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IR laser manipulation of *cis*↔*trans* isomerization of 2-naphthol and its hydrogen-bonded clusters

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The *cis*↔*trans* isomerization reaction has been carried out for 2-naphthol and its hydrogen (H) bonded clusters by infrared (IR) laser in the electronic excited state (S_1) in supersonic jets. A specific isomer in the jet was pumped to the X–H stretching vibration in the S_1 state, where X refers to C, O, or N atom, by using a stepwise UV-IR excitation, and the dispersed emission spectra of the excited species or generated fragments were observed. It was found that the isomerization occurs only in the H-bonded clusters but a bare molecule does not exhibit the isomerization in the examined energy region of $E_v \leq 3610\ \mathrm{cm}^{-1}$, indicating a reduction of the isomerization barrier height upon the H bonding. The relative yield of the isomerization was observed as a function of internal energy. The isomerization yield was found to be very high at the low IR frequency excitation, and was rapidly reduced with the IR frequency due to the competition of the dissociation of the H bond within the isomer. Density-functional theory (DFT) and time-dependent DFT calculations were performed for estimating the barrier height of the isomerization for bare 2-naphthol and its cluster for electronic ground and excited states. The calculation showed that the isomerization barrier height is highly dependent on the electronic states. However, the reduction of the height upon the hydrogen bonding was not suggested at the level of our calculation.
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I. INTRODUCTION

2-naphthol has two rotational isomers, *cis* and *trans*, depending on the orientation of the OH group with respect to the naphthalene ring. A systematic spectroscopic study on the structural determination of the isomer was first carried out by Oikawa *et al.* by measuring the electronic spectra in a supersonic free jet.[1] Later, Johnson *et al.* measured rotationally resolved electronic spectra and determined their structures.[2] Since then, there are several spectroscopic experiments on the stability of the isomers and their hydrogen (H) bonded clusters.[3–9] It is reported that the *cis* isomer is 140 cm^{-1} more stable than the *trans* in the electronic ground state (S_0) of 2-naphthol, while in S_1 the *trans* isomer becomes 174 cm^{-1} more stable than the *cis*.[2,9] The barrier height of the *cis-trans* isomerization in S_0 is estimated to be 1200 cm^{-1} from the analogy of phenol.[10] The barrier height in S_1 is thought to be much larger, because the torsional barrier height of phenol in S_1 is reported to be 4710 cm^{-1}.[11]

The *cis*↔*trans* isomerization and its control by the use of a laser light have been discussed by several groups from their points of view that they are very challenging themes and that the dynamics of isomerization along a flexible bond is very important to understand the conformational isomerization of flexible molecules. In our previous paper, we reported a first attempt of the laser-induced *cis-trans* isomerization of 2-naphthol and its hydrogen (H) bonded clusters in S_1 state by a UV-IR stepwise excitation.[12] As a result, it was demonstrated that the excitation of the X–H stretch vibration by an IR laser light, where X refers to O, C, or N atom, can induce the isomerization especially for the H-bonded system. We found that the isomerization reaction occurs after the intracluster vibrational energy redistribution and the isomerization yield is very sensitive to the excitation frequency. Very recently, another type of the laser-induced isomerization study on such a flexible molecule in the ground electronic state has been also reported by Zwier's group. They used stimulated emission pumping for the vibrational excitation and succeeded in isomerizing the molecule.[13]

In this work, we report a further study on the *cis*↔*trans* isomerization of 2-naphthol. We extended the work to the several H-bonded clusters of 2-naphthol with different H-bonding energies and investigated the excitation energy dependence to examine the effect of the H-bonding strength on the isomerization dynamics. In parallel, we carried out density-functional theory (DFT) and time-dependent DFT calculations to estimate the isomerization barrier height for different electronic states for a bare molecule and a H-bonded cluster.

II. EXPERIMENTAL

The excitation scheme and the experimental setup of an UV-IR pump-probe spectroscopy were already described in previous papers.[8,12,14] Briefly, a specific isomer or its

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H-bonded cluster of 2-naphthol in a jet was pumped to the zero-point level of S_1 by an UV laser pulse and is further excited to the X–H stretch levels by a tunable IR laser light, where X refers to C, O, or N atom, respectively. The vibrationally excited molecules or clusters will be immediately relaxed by intramolecular (intracluster) vibrational energy redistribution (IVR) and emit broad fluorescence. When the energy is large enough to overcome the barrier height of isomerization or to break the hydrogen bond, the generated species, isomer or fragment, emits fluorescence at different wavelengths. The IR spectrum in the S_1 electronic state, here we call UV-IR spectra, is thus obtained by scanning the IR laser frequency while monitoring either the broad emission from the IVR redistributed levels or the emission of fragments by the use of a monochromator. Then, the dispersed fluorescence spectrum was obtained to identify the emitting species.

A tunable UV laser light was the second harmonics of the Nd:yttrium aluminum garnet (YAG) laser- (Continuum Surelite III) pumped dye laser (LAS LDL20505) and a tunable IR output was obtained by difference frequency mixing between the second harmonics of another Nd:YAG laser (Quantaley GCR-250) and the laser-pumped dye laser (Continuum ND6000) with an LiNbO3 crystal. The laser beams were collinearly introduced into a vacuum chamber to cross the jet 10 mm downstream of the pulsed nozzle. The delay time between the UV and the IR laser pulses was set to a few nanoseconds by the use of a pulsed delay generator (SRS DG 535). The emission of the molecules or clusters was collected by a series of lenses and focused on the slit of a monochromator (Nikon P250). A dispersed emission was detected by a photomultiplier tube (Hamamatsu Photonics R928) and the signal was processed by a boxcar integrator (Par 4400) connected with a personal computer. The jet-cooled 2-naphthol and their clusters were generated by a supersonic expansion of the gaseous mixture of 2-naphthol, solvent molecule, and He. 2-naphthol were heated in sample housing at 90 °C to obtain enough vapor pressure, and the concentration of solvent molecules were kept less than 5% of the total pressure by the use of a thermoregulator. 2-naphthol was purchased from Wako Chemicals and was used without further purification.

III. RESULTS

A. IR spectra of 2-naphthol and its H-bonded clusters in S_1

Figure 1 shows the UV-IR double-resonance spectra of 2-naphthol and its H-bonded clusters. In this measurement, the UV laser frequency was fixed to the 0,0 band of each species, and the laser frequency of the IR light, introduced at a delay time of a few nanoseconds after the UV pulse excitation, was scanned while monitoring the emission from the IVR redistributed levels or that of the 2-naphthol photofragment. The OH stretching vibration of a bare 2-naphthol in S_1 appears at 3609 cm^{-1}, which is 43 cm^{-1} redshifted from the OH stretching frequency in S_0. In the H-bonded clusters, the OH stretching frequency decreases with an increase of the proton affinity of the proton acceptors. In addition to the redshift, the OH stretch band is significantly broadened, indicating a very rapid relaxation in this level. The obtained OH stretching frequencies in S_1 together with those in S_0 are listed in Table I. The magnitude of the redshift upon the H bonding in S_1 is roughly 1.4 times larger than those in S_0, which is attributed to an increase of acidity of 2-naphthol in S_1.[15,16] In Fig. 1, several other vibrational bands are also seen in the spectra, in addition to the OH stretching vibration. Some of them are assigned to the CH stretch vibrations of 2-naphthol, CH_3OH, and $(CH_3)_2O$, the OH stretching vibration of CH_3OH and the NH stretching vibrations of NH_3 and $NH(CH_3)_2$, respectively. In the spectra of 2-naphthol-CH_3OH, and -$(CH_3)_2O$, several vibrational bands are seen at the higher frequency side of the H-bonded OH stretch. There is no fundamental band in such a region and can be assigned to the intermolecular vibrational bands associated to the H-bonded OH stretch. We fixed the IR frequency to each band and measured the dispersed fluorescence (DF) spectra.

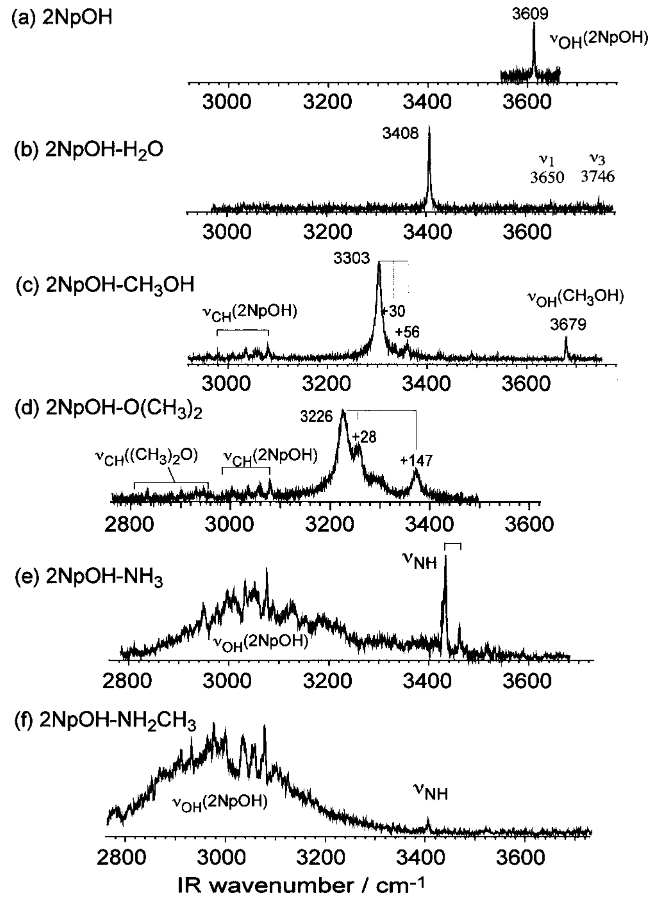

FIG. 1. IR spectra of (a) *cis*-2-naphthol and [(b)–(f)] its hydrogen-bonded clusters in S_1 obtained by UV-IR double-resonance spectroscopy.

B. Dynamics after UV-IR excitation of bare 2-naphthol

Figure 2(a) shows the DF spectra of bare *cis*- and *trans*-2-naphthtol, and Fig. 2(b) shows enlarged portions of the 0,0 band with and without the IR excitation of the OH stretching vibration in S_1. Here, the UV and IR frequencies were fixed to the 0,0 band of each isomer and its OH stretching vibration, respectively. In both spectra with the IR laser

TABLE I. Frequencies of OH stretching vibration of 2-naphthol (all data are for the *cis* form) and its hydrogen-bonded clusters in S_0 and S_1.

	S_0		S_1		
	ν_{OH} (cm^{-1})	Δ[a] (cm^{-1})	ν_{OH} (cm^{-1})	Δ[a] (cm^{-1})	PA[b] (kcal mol^{-1})
2-NpOH	3652	⋯	3609	⋯	
2-NpOH-H_2O	3519	−133	3408	−201	166.5[c,d]
2-NpOH−CH_3OH	3443	−209	3303	−306	181.9[c,d]
2-NpOH−$O(CH_3)_2$	3389	−263	3226	−383	189[c,d]
2-NpOH−NH_3	3263	−389	3050	−559	204.0[c,d]
2-NpOH−NH_2CH_3	3120	−532	3000	−609	214[c,d]

[a] Frequency shift with respect to bare 2-naphthol.

[b] Proton affinity of acceptor.

[c] Reference 18.

[d] Reference 19.

on, a broad emission is seen beneath of the 0,0 band of each isomer, which is attributed to the emission from the redistributed levels generated by IVR of the OH stretching vibration. We investigated whether the IR laser-induced isomerization occurs or not from the broadened DF spectra with IR on. As seen in Fig. 2, the 0,0 band of *cis* isomer is located at the higher frequency side of that of *trans* isomer. Then, we expect an appearance of the 0,0 band of *cis*-isomer emission in the DF spectrum of *trans* isomer if the IR induced *trans*→*cis* isomerization occurs. In Fig. 2(b), however, though a broad emission is extended to the 0,0 band region of *trans* isomer in the DF spectrum, we do not find any peaks due to the *trans* isomer. Actually, as will be shown later, we observed a steplike feature in the DF spectra when *cis*-2-naphthol-NH_3 and -NH_2CH_3 isomerize to the *trans* form. To demonstrate the similarity of the DF spectra of both isomers with IR on, the DF spectrum of the *cis* isomer is overlaid to that of the *trans* isomer in Fig. 2(c) so that their 0,0 bands are overlapped. In the figure, the broad feature of the spectra is very similar with each other, suggesting that only IVR is occurring in each isomer after the IR excitation to their OH stretching vibrations. Thus, we conclude that the input energy (3609 cm^{-1}) is not large enough to cause the isomerization in bare 2-naphthol. As will be discussed later, this lower limit of the isomerization energy in S_1 is consistent with the torsional barrier height of other aromatic molecule such as phenol.

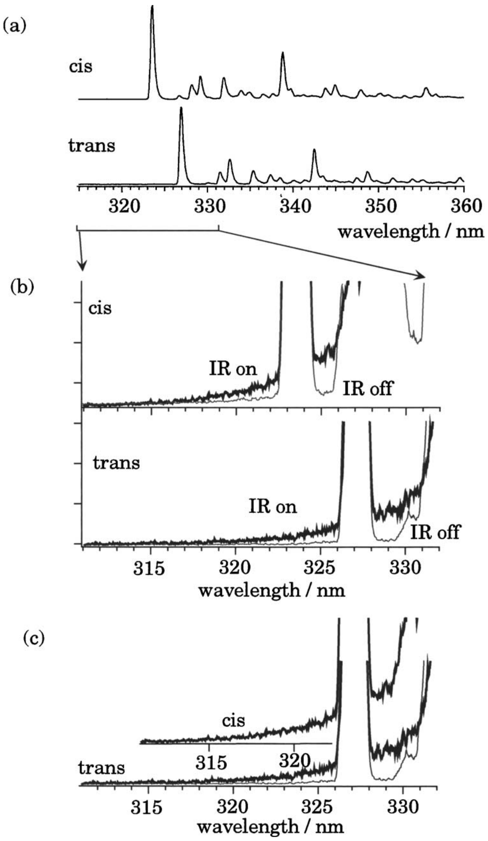

FIG. 2. (a) Dispersed fluorescence (DF) spectra of bare *cis*- and *trans*-2-naphthols from the band origins. (b) Enlarged DF spectra from the band origins with and without IR excitation (ν_{IR}=3609 cm^{-1}) to the OH stretching vibration. (c) DF spectra from the band origins with and without IR excitation to the OH stretching vibration. The two spectra are shown in the manner that the positions of the band origin are overlapped.

C. Dynamics after UV-IR excitation of H-bonded clusters

The *cis-trans* isomerization was observed in all the H-bonded clusters examined. Figures 3–6 show the DF spectra after the UV-IR double-resonant excitation of *cis*- and *trans*-2-naphthol-H_2O, -CH_3OH, -NH_3, and -NH_2NH_3. In all figures, the DF spectra without the IR excitation are shown for reference, as well as those from the 0,0 band of bare *cis*- and *trans*-2-naphthol.

1. *2-naphthol*-H_2O

In the DF spectra of 2-naphthol-H_2O with the UV-IR double-resonant excitation, Fig. 3, new broadbands appear at the shorter wavelength side of the 0,0 band of the clusters, a band *C* for *cis*-2-naphthol-H_2O and a band *T* for *trans*-2-naphthol-H_2O. By comparing these bands with the DF spectra of the bare *cis*- and *trans*-2-naphthol, they can be assigned to the emission of each isomer of bare 2-naphthol fragment, which are generated by the vibrational predissociation (VP) of the parent clusters having the same isomeric forms. Thus, we conclude that in both cases only the VP takes place after the IR excitation. Interestingly, the position

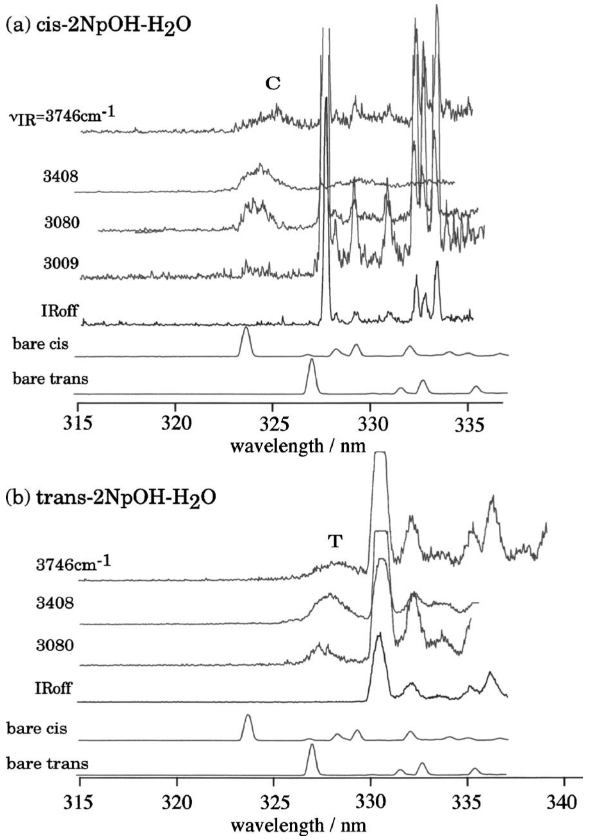

FIG. 3. (a) DF spectra of *cis*-2-naphthol-H_2O cluster from the band origin with the IR excitations to various bands in S_1. The excited IR frequencies are shown at the left of the spectra. The DF spectra of *cis*-2-naphthol-H_2O and bare *cis*- and *trans*-2-naphthols without IR excitation are also shown. (b) DF spectra of *trans*-2-naphthol-H_2O cluster from the band origins with the IR excitation in S_1.

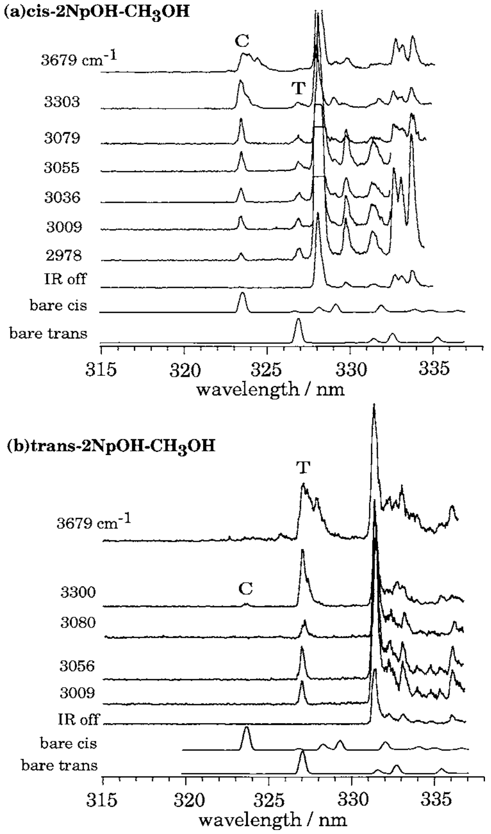

FIG. 4. (a) DF spectra of *cis*-2-naphthol-CH_3OH from the band origin with the IR excitations to various bands in S_1. The excited IR frequencies are shown at the left of the spectra. The DF spectra of *cis*-2-naphthol-CH_3OH and bare *cis*- and *trans*-2-naphthols without IR excitation are also shown. (b) DF spectra of *trans*-2-naphthol-CH_3OH from the band origins with the IR excitation in S_1.

of the maximum of each broadband shifts to red with the excitation frequency, indicating that the generated fragments become internally hot with the excitation energy. As will be discussed later, the fact that we did not observe the isomerization in this system does not mean that the input IR energy is not enough to overcome the barrier height.

2. *2-naphthol*-CH_3OH

The DF spectra of 2-naphthol-CH_3OH after the UV-IR excitation are quite different from those of 2-naphthol-H_2O. In the DF spectra of *cis*-2-naphthol-CH_3OH with the UV-IR excitation, Fig. 4(a), two new bands appear at the shorter wavelength side of the 0,0 band of the clusters, which are easily assigned to the emission of the *cis*- and the *trans*-2-naphthol fragments. Thus, the isomerization accompanied with VP is prominent in this case and its yield is comparable to VP within a same isomeric species. There are two important issues to be addressed from these spectra. First is that the ratio of the two fragment bands, which we call the "*cis*/*trans* ratio," changes with the IR excitation frequency. At the lowest energy of $\tilde{\nu}_{\mathrm{IR}}=2978\ \mathrm{cm}^{-1}$, the isomerized fragment, *trans*-2-naphthol, is generated more than the *cis*-2-naphthol fragment. With the increase of the energy, the *cis*-2-naphthol fragment ratio rapidly increases, and it is striking that only the *cis*-2-naphthol fragment is generated at highest frequency excitation $\tilde{\nu}_{\mathrm{IR}}=3679\ \mathrm{cm}^{-1}$. Second is that the bandwidths of the emission of both the fragments are rather sharp compared with the case of 2-naphthol-H_2O with the same IR excitation frequency, and the width increases with the frequency. The narrower bandwidth of the 2-naphthol fragment from 2-naphthol-CH_3OH than that from 2-naphthol-H_2O is due to that the H-bond binding energy of the former cluster is larger than the latter.

In contrast with the prominent *cis*→*trans* isomerization, the yield of the opposite process, "*trans*→*cis* isomerization," is very small as seen in Fig. 4(b). In the DF spectra of *trans*-2-naphthol-CH_3OH with the UV-IR excitation, only the *trans*-2-naphthol fragment is generated except $\tilde{\nu}_{\mathrm{IR}}=3300\ \mathrm{cm}^{-1}$. Even at $\tilde{\nu}_{\mathrm{IR}}=3300\ \mathrm{cm}^{-1}$, the *trans/cis*-2-naphthol ratio is larger than 20. Thus, it is suggested that the isomerization is almost a one-sided process. Similar to *cis*-2-naphthol-CH_3OH, the bandwidth of the fragment emission is sharp at low energy and becomes broad with the energy.

3. *2-naphthol*-NH_3 *and 2-naphthol*-NH_2CH_3

The DF spectra of *cis*-2-naphthol-NH_3, Fig. 5(a), show another spectral feature in addition to those observed in 2-naphthol-H_2O and -CH_3OH. In Fig. 5(a), at high IR frequency excitation such as $\tilde{\nu}_{\mathrm{IR}}=3435\ \mathrm{cm}^{-1}$, the two isomeric fragments, bands *C* and *T*, are equally produced. At low IR frequency such as $\tilde{\nu}_{\mathrm{IR}}=3260\ \mathrm{cm}^{-1}$, on the other hand, only *trans*-2-naphthol (band *T*) is generated. When $\tilde{\nu}_{\mathrm{IR}}$ is lower

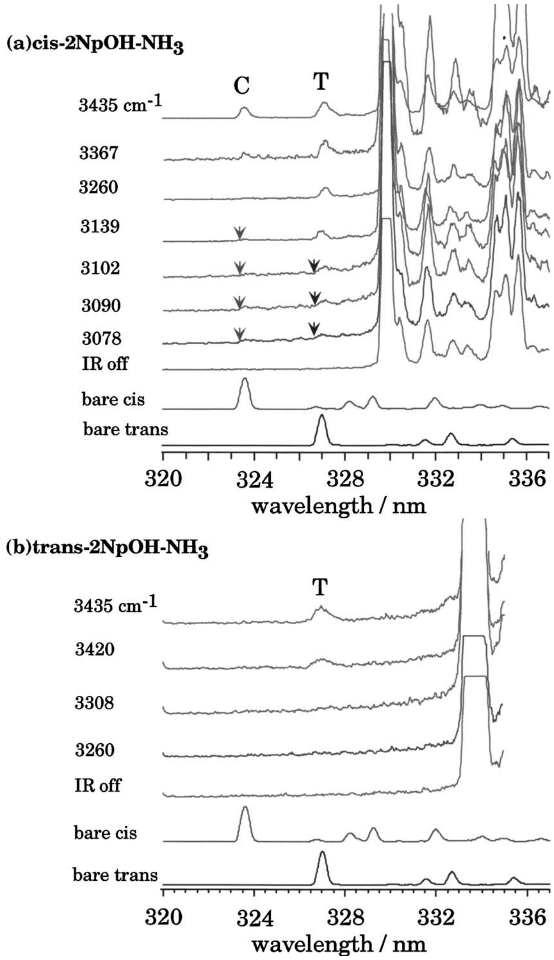

FIG. 5. (a) DF spectra of *cis*-2-naphthol-NH$_3$ from the band origin with the IR excitations to various bands in S_1. The excited IR frequencies are shown at the left of the spectra. The DF spectra of *cis*-2-naphthol-NH$_3$ and bare *cis*- and *trans*-2-naphthols without IR excitation are also shown. (b) DF spectra of *trans*-2-naphthol-NH$_3$ from the band origins with the IR excitation in S_1.

than 3100 cm^{-1}, no sharp peak due to the fragment is observed. Instead, the DF spectra show steplike features at the positions of the 0,0 bands of bare 2-naphthols, which are indicated as arrows. As will be discussed later, the steplike emissions are attributed to the emission of internally hot *cis*- and *trans*-2-naphthol-NH$_3$ clusters. In the low IR frequency excitation, only the isomerization occurs and the H bond is not broken. Thus, *cis*- and *trans*-2-naphthol-NH$_3$ clusters are internally very hot, exhibiting a broad emission. Thus, the isomerization is not necessarily accompanied with the dissociation of H bond.

The DF spectra of *cis*-2-naphthol-NH$_2$CH$_3$ in Fig. 6 show only a steplike feature and no emission due to the 2-naphthol fragment is seen in all the examined energy regions. Thus, in this case only the isomerization is occurring within the cluster.

IV. DISCUSSION

A. Energetics and dynamics of isomerization/fragmentation of 2-naphthol H-bonded clusters in S_1

In the present system, three processes are involved after the IR excitation of the X–H stretch vibrations, that is, IVR, the *cis*↔*trans* isomerization, and the dissociation of H bond. Another interesting feature is that the *cis*→*trans* isomerization takes place with high efficiency, while the efficiency of the reverse isomerization, that is, the *trans*→*cis* process, is very small. Such a one-sided reaction is essentially ascribed by the difference of the energy between the *cis* and the *trans* isomers in S_1. Figure 7 shows the energy diagrams for (a) 2-naphthol-H$_2$O, (b) 2-naphthol-CH$_3$OH, (c) 2-naphthol-NH$_3$, and (d) 2-naphthol-NH$_2$CH$_3$ obtained on the basis of the present work, and the reported dissociation energies of the clusters[17] in S_0 and the electronic transition energies. In the following, we discuss the energetics and the dynamics according to the energy diagrams and the input excitation energies.

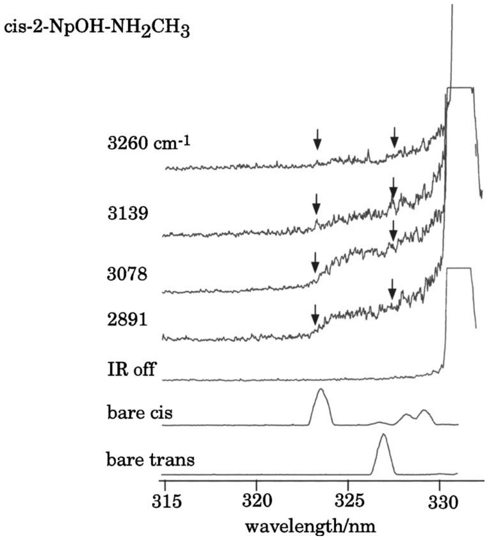

FIG. 6. DF spectra of *cis*-2-naphthol-NH$_2$CH$_3$ from the band origin with the IR excitations to various bands in S_1. The excited IR frequencies are shown at the left of the spectra. The DF spectra of *cis*-2-naphthol-NH$_2$CH$_3$ and bare *cis*- and *trans*-2-naphthols without IR excitation are also shown.

1. Low IR frequency excitation

As was described in the Introduction, the *trans* isomer is about 170–200 cm^{-1} more stable than the *cis* isomer in S_1. When the energy put into the *cis*-2-naphthol H-bonded cluster is large enough to overcome the barrier but less than the H-bonding energy, the *cis* form cluster will isomerize to the *trans* form within the lifetime of S_1. This situation corresponds to the excitation scheme (1) in Fig. 7. The generated isomer in such a way is internally very hot and emits a broad fluorescence. Typical examples are the DF spectra of 2-naphthol-NH$_3$ with the low frequency IR excitation. As seen in the lower portion of Fig. 5, the DF spectrum exhibits a broad emission with a steplike feature near the 0,0 band of the each isomer of bare 2-naphthol. They are assigned to the emission from the redistributed levels of *cis*-2-naphthol-NH$_3$ and *trans*-2-naphthol-NH$_3$. The steplike feature of the vibrationally hot 2-naphthol clusters in the DF spectra is described based on the emission pattern of Fig. 8, where schematic potential curves of S_0 and S_1 as a function of intermolecular coordinate are shown. The emission of the vibrationally excited cluster consists of many $v' \rightarrow v''$ transitions. Among them, the transitions of less internally excited clusters will be

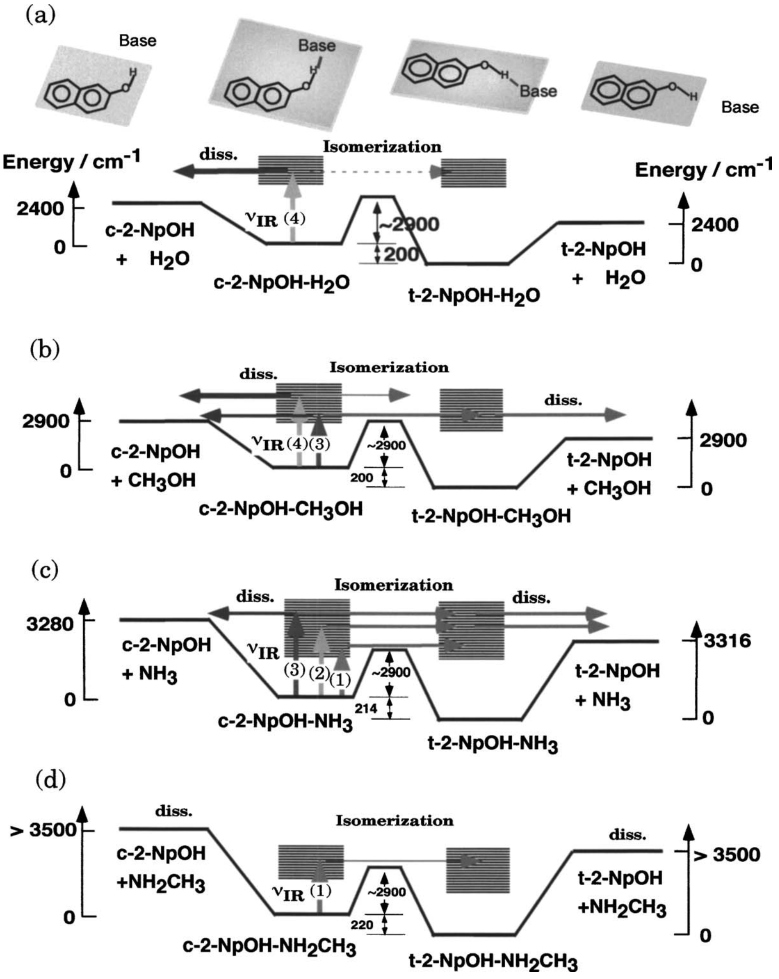

FIG. 7. Energy-level diagrams of the hydrogen-bonded clusters of 2-naphthol in S_1 and relaxation pathways after the vibrational excitation by IR light: (a) 2-naphthol-H_2O, (b) 2-naphthol-CH_3OH, (c) 2-naphthol-NH_3, and (d) 2-naphthol-NH_2CH_3. Several pathways are shown for different IR frequencies: (1) low, [(2) and (3)] middle, and (4) high frequency. See the text.

located in the 0,0 band region, "transition D," and those of most excited cluster will be located in the region close to the 0,0 band of the bare molecule, "transition A." Thus, the internally hot clusters will emit broad fluorescence in the wavelengths between the 0,0 bands of the bare molecule and the cluster, giving a steplike feature at the 0,0 band of the bare molecule.

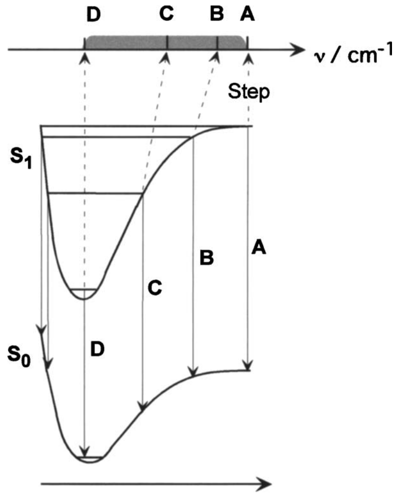

FIG. 8. Schematic intermolecular potential curves and expected frequencies of the emission of the vibrationally excited cluster.

Similar steplike features are seen in all the DF spectra of *cis*-2-naphthol-NH_2CH_3 in Fig. 6. Since the H-bonding energy of 2-naphthol-NH_2CH_3 is larger than that of 2-naphthol-NH_3 due to the larger proton affinity of NH_2CH_3 than that of NH_3,[18,19] the energy put by the IR light is not enough to break the H bond. The H-bonding energy of 2-naphthol-NH_2CH_3 in S_1 is estimated to be larger than 3600 cm^{-1}.

2. Intermediate IR frequency excitation

When the IR energy is larger than the H-bonding energy, the cluster can dissociate to generate a bare 2-naphthol as a fragment. This situation corresponds to the excitation scheme (2) in Fig. 7. Since the energy of the *trans* isomer is lower than that of the *cis* isomer, the *trans*-2-naphthol fragment will be first generated at a low-energy region. A typical example is seen in the DF spectra of *cis*-2-naphthol-NH_3 cluster at $\nu_{IR}=3139$ and 3260 cm^{-1} excitations. The spectra exhibit a sharp peak due to the *trans*-2-naphthol fragment which is marked by *T*, and the steplike broad fluorescence emitted by the internally hot *cis*-2-naphthol-NH_3 cluster. Thus in these excitation energies, part of the internally excited *cis*-2-naphthol-NH_3 isomerizes to the *cis* form which is followed by the dissociation.

In the spectra with the higher frequency excitations, such as $\nu_{IR}=3367$ and 3435 cm^{-1}, of *cis*-2-naphthol-NH_3, the peaks of the *cis*- and *trans*-2-naphthol fragments appear in

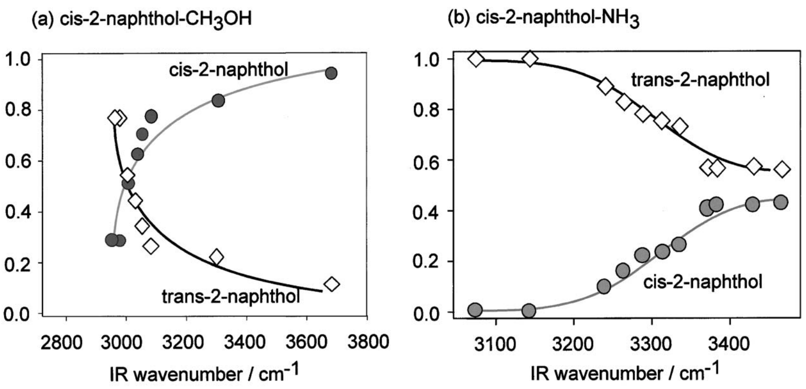

FIG. 9. Plots of the *cis*- and *trans*-2-naphthol fragment ratio after the IR excitation of (a) *cis*-2-naphthol-CH_3OH and (b) *cis*-2-naphthol-NH_3 as a function of input IR frequency. The ratio is normalized so that the sum of the two fragments becomes unity.

the DF spectra. Thus at these energies, both the dissociation channels are possible. This situation corresponds to the excitation scheme (3) in Fig. 7. The production of the two fragments is also seen in *cis*-2-naphthol-CH_3OH, as shown in Fig. 4, with much wider range of the ν_{IR} excitation frequency. The interesting point is that the *trans/cis* fragment ratio rapidly changes with the IR frequency. Figure 9 shows the plots of the ratio as a function of IR frequency for *cis*-2-naphthol-NH_3 and *cis*-2-naphthol-CH_3OH. In case of *cis*-2-naphthol-CH_3OH, the ratio is 1.5 at $\nu_{IR}=2978\ \text{cm}^{-1}$, while it is almost zero at $\nu_{IR}=3679\ \text{cm}^{-1}$. Thus, with the increase of the energy, the rate constant of the H-bond dissociation becomes much larger than that of the isomerization.

3. High IR frequency excitation

At the high IR frequency excitation, the dissociation of the H bond within the isomer becomes dominant, as seen in the DF spectrum with $\nu_{IR}=3679\ \text{cm}^{-1}$ of *cis*-2-naphthol-CH_3OH in Fig. 4(a). This situation corresponds to the excitation scheme (4) in Fig. 7. In the case of *cis*-2-naphthol-H_2O, the exclusive H-bond dissociation occurs even at lower IR frequency excitations. This is due to that the H-bond energy of *cis*-2-naphthol-H_2O, 2400 cm^{-1}, is smaller than *cis*-2-naphthol-CH_3OH, 2900 cm^{-1}, so that the H-bond dissociation of 2-naphthol-H_2O occurs at the lower energy than 2-naphthol-CH_3OH. The excess energy after the H-bond dissociation is distributed into the internal and the translational motion of the fragments. The result is reflected in the bandwidth of the 2-naphthol fragment emission, exhibiting a broader feature with the increase of the IR frequency. Though it is not clear whether the isomerization/dissociation of H-bond processes occur statistically, the exclusive production of the *cis* fragment at the higher energy can be explained by the larger density of states for the dissociation channel than that of the isomerization channel. The density of states of the latter channel is composed of the quantum levels of the free internal rotations and vibrations of the fragments, while that of the former channel is composed of the quantum levels of the inter- and intramolecular vibrations of the clusters. Since the energy spacing of the rotational motions is much smaller than the intermolecular vibrations, the density of states of the former (dissociation) channel increases much faster with the energy than the latter (isomeriation) channel, leading the dissociation as the main channel at high energy.

It should be noted that the larger rate constant of the H-bond dissociation at high internal energy can describe the very small yield of the reverse *trans*→*cis* isomerization process. As presented in the energy diagram of Fig. 7, the H-bond energy is comparable to the isomerization energy, and the two channels become open at almost equal energy in the case of *trans*-2-naphthol clusters. Thus, even if the isomerization is energetically possible, the H-bond dissociation occurs much faster than the isomerization.

B. DFT calculation of the isomerization barrier height

From the obtained data, there are two issues to be addressed for the barrier height of the isomerization. First is the difference in the height between S_1 and S_0, and second is the dramatic reduction of the height by the H-bond formation. To answer these questions, we calculated the barrier height for 2-naphthol and its H-bonded cluster with ammonia for S_0 and S_1. For S_0, a DFT calculation was employed, and the TD-DFT calculation for S_1 with B3LYP/cc-PVDZ level with GAUSSIAN 98 software.[20] In S_0, the structure is optimized for the different torsional angles of the OH group along the CO axis. The energy of S_1 is calculated for the same structures with those of the ground state. Figure 10 shows the calculated barrier height. In S_0, the barrier heights of the bare 2-naphthol and 2-naphthol-NH_3 are 1650 and 1700 cm^{-1}, respectively. The obtained value for the bare 2-naphthol is slightly larger than the reported torsional barrier height of phenol in S_0. For the height of the cluster, the effect of the H bonding seems to be negligibly small.

In S_1, the calculated barrier heights were 3050 and 3100 cm^{-1} for the bare 2-naphthol and 2-naphthol-NH_3. These values are almost twice of S_0. The enhancement of the height upon the electronic excitation is qualitatively in good agreement with that of phenol, whose torsional barrier height in S_1 is obtained to be 4710 cm^{-1} by Berden and Meerts from the analysis of the high-resolution S_1-S_0 spectrum.[11] This common feature between 2-naphthol and phenol indicates the similarity of the electronic structure between them. The increase of the barrier height in S_1 may be described by that they tend to form quinoidal structure in S_1, resulting in the increase of its double-bond character in the C–O bond. As to the effect of H bonding on the barrier height in S_1, the present calculation did not show the reduction of the height of 2-naphthol-NH_3 compared with the bare 2-naphthol. This result suggests that the decrease of the barrier height upon

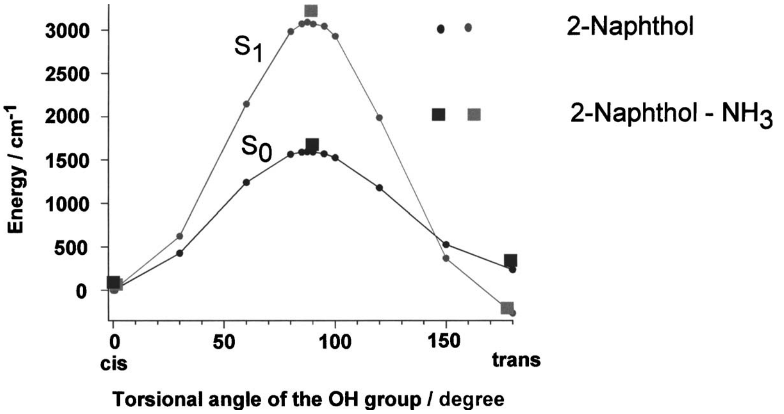

FIG. 10. Plots of relative energies of 2-naphthol and 2-naphthol-NH_3 in S_0 and S_1 as a function of the OH torsional angle. For S_0, O–H−−NH_3 angle was assumed to be linear with other geometry optimized with DFT calculation with B3LYP/cc-PVDZ level. For S_1, TD-DFT calculation was employed for the same geometry with S_0.

the H bonding is not intrinsic to S_1. Thus, it is suggested that the reduction of the barrier height is caused by the interaction with the higher excited state(s). One of such the possible states is the $\pi\sigma^*$ state which is predicted to locate above S_1.[21–23] The $\pi\sigma^*$ state has a repulsive potential curve along the O–H bond, and causes the excited-state hydrogen transfer (ESHT) reaction in the H-bonded cluster via the conical intersection between the photoexcited $\pi\pi^*$ state and the $\pi\sigma^*$ state. In the present system, however, we did not observe the ESHT reaction and there has been no report on this reaction in the H-bonded system of 2-naphthol. Thus, it is not clear whether the $\pi\sigma^*$ state affects the isomerization barrier height of the $\pi\pi^*$ state in 2-naphthol. Further calculation including for the geometry optimization including higher excited states will be necessary for more detailed discussion.

V. SUMMARY

In the present work, we used an IR laser light to promote the *cis-trans* isomerization of 2-naphthol and its H-bonded clusters in the excited electronic states. We found that the barrier height is larger than 3610 cm^{-1} for the bare molecule, and is reduced to less than 3000 cm^{-1} in the H-bonded clusters. In the cluster, the *cis*→*trans* isomerization yield is very high, while the yield of the reverse process, *trans*→*cis*, is very low, which is ascribed by the difference in energy between them. In addition, the *cis* → *trans* isomerization yield drastically changes as a function of the IR frequency. The yield is very high at low IR frequency, and rapidly decreases with the frequency because of the dominance of the H-bond dissociation within the isomer at high energy. Though we could not obtain the theoretical support for the reduction of the barrier height upon the H bonding, the interaction with S_2 excited state is suggested for the reduction.

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