IR induced cis→trans isomerization of 2-naphthol: Catalytic role of hydrogen-bond in the photoinduced isomerization

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An infrared laser induced cis→trans isomerization has been investigated for 2-naphthol and its hydrogen(H)-bonded cluster with NH3 in the S1 electronic state by UV–IR double resonance excitation in a supersonic jet. A specific isomer was pumped to a X–H (X=O, C or N) stretching vibration in S1 by a sequential UV–IR two-photon excitation, and the resultant product species were analyzed by dispersing their fluorescence. It was found that the IR excitation induces the isomerization for the H-bonded cluster with the excitation less than 3000 cm⁻¹, while no isomerization was found to occur for bare 2NpOH even with an input energy of 3610 cm⁻¹. The substantial reduction of the isomerization barrier height represents evidence of the catalytic nature of H-bonding in the conformational isomerization. It was also found that the isomerization efficiency is very high at low IR frequency and exhibits a marked IR frequency dependence.


The existence and discrimination of the rotational isomers of 2-naphthol (2NpOH) was first demonstrated by Ito and co-workers using electronic spectroscopy combined with a supersonic free jet technique.¹ The rotamers, cis and trans, originate from the difference in conformation of the OH group with respect to the naphthalene ring. Later, Pratt and co-workers distinguished the two isomers by measuring high resolution electronic spectra.² It is reported that the cis-isomer is 140 cm⁻¹ more stable than the trans-isomer in S0, while in S1 the trans-isomer becomes 180 cm⁻¹ more stable than the cis-isomer.³ Though the barrier height of the isomerization along the torsional coordinate of the OH group in 2NpOH has not been reported in either state, it is thought to be very similar to that of phenol, 1200 cm⁻¹ in S0,⁴ and 4710 cm⁻¹ in S1, respectively.⁵ The dynamics and mechanism of the conformational isomerization has recently been paid much attention because of the fundamental importance in chemistry, as well as in biochemistry, especially for understanding the three dimensional structure of flexible bio-relevant molecules.⁶

In this Communication, we report a study on laser assisted cis→trans isomerization of 2NpOH and its hydrogen(H)-bonded cluster with NH3 in S1 by using UV–IR double resonance spectroscopy. A specific isomer or its cluster in a jet is pumped to a X–H stretching vibration in S1 by a sequential UV–IR two-photon excitation, where X refers to O, C, or N atom. The isomerization will occur when the X–H stretching energy flows into the torsional vibration of the OH group, exceeding the barrier height of the isomerization. We investigated the process putting our emphasis on the following issues: The first is whether cis→trans isomerization actually occurs in the energy region examined in the present work. The second is whether this reaction exhibits any selectivity. In such a case, what is a major factor for the selectivity? The third is how the barrier height and the dynamics of the isomerization are affected by H-bonding to the OH group. We will verify those issues under a challenging attempt for the laser control of the isomerization.

The experimental setup of UV–IR double resonance spectroscopy has been described in our previous papers.⁷⁻⁹ Jet-cooled 2NpOH and its cluster with NH3 were produced by the supersonic expansion of 2NpOH/NH3 gaseous mixture, seeded in helium carrier gas. A specific species in the jet was pumped to the zero-point level in S1 with a UV light, followed by an IR excitation to the X–H stretching vibration. The vibrationally-excited molecules or clusters in S1 will immediately relax by intramolecular or intracluster vibrational energy redistribution (IVR) and emit broad fluorescence in the wide frequency region. If isomerization occurs, the generated isomer emits fluorescence in different frequency region from the initial species because each isomer has own electronic transition frequency. Thus we can discriminate IVR or isomerization by dispersing the emission by using a monochromator. The X–H stretching energies are, in general, larger than the H-bonding energy, and the vibrationally excited clusters may predissociate and generate 2NpOH fragments in S1. Since most of the input energy is consumed for the dissociation of the H-bond, the generated 2NpOH will be internally cool and emit sharp fluorescence in the band origin region, which can also be discriminated. The IR spectra of 2NpOH and its cluster in S1 are obtained by scanning the IR frequency while monitoring either the emission from the IVR generated levels⁹ or the photofragment emission.⁸

The UV light was a second harmonic of Nd:YAG laser pumped dye laser. Tunable IR laser light in the 3 μm region was obtained by difference frequency generation between the second harmonic of another Nd:YAG laser and the Nd:YAG laser pumped dye laser output by using a LiNbO3 crystal. The delay time between the UV and IR pulses was set to ten
nanoseconds. The laser beams were coaxially introduced into a vacuum chamber, crossing the free jet. An \( f = 250 \text{ mm} \) monochromator was used to disperse the fluorescence. Typical slit width was 100 \( \mu \text{m} \).

The electronic transitions of 2NpOH and its H-bonded clusters have been reported by several groups,\(^{1,10-13}\) The band origin of cis- and trans-isomer of bare 2NpOH is located at 30 903 and 30 585 cm\(^{-1}\), respectively, and that of the 1:1 H-bonded cluster with \( \text{NH}_3 \) is located at 30 318 and 29 964 cm\(^{-1}\), respectively. Figure 1(A) shows the IR spectra of bare cis-2NpOH and cis-2NpOH-NH\(_3\) in \( S_1 \) state. The OH stretch of bare cis-2NpOH appears at 3609 cm\(^{-1}\). In cis-2NpOH-NH\(_3\), we see two sharp peaks at 3400–3500 cm\(^{-1}\) and a broadband at 2800–3300 cm\(^{-1}\) with its center frequency at 3050 cm\(^{-1}\). From a comparison of the IR spectrum in \( S_1 \) with the reported spectrum in \( S_0 \),\(^{13}\) we assign the sharp bands to the NH stretching vibrations of \( \text{NH}_3 \), and the broadband to the H-bonded OH stretching vibration of 2NpOH. A large reduction of the OH stretch frequency (560 cm\(^{-1}\)) is due to a strong H-bonding between 2NpOH in \( S_1 \) (Ref. 14) and a strong base, \( \text{NH}_3 \).

We examined the IR laser induced isomerization for both bare 2NpOH and 2NpOH-NH\(_3\) in \( S_1 \). As a result, we found that the isomerization occurs only in the cluster but not in the bare molecule in the examined energy region of 2900–3610 cm\(^{-1}\). We first present the result of 2NpOH-NH\(_3\) and then discuss the result of bare molecule. Since the IR spectrum of 2NpOH-NH\(_3\) is extremely broad as seen in Fig. 1(A), we were able to pump the cluster to various energies by tuning the IR laser frequency along the broad IR band. In Fig. 1(B), traces (a)–(e) represent the dispersed fluorescence (DF) spectra of cis-2NpOH-NH\(_3\) observed after the UV–IR excitation with various IR frequencies, being compared with the DF spectrum obtained without IR excitation, trace (f). In the DF spectra with low IR frequency excitations, traces (c)–(e), a broad emission is seen at 30 300–30 920 cm\(^{-1}\). The broadness indicates that the emitting species is internally very hot, so that we assign the broad emission as the fluorescence from the levels generated by IVR of the cluster. In the broad emission spectrum, traces (c)–(e), we notice that there is a step-like feature at 30 920 and 30 600 cm\(^{-1}\), which are marked by arrows. We will discuss the step-structure later. In the DF spectrum with 3260 cm\(^{-1}\) excitation, trace (b), a sharp band (band T) emerges at 30 580 cm\(^{-1}\), which is overlapped with the broad emission having a step at 30 920 cm\(^{-1}\). In the case of the 3435 cm\(^{-1}\) excitation, trace (a), another sharp band (band C) emerges at 30 900 cm\(^{-1}\). It should be noticed that the broad emission is not seen in trace (a).

The new bands T and C, are undoubtedly assigned to the band origins of bare trans- and cis-2NpOH, respectively, by the comparison with the \( S_1-S_0 \) excitation spectrum. Actually, the DF spectra of bare cis- and trans-2NpOH from their band origins, traces (g) and (h), clearly show a good coincidence of the bands T and C to the band origins of trans- and cis-2NpOH, respectively. Thus, we conclude that these species are generated by predissociation of the vibrationally excited cis-2NpOH-NH\(_3\) in \( S_1 \). The important point from this observation is that the trans-2NpOH fragment is generated from cis-2NpOH-NH\(_3\), that is, the cis—trans isomerization is occurring in cis-2NpOH-NH\(_3\). Furthermore, in the 3260 cm\(^{-1}\) excitation, only the trans-2NpOH fragment is generated as seen in trace (b), indicating that the isomerization proceeds with almost 100% efficiency at this energy.

In order to make these characteristics clear, we observed relative yields of the two fragments as a function of the IR frequency. Figure 2(a) shows the trans-2NpOH fragment yield spectrum by the UV–IR excitation of cis-2NpOH-NH\(_3\), representing that the appearance energy of the trans-2NpOH fragment from 2NpOH-NH\(_3\) is 3090 (±10) cm\(^{-1}\). We carried out similar measurement for the cis-2NpOH fragment. However, the IR absorption intensity was weak at the appearance energy of this fragment and we could not obtain cis-2NpOH yield spectrum with a good S/N ratio. Instead, we determined the appearance energy of the cis-2NpOH fragment by measuring the relative ratio of the two fragments as a function of the IR frequency as shown in Figs. 2(b) and 2(c). From Fig. 2(c), the appearance energy of the cis-2NpOH fragment was determined to be 3280 (±10) cm\(^{-1}\).
Acidity of 2NpOH drastically increases from $S_0$ ($pK_a = 9.8$) to $S_1$ ($pK_a = 2.4$), leading to the excited state proton transfer (ESPT) reaction in condensed phase. Though the ESPT reaction is not reported in the 1:1 cluster, it is quite possible that the OH bond is largely lengthened in the H-bonded cluster in $S_1$. As the O–H bond stretches, the Coulombic contribution to the H-bonding will increase in the cluster, which may lead to a loss of the bond directionality and a reduction of the barrier height along the torsional coordinate of the OH group. The other origin is the interaction of the nearby $\pi\sigma^*$ state. The importance of this state on the photochemistry of aromatic hydrocarbons has been recently proposed by Sobolewski et al.\textsuperscript{15–17} This state is predicted to be located nearby $S_1$ and may cause the excited state hydrogen transfer reaction (ESHT) in the clusters.\textsuperscript{18,19} In case of aniline, in fact, we have experimentally proved the existence of this state.\textsuperscript{9} A theoretical support is highly demanded for the information of the transition state structure and the barrier height.

So far, we did not discuss the possibility of the isomerization below the H-bond dissociation energy. It will be very important to reveal whether the isomerization is accompanied with the H-bond dissociation. As we mentioned before, we found step-like features at 30 920 and 30 600 cm$^{-1}$ in the DF spectra when the IR excitation energy was lower than the dissociation limit. The difference 320 cm$^{-1}$ between the two steps is very close to the difference of the electronic transition frequencies of the cis- and trans-2NpOH-NH$_3$ clusters. Thus, the steps at 30 920 and 30 600 cm$^{-1}$ are thought to be high frequency limits of the emission from the redistributed levels of cis- and trans-2NpOH-NH$_3$, respectively, generated by IVR and/or isomerization of the IR excited cis-2NpOH-NH$_3$. Therefore, we conclude that the isomerization occurs without accompanying the H-bond dissociation, and the upper limit of the isomerization barrier height is determined to be 2891 cm$^{-1}$.

Another noticeable feature is that the production efficiency of the isomerized fragment is very high at low IR excitation energy. As was described before, we have obtained the threshold energies of the productions of trans- and cis-2NpOH fragments from cis-2NpOH-NH$_3$ to be 3090 and 3280 cm$^{-1}$, respectively. This means that only the trans-2NpOH fragment is produced from cis-2NpOH-NH$_3$ at 3090–3280 cm$^{-1}$. This high selectivity at the low IR frequency excitation can be explained from heat of formation of each species. Figure 3 shows the energy diagram of 2NpOH and 2NpOH-NH$_3$ in $S_0$ and $S_1$. The H-bond energy of cis-2NpOH-NH$_3$ in $S_1$ can be set to 3280 cm$^{-1}$ from the appearance energy of cis-2NpOH fragment as shown in Fig. 2(c). Accordingly, the binding energy in $S_0$ is obtained to be 2695 $(\pm 10)$ cm$^{-1}$ from the binding energies in $S_1$ and electronic transition frequencies of bare cis-2NpOH and cis-2NpOH-NH$_3$. By assuming the H-bond energy is the same between the cis- and the trans-forms in $S_0$, we obtain the H-bond energy of trans-2NpOH-NH$_3$ in $S_1$ to be 3316 $(\pm 10)$ cm$^{-1}$, from the $S_1$–$S_0$ transition frequencies. It should be mentioned that the obtained H-bonding energy for 2NpOH-NH$_3$ in $S_0$ is in good agreement with that of 1NpOH-NH$_3$ (2680 cm$^{-1}$) reported by Bürgi et al.\textsuperscript{20}
Based on the energy levels in Fig. 3, we discuss the competitive channels for the isomerization and the dissociation. In $S_1$ of 2NpOH-NH$_3$, trans-isomer is 214 cm$^{-1}$ more stable than that of cis-isomer. When the cis-2NpOH-NH$_3$ cluster is excited to the vibrational levels below 3280 cm$^{-1}$ (case 1 in Fig. 3), the energy is not large enough to break the H-bond in the cis-form. However, if the cis-form cluster isomerizes to the trans-form, it can dissociate into trans-2NpOH (in $S_1$) and NH$_3$, because the total energy of 3494 ($=214+3280$) cm$^{-1}$ is higher than the dissociation energy of trans-2NpOH-NH$_3$. Thus, only the cis$\rightarrow$trans isomerization/dissociation channel is possible at 3090–3280 cm$^{-1}$. On the contrary, when cis-2NpOH-NH$_3$ is excited above 3280 cm$^{-1}$ (case 2), the dissociation channel of the cis-2NpOH-NH$_3$ becomes open and the two channels will compete, and we will observe the emission of both the cis- and trans-2NpOH fragments. To verify the energy constraint reaction mechanism, we carried out the similar study for the trans-2NpOH-NH$_3$ cluster. In the examined IR frequency region of 3330–3435 cm$^{-1}$, we identified only the trans-2NpOH production channel, which is in good agreement with the energy diagram of Fig. 3. Even the highest energy of 3435 cm$^{-1}$ is 59 cm$^{-1}$ lower than the cis-2NpOH production channel. The experiment for higher IR excitation could not be performed because of the weak absorption of trans-2NpOH-NH$_3$ compared to that of cis-2NpOH-NH$_3$.

In conclusion, IR laser assisted cis$\rightarrow$trans isomerization has been applied to the H-bonded cluster of 2NpOH in $S_1$, using UV–IR double resonance spectroscopic method. We found that the H-bonding to the OH group substantially reduces barrier height of the conformational isomerization. The isomerization starting from the cis-form H-bonded cluster showed a characteristic energy dependence. At low internal energies the cis$\rightarrow$trans isomerization followed by the H-bond dissociation is dominant, resulting in the high yield of the isomerized photofragment. With the energy increases, the predissociation channel within the cis-form cluster competes with the isomerization. Further studies on other clusters with wider energy range are now in progress for the detailed understanding of the dynamics of the isomerization and the predissociation.

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