusters, their ion signals were very weak and we could not determine their masses. As will be discussed later, however, their IR spectra in the ν_{OH} region provide the conclusive evidence for the size and the structure. Table I lists observed frequencies of the 0-0 bands of 2-naphthol-$(H_2O)_{n=0-3,5}$.

As seen in Fig. 1(b), there is a remarkable tendency for the shift of the 0-0 bands of the S_1-S_0 electronic transition, which are common in both isomers. That is, though the 0-0 band of the $n=1$ cluster shifts to red, those of the clusters with $n\geqslant 2$ shift to blue with respect to that of the $n=1$ cluster. In addition, it is seen that the 0-0 band of the $n=2$ cluster shows different features from other clusters. The 0-0 band of *trans*-2-naphthol-$(H_2O)_2$ is very weak and a progression of low frequency vibration ($\sim 20\ \text{cm}^{-1}$) is seen. For *cis*-2-naphthol-$(H_2O)_2$ the band is broad and is observed weakly beneath the sharp 0-0 band of *cis*-2-naphthol-$(H_2O)_3$. These spectral features of the $n=2$ clusters indicate that their stable structures are quite different between S_0 and S_1. A similar spectral feature was seen in the S_1-S_0 electronic spectrum of phenol-$(H_2O)_n$.[26]

B. IR spectra of bare 2-naphthol

Figure 3(a) shows the FDIR spectra of the OH stretching vibrations (ν_{OH}) of bare 2-naphthol. When the UV frequency was tuned to the band at 30 903 cm^{-1}, the ν_{OH} band was observed at 3654 cm^{-1}. When the UV frequency was fixed to the band at 30 585 cm^{-1}, another ν_{OH} band was observed at 3661 cm^{-1}. Thus, these results show that the two electronic bands belong to the two different isomers and their ν_{OH} frequencies differ from each other by 7 cm^{-1}. Figure 3(b) shows the IR spectra of the ν_{OH} vibrations obtained by *ab initio* calculations. The calculated ν_{OH} vibrational frequencies were 3654 and 3661 cm^{-1} for the *cis*- and *trans*-rotamer, respectively. Thus, the frequency of the *cis*-rotamer is lower than that of the *trans*-rotamer by 7 cm^{-1}, which agrees fairly well with the observed difference of 7 cm^{-1}. Thus, the assignment of the *cis*- and *trans*-rotamers provided by Johnson and co-workers in the electronic spectra is confirmed. The result represents that observation of ν_{OH}, and simulation of the spectra gives us conclusive evidence for the identification of rotamers.

In the *ab initio* calculations, the energy difference of the zero-point level between the two rotamers was also obtained

TABLE I. Observed frequencies of the 0-0 bands of 2-naphthol-$(H_2O)_n$ $(n=0-5)$. Also shown are the red-shifts of the 0-0 band from that of bare 2-naphthol.

	Observed frequencies (red-shift from the 0-0 band of bare 2-naphthol)/cm^{-1}					
	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
cis-2-naphthol-$(H_2O)_n$	30 903	30 532 (−371)	~30 670(~233)[a]	30 677 (−226)	⋯	⋯
trans-2-naphthol-$(H_2O)_n$	30 585	30 253 (−332)	30 376 (−109)	30 578 (−7)	⋯	30 263 (−322)

[a]This value is the frequency at maximum intensity of the broad band due to *cis*-2-naphthol-$(H_2O)_2$.

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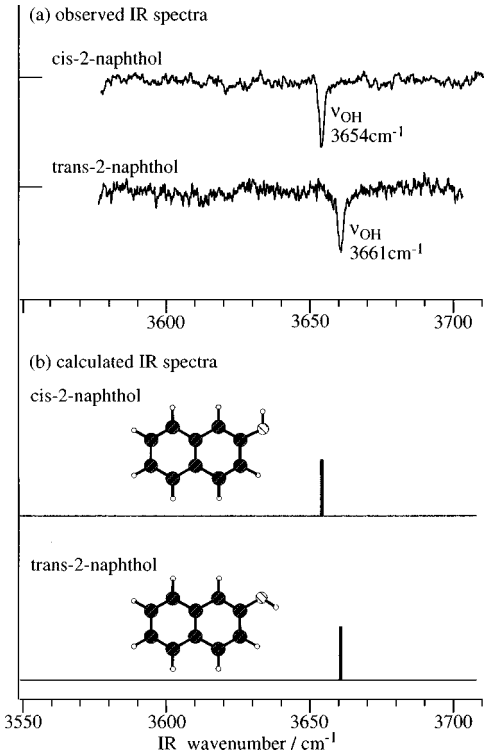

FIG. 3. (a) Fluorescence detected infrared (FDIR) spectra of *cis*- and *trans*-2-naphthol obtained by fixing UV laser frequencies to the bands at 30 903 and 30 585 cm^{-1}, respectively. (b) IR spectra (stick diagram) of *cis*- and *trans*-2-naphthol obtained by *ab initio* calculation with HF/6-31G basis set.

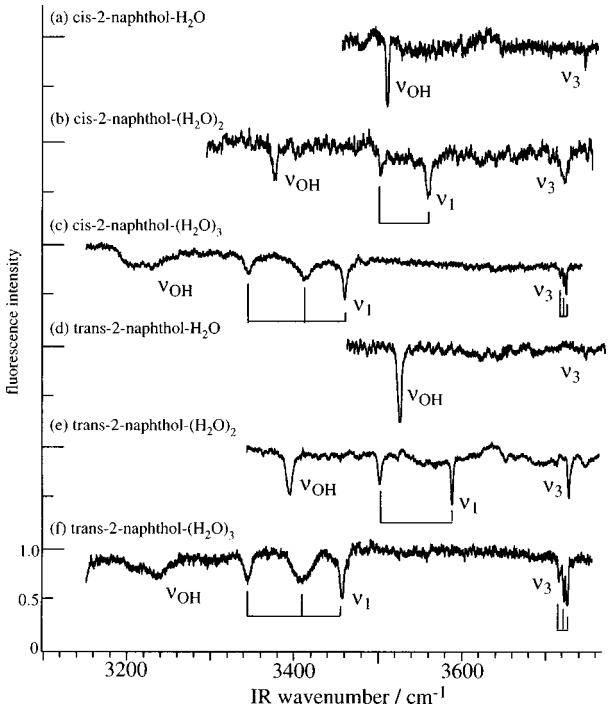

FIG. 4. Fluorescence detected infrared (FDIR) spectra of 2-naphthol-$(H_2O)_n$ ($n=1-3$); (a)–(c) *cis*-rotamers, (d)–(f) *trans*-rotamers.

and the result showed the *cis*-form is more stable than the *trans*-form by 312.5 cm^{-1}. This result agrees with the study by Schütz and co-workers, who calculated the structures by using the HF/6-31G(d,p) basis set.[16] The stable *cis*-rotamer is also confirmed experimentally in the LIF spectrum, in which the intensity of the 0-0 band of *cis*-2-naphthol is three times larger than that of *trans*-2-naphthol. It is known that the thermal population of the isomers is preserved even after the jet expansion, if there exists a substantial potential barrier to isomerization. By using the calculated energy difference, the population ratio of the *cis*- to *trans*-rotamers at 360 K, which is the sample temperature before the expansion, is estimated to be about 3.5. This value is in good agreement with the observed ratio.

C. IR spectra of 2-naphthol-$(H_2O)_n$

Figures 4(a)–4(f) show the FDIR spectra of the ν_{OH} vibrations of *cis*- and *trans*-2-naphthol-$(H_2O)_n$ ($n=1-3$) clusters, which were obtained by fixing the UV laser frequency to the corresponding peaks in Fig. 1(b). The frequencies of the observed vibrational bands are listed in Table II. Also listed are the ν_{OH} frequencies obtained by the *ab initio* calculation. The size dependence of the FDIR spectra of 2-naphthol-$(H_2O)_n$ is found to be quite similar to that of phenol-$(H_2O)_n$ (see Fig. 3 of Ref. 26). In the following section, we discuss the observed spectra and the structures of each species in detail.

1. *cis- and trans-2-naphthol*-H_2O

Figures 5(a) and 5(b) show the FDIR spectra of *cis*- and *trans*-2-naphthol-H_2O. Also shown are the spectra of bare 2-naphthol for comparison. The IR spectrum of 2-naphthol-H_2O shows two ν_{OH} bands at 3512 and 3749 cm^{-1} for the *cis*-form, and at 3523 and 3748 cm^{-1} for the *trans*-form. In each rotamer, the intense lower frequency band is assigned to ν_{OH} of the 2-naphthol site, while the higher frequency band is due to the antisymmetric vibration (ν_3) of the H_2O site. The red-shift of υ_{OH} from that of bare 2-naphthol is 142 and 138 cm^{-1} for the *cis*- and *trans*-forms, respectively, indicating that the OH bond strength of the 2-naphthol site is reduced by the H-bond formation with H_2O. In contrast, the ν_3 band of the H_2O site is slightly red-shifted from the bare H_2O molecule (3755.79 cm^{-1}),[39] which means that the effect of the H-bond formation on the ν_3 vibration is very small. This characteristic feature shows that 2-naphthol is acting as a proton donor, and the H_2O molecule is acting as a proton acceptor. The similar feature of the ν_{OH} bands was also observed in the phenol-H_2O clusters,[26] whose OH frequencies are also listed in Table II, to be compared with those of the 2-naphthol-$(H_2O)_n$ clusters. The observed red-shifts of ν_{OH} of 2-naphthol are slightly larger than those of phenol (133 cm^{-1}), corresponding to the larger acidity of 2-naphthol than phenol. Actually, it has been shown that the red-shifts of ν_{OH} of the 1:1 cluster of phenol with various solvent molecules are closely related to the enthalpy changes upon the cluster formation.[27] In this respect, the red-shift is also a measure of acidity of the proton donor. The similar red-shift value of the two rotamers of 2-naphthol indicates that the difference in acidity between *cis*- and *trans*-form is very small. Figures 6(a) and 6(b) show the most stable forms of *cis*- and *trans*-2-naphthol-H_2O obtained by the *ab initio* calculations, re-

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TABLE II. Observed and calculated frequencies (cm^{-1}) of OH stretching vibrations of *cis*- and *trans*-2-naphthol-$(H_2O)_n$ ($n=0-3$). Also listed are the vibrations of phenol-$(H_2O)_n$ ($n=0-3$) (Ref. 26).

	Observed			Calculated
	Frequency/cm^{-1}	Assignment	$\Delta\nu_{OH}$/cm^{-1}[a]	Frequency/cm^{-1}[b]
$n=0$ (*cis*)	naphthol site			
	3654	ν_{OH}	···	3654
$n=0$ (*trans*)	naphthol site			
	3661	ν_{OH}	···	3661
$n=1$ (*cis*)	H_2O site			
	3749	ν_3		3751
	···	ν_1		3615
	naphthol site			
	3512	ν_{OH}	−142	3465
$n=1$ (*trans*)	H_2O site			
	3748	ν_3		3749
	···	ν_1		3614
	naphthol site			
	3523	ν_{OH}	−138	3478
$n=2$ (*cis*)	H_2O site			
	3726	ν_3		3729
	···	ν_3		3726
	3560	ν_1		3514
	3503	ν_1		3440
	naphthol site			
	3376	ν_{OH}	−278	3336
$n=2$ (*trans*)	H_2O site			
	3723	ν_3		3730
	···	ν_3		3724
	3585	ν_1		3509
	3498	ν_1		3434
	naphthol site			
	3392	ν_{OH}	−269	3346
$n=3$ (*cis*)	H_2O site			
	3722	ν_3		3721
	3719	ν_3		3721
	3715	ν_3		3720
	3458	ν_1		3408
	3411	ν_1		3329
	3343	ν_1		3272
	naphthol site			
	3226	ν_{OH}	−428	3174
$n=3$ (*trans*)	H_2O site			
	3723	ν_3		3722
	3719	ν_3		3720
	3713	ν_3		3719
	3454	ν_1		3400
	3407	ν_1		3322
	3342	ν_1		3270
	naphthol site			
	3233	ν_{OH}	−428	3181
phenol	phenol site			
	3657	ν_{OH}	···	3683
phenol-H_2O	H_2O site			
	3748	ν_3		3779
	3650	ν_1		3642
	phenol site			
	3524	ν_{OH}	−133	3503
phenol-$(H_2O)_2$	H_2O site			
	3725	ν_3		3757
	3722	ν_3		3754
	3553	ν_1		3534
	3505	ν_1		3463
	phenol site			
	3388	ν_{OH}	−269	3369
phenol-$(H_2O)_3$	H_2O site			
	3722	ν_3		3750
	3719	ν_3		3749
	3715	ν_3		3748
	3451	ν_1		3426
	3401	ν_1		3350
	3345	ν_1		3298
	phenol site			
	3236	ν_{OH}	−421	3208

[a]The red-shift of ν_{OH} from that of monomer.
[b]Each frequency is multiplied by a scaling factor of 0.9034.

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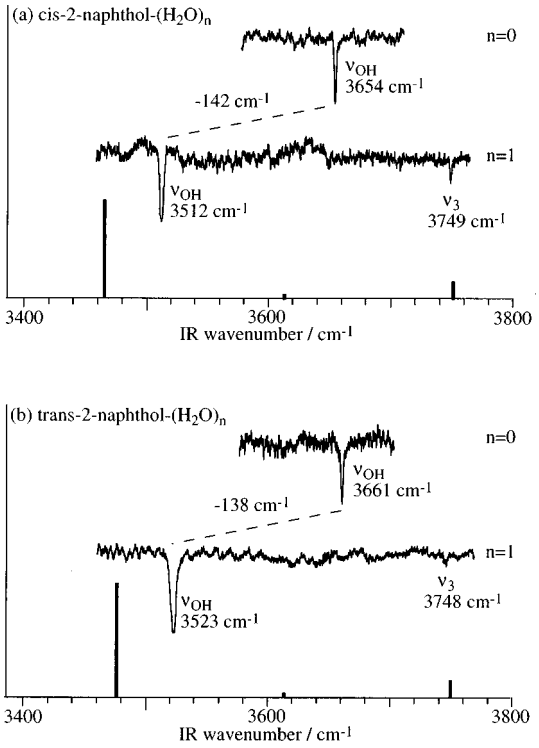

FIG. 5. FDIR spectra and the IR spectra obtained by *ab initio* calculation of (a) *cis*-2-naphthol-H_2O and (b) *trans*-2-naphthol-H_2O. The FDIR spectra of bare 2-naphthol are also shown for comparison.

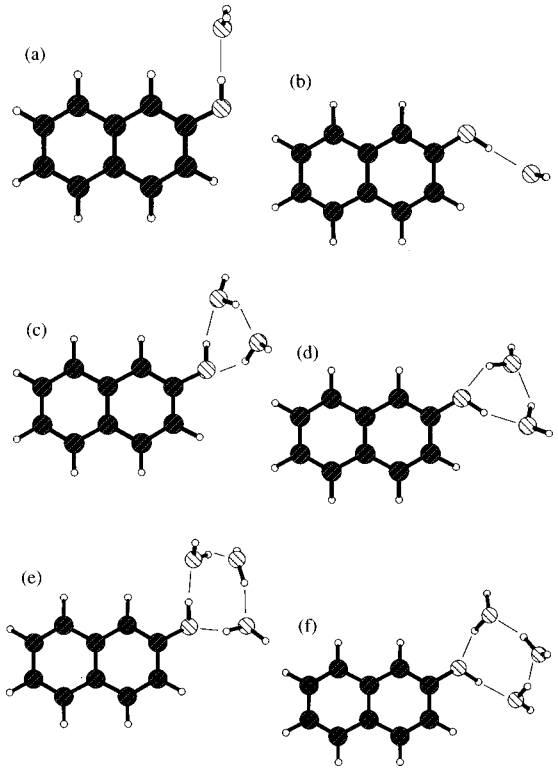

FIG. 6. Structures of 2-naphthol-$(H_2O)_n$ $(n=1-3)$ obtained by *ab initio* calculation. The figures are drawn using the MOLCAT program (Ref. 42).

spectively. As described above, it is seen that 2-naphthol is acting as a proton donor and H_2O is a proton acceptor. As can be seen in the figure, the clusters have a C_s symmetry, in which the plane of the H_2O molecule is perpendicular to the plane of the naphthalene ring similar to that of the phenol-H_2O cluster. The simulated IR spectra for this form are also shown in Fig. 5 as a stick diagram. A good agreement is seen between the observed and calculated spectra.

2. 2-naphthol-$(H_2O)_n$ n=2,3; ring-form structures

a. 2-naphthol-$(H_2O)_2$. The FDIR spectrum of *cis*-2-naphthol-$(H_2O)_2$ is shown in the upper part of Fig. 7(a). Four intense bands occur at 3376, 3503, 3560, and 3726 cm^{-1}. The bands exhibit the characteristic feature of the ring-form cluster similar to the phenol-$(H_2O)_2$ cluster. In the ring-form cluster, as seen in Fig. 6(c), there are three H-bonded OH oscillators in the ring and two OH oscillators protruding out of the ring. Assuming a local mode picture for the OH vibration, the band at 3376 cm^{-1} is assigned to ν_{OH} of the 2-naphthol site, and those at 3503 and 3560 cm^{-1} are assigned to the H-bonded OH oscillators of H_2O molecules in the ring. The band at 3726 cm^{-1} is assigned to the stretching vibrations of OH groups of H_2O molecules protruding out of the ring, where the two bands are overlapped. The simulated IR spectrum of the ring-form *cis*-2-naphthol-$(H_2O)_2$ is shown in the lower part of Fig. 7(a). The spectrum was obtained from the energy-optimized ring-form structure, which is shown in Fig. 6(c). The calculated frequencies are also listed in Table II. As can be seen in the figure, the simulated spectrum reproduces very well the observed one with respect to the frequencies as well as the relative intensities.

Figures 8(a)–8(e) show the vector models of each vibrational mode of *cis*-2-naphthol-$(H_2O)_2$ with the corresponding harmonic frequencies obtained by the *ab initio* calculations. As seen in the figure, the lowest vibration is assigned to ν_{OH} localized mainly in 2-naphthol. The displacement vectors of the other modes represent more details of the characters of the vibrations; for example, both low frequency OH vibrations of Figs. 8(b) and (c) exhibit in-phase displacements of the two OH oscillators of a H_2O unit, although the amplitudes of the OH oscillations are not symmetry any more. In this respect, these other two modes are assigned to the ν_1-type vibrations localized mainly on each H_2O molecule, rather than being assigned as the H-bonded OH oscillators. The higher frequency bands, in contrast, exhibit out-of-phase displacements of the two OH oscillators of the H_2O unit, so that they are called ν_3-type vibrations. In this respect, these two modes are also assigned to the ν_3-type vibrations of two H_2O molecules, rather than as the OH oscillators free from the ring.

Figure 7(b) shows the observed FDIR and the simulated IR spectra of *trans*-2-naphthol-$(H_2O)_2$. Four ν_{OH} bands at 3392, 3498, 3585, and 3723 cm^{-1} are assigned as ν_{OH} of naphthol site, two ν_1 of H_2O sites, and ν_3 of H_2O sites, respectively. It is seen that the spectral features of the clusters of the two rotamers are essentially the same. So, the structure of the *trans*-2-naphthol-$(H_2O)_2$ cluster is also expected to be the ring form. The lower part of Fig. 7(b) shows the simulated IR spectrum of the energy-optimized ring-form

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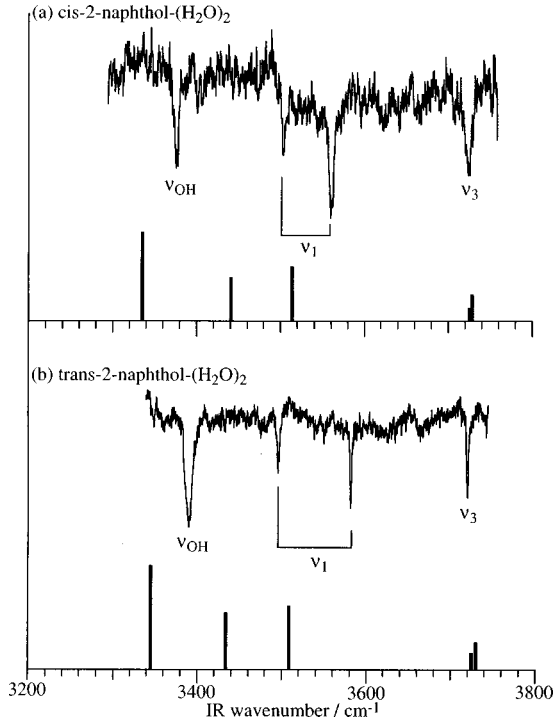

FIG. 7. FDIR spectra and the simulated IR spectra of (a) *cis*-2-naphthol-$(H_2O)_2$ and (b) *trans*-2-naphthol-$(H_2O)_2$ obtained by *ab initio* calculation.

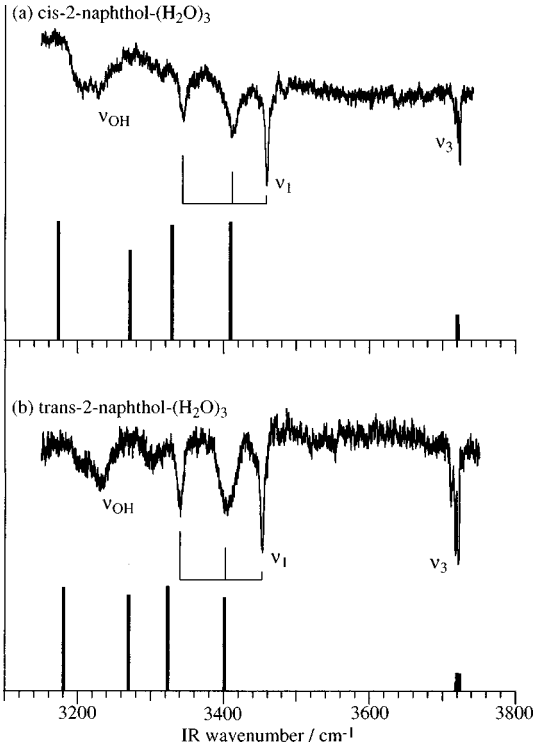

FIG. 9. FDIR spectra and the calculated IR spectra of (a) *cis*-2-naphthol-$(H_2O)_3$ and (b) *trans*-2-naphthol-$(H_2O)_3$.

trans-2-naphthol-$(H_2O)_2$. A good agreement is obtained between the observed and the calculated IR spectra, confirming that the structure of *trans*-2-naphthol-$(H_2O)_2$ is also of ring form.

Though the vibrational structure is very similar between the two rotamers of 2-naphthol-$(H_2O)_2$, a remarkable difference is seen in the observed spectra shown in Figs. 7(a) and 7(b); the interval of the ν_1 vibrations of the H_2O sites is substantially larger in the *trans*-form (b) than that of the *cis*-form (a). Such differences of the OH bands represent the difference in the intermolecular interaction between the clusters of the two rotamers. The 2-naphthol-$(H_2O)_2$ cluster is the smallest size ring-form cluster similar to phenol-$(H_2O)_2$ or $(\text{phenol})_3$, and it has been pointed out that such a small H-bond ring has a strain in its intermolecular bonds, so that the structure is subject to a balance between the stress and the stabilization by the ring form. The observed differences of the OH bands of the 2-naphthol-$(H_2O)_2$, therefore, seem to be closely related to the balance of the ring formation of both the rotamers. Unfortunately, the simulated spectra by *ab initio* calculation does not reproduce the difference of the band splitting of the ν_1 vibrations of the H_2O sites between the two rotamers. From the normal coordinate analysis, it was revealed that the ν_1 bands at higher energy side ($\sim$3550 cm^{-1}) are due to those of the H_2O molecule, which acts as the proton donor to the oxygen atom of the 2-naphthol site. Therefore, the difference in the band splitting of ν_1 is thought to be due to the difference in the H-bond strength between the oxygen of the OH group of 2-naphthol and the hydrogen of donor H_2O. Such a rotamer difference may arise from the difference in ''through space'' interaction between the OH oscillator and the second aromatic ring of 2-naphthol rotamers.

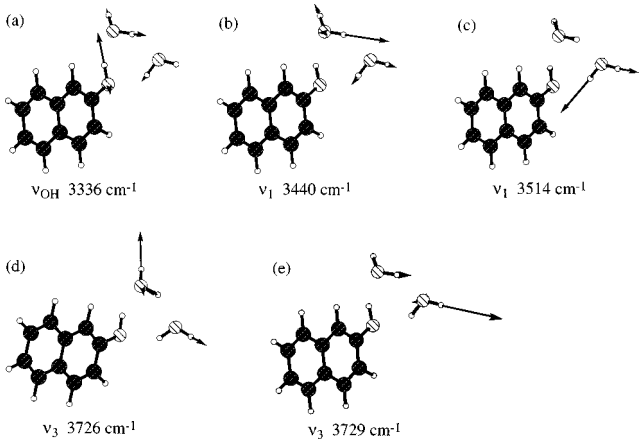

FIG. 8. The vector model of ν_{OH} vibrations of *cis*-2-naphthol-$(H_2O)_2$ with corresponding harmonic frequencies: (a) ν_{OH} of naphthol site, (b) and (c) ν_1 of H_2O site, (d) and (e) ν_3 of H_2O site. These are obtained by *ab initio* calculation, and multiplied by a scaling factor of 0.9034.

b. 2-naphthol-$(H_2O)_3$. The FDIR spectrum of *cis*-2-naphthol-$(H_2O)_3$ is shown in the upper part of Fig. 9(a). Seven OH stretching vibrational bands were observed, representing a typical feature of the ring-form cluster. Four of them are lower than 3500 cm^{-1} and the remaining three are located close to each other at $\sim$3720 cm^{-1}. The band at 3226 cm^{-1} is assigned to ν_{OH} of the naphthol site, and those at 3343, 3411, and 3458 cm^{-1} are assigned to ν_1 vibrations of the H_2O molecules in the H-bond ring, that is, H-bonded OH groups of H_2O. The three bands at $\sim$3720 cm^{-1} are assigned to ν_3 vibrations of the three members of H_2O, which corre-

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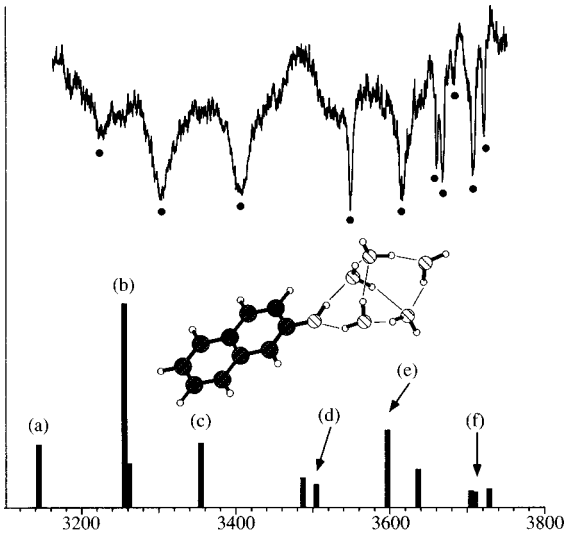

FIG. 10. (upper) FDIR spectrum obtained by tuning UV laser to the band at 30 263 cm^{-1} and (lower) the calculated IR spectrum (stick diagram) of 2-naphthol-$(H_2O)_5$ ice (*I*) structure. The observed OH stretching bands are marked by dots. Also shown is the optimized structure of 2-naphthol-$(H_2O)_5$ with ice (*I*) structure.

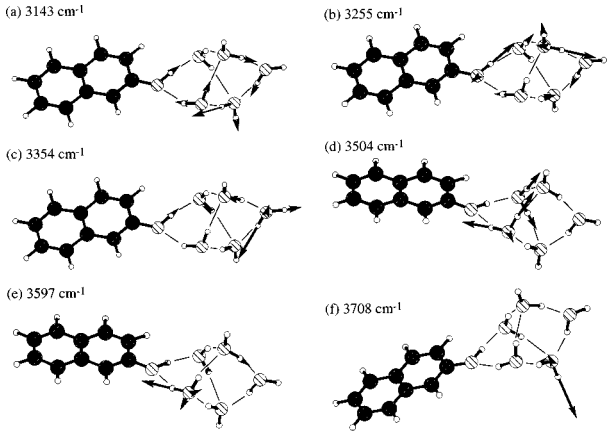

FIG. 11. The vector model of ν_{OH} vibrations of 2-naphthol-$(H_2O)_5$ [ice (*I*)] with corresponding harmonic frequencies (scaled by a factor of 0.9034) obtained by *ab initio* calculation. Each mode corresponds to the band of the simulated IR spectrum in Fig. 10.

spond to the OH oscillators protruding out of the ring. There is a large interval between the H-bonded OH band group and the ν_3 groups, and the interval is called the window region.[26] The stick diagram in the lower part of Fig. 9(a) shows the IR spectra of the energy-optimized ring-form cluster of 2-naphthol-$(H_2O)_3$, which is shown in Fig. 6(e). It is clear that the simulated IR spectrum of the ring-form structure reproduces well the observed ones. The calculated frequencies are also listed in Table II.

The FDIR spectrum of *trans*-2-naphthol-$(H_2O)_3$ is shown in Fig. 9(b). Seven bands were also observed similar to those of *cis*-rotamer, and the spectral feature of *trans*-rotamer is very similar to that of *cis*-rotamer. Frequencies of these bands are listed in Table II. The lower part of Fig. 9(b) shows the simulated IR spectrum of *trans*-2-naphthol-$(H_2O)_3$, obtained from the energy-optimized ring-form structure. The calculated spectrum reproduces well the observed one, and it is confirmed that the structure of *trans*-2-naphthol-$(H_2O)_3$ is also of ring-form. Therefore, similar to 2-naphthol-$(H_2O)_2$, the stable structures of 2-naphthol-$(H_2O)_3$ are of ring-form in both rotamers.

3. 2-naphthol-$(H_2O)_5$; ice (I) structure

In the S_1-S_0 LIF spectrum shown in Fig. 1(b), there is an additional band at 30 263 cm^{-1}, which is close to the *trans*-2-naphthol-H_2O band. Mass-selected MPI spectra did not provide its definite size because of a fragmentation of the cluster after the ionization. So we applied FDIR spectroscopy to this cluster to determine the structure. The upper part of Fig. 10 shows the FDIR spectrum obtained by tuning the UV laser to the band at 30 263 cm^{-1}. Seven sharp IR bands occur in the region of 3500–3700 cm^{-1}, and three broad bands occur in the region of 3200–3400 cm^{-1}. Since the spectrum consists of more than nine ν_{OH} bands, the band at 30 263 cm^{-1} in the LIF spectrum is assigned to the cluster with $n=5$. As seen in the spectrum, the characteristic feature is that five ν_{OH} bands are observed between 3550 and 3700 cm^{-1}, that is in the window region. The existence of the ν_{OH} bands in the window region indicates that the structure of this cluster is different from the ring-form structure described above. From the theoretical investigation of phenol-$(H_2O)_n$ structures by Watanabe and Iwata, it was demonstrated that the appearance of the OH bands in this region is associated with the presence of one or more H_2O molecules acting as a double proton donor. Especially for the phenol-$(H_2O)_5$, the IR spectrum of ice (*I*) showed similar vibrational structure with the observed one among the possible isomers whose stabilization energy is within 5 kJ/mol. In the ice (*I*) structure, two H_2O molecules are acting as double proton donors and they exhibit ν_{OH} vibrations in the window region.[31]

In a similar manner, we also calculated the optimized structure of 2-naphthol-$(H_2O)_5$ and compared the calculated IR spectrum with the observed one. In the lower part of Fig. 10 is shown the simulated IR spectra of ν_{OH} vibrations for the optimized ice (*I*) structure of 2-naphthol-$(H_2O)_5$. Here, we assumed that this cluster belongs to *trans*-rotamer, since the bands of S_1-S_0 transition of this cluster appeared in the *trans*-rotamer region in the LIF spectrum [Fig. 1(b)]. As seen in Fig. 10, the simulated IR spectrum exhibits several bands in the window region, and well reproduces the observed spectrum with respect to the bands in the 3200–3400 cm^{-1}. So it is concluded that the band at 30 263 cm^{-1} in LIF spectrum [Fig. 1(b)] is due to 2-naphthol-$(H_2O)_5$ and the structure of this cluster is of ice (*I*) type.

Figures 11(a)–11(f) show the vector model of the normal modes for ice (*I*) 2-naphthol-$(H_2O)_5$ obtained by *ab initio* calculations. Each mode corresponds to the bands indicated in the simulated IR spectrum in Fig. 10. As seen in the figure, the bands (a) to (c) mainly involve the ν_{OH} vibrations of naphthol and the H_2O sites. Different from the ring-form structure such as *cis*-2-naphthol-$(H_2O)_2$ shown in Fig. 8, it is seen that the OH stretching vibrations in the region of 3200–3400 cm^{-1} are rather delocalized among the OH group of 2-naphthol and five H_2O molecules. The vibrations (d) and (e) are those appearing in the 3500–3700 cm^{-1}, that is, in the

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window region. The band (d) corresponds to ν_1 and the band (e) corresponds to ν_3 of the H_2O molecule, which acts as the double proton donor in the H-bonding network. From these results, it is evident that the bands in the region of 3500–3700 cm^{-1} in the IR spectrum are due to the existence of ''double proton donor H_2O molecules.'' The mode (f) corresponds to one of the ν_3 of three ''single proton donor H_2O molecules.''

As to 2-naphthol-$(H_2O)_4$, we could not observe the 0-0 band of this cluster in the LIF spectrum. The reason why the band of 2-naphthol-$(H_2O)_4$ is missing is not clear. The band might not locate in the energy region observed in Fig. 1, or might be broadened by very fast nonradiative process in the S_1 state. The analysis of the electronic spectrum in Fig. 1 is, in that sense, very important in order to characterize the dynamics of the clusters in the S_1 state, which will be the subject of future work.

In summary, the H-bonding structures of 2-naphthol-$(H_2O)_n$ clusters have been investigated based on the analysis on their OH stretching vibrations. The observations of the OH stretching vibrations of the size-selected clusters could be performed by highly sensitive IR-UV double-resonance spectroscopy. By the comparison between the observed IR spectra with those obtained by *ab initio* calculation, the cluster structures were determined. The stable structures of 2-naphthol-$(H_2O)_{n=2,3}$ are determined to be of ring form, while that of 2-naphthol-$(H_2O)_5$, which is a larger size cluster, is of ice (*I*) form. A similar change of the stable structure from ring to ice with the cluster size is also observed in $(H_2O)_n$ and in benzene-$(H_2O)_n$.[40,41] Finally, it should also be pointed out that this spectroscopy is also useful in identifying the two rotamers of bare 2-naphthol.

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