Torsional Potential of Methyl Group in *m*-Tolunitrile-H_2O and *m*-Tolunitrile-N_2O Complexes Studied by Laser-Induced Fluorescence and Hole-Burning Spectroscopies

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Torsional vibronic bands of the methyl group of *m*-tolunitrile-H_2O and *m*-tolunitrile-N_2O complexes in their S_1 (first excited singlet electronic) states were observed under the supersonic-jet condition by laser-induced fluorescence and hole-burning spectroscopies. Torsional potentials determined from the observed frequencies revealed that the complex formation similarly affects for the H_2O and N_2O complexes. Two isomers were assumed for both the H_2O and the N_2O complexes: One showed vibrational frequencies of torsion similar to those of the monomer, whereas torsional potentials for the other complexes were lower than that in the monomer and of nearly 6-fold symmetry. The geometries of the complexes were evaluated by molecular-orbital calculations.

Introduction

Because torsional motions of methyl groups in aromatic molecules, one of the large-amplitude vibrations, play an important role in the dynamics of molecules and molecular complexes, extensive studies on toluene derivatives have been performed. For example, Moss et al.[1−3] reported that the torsional motion of the methyl group in *p*-fluorotoluene accelerates intramolecular vibrational redistribution. In our previous paper, we found that the vibrational predissociation of anisole-argon complex, which has a methyl torsional motion, takes place more rapidly than that of benzonitrile-argon complex, which has no torsional mode.[4,5] A similar trend was found in studies on the anisole-benzene complex[6] and benzene dimer;[7,8] the lifetimes of the excited vibrational states for the former are appreciably shorter than those for the latter. These results imply that the fast dynamics of the complex containing a methyl group is related to either (1) increasing state density caused by low-frequency torsional motion or (2) lowering symmetry from a plane of aromatic ring caused by a nonplanar methyl group, resulting in strong coupling between intramolecular and intermolecular vibrational modes. However, the effect of the methyl group on dynamics of complexes has not been elucidated clearly.

Most researches on torsional potentials have been done for isolated monomer molecules in supersonic jets, although detailed investigation of the changes of torsional potentials upon the complex formation seems profitable to elucidate the role of torsional motion in dynamics. On the other hand, fewer reports on the analyses of torsional potentials of molecules forming complexes with other molecules have been found in the literature.[9,10]

We have previously reported the change of methyl torsional potential of *m*-tolunitrile on the 1:1 complex formation with neon, argon or krypton,[11] where torsional frequencies in the S_1 (the first excited singlet electronic) states of the complexes were measured by the LIF (laser-induced fluorescence) and hole-burning spectroscopies. The torsional potentials and the reduced rotational constants for the methyl groups were estimated from the observed torsional frequencies. The barrier height of the potential decreases and the reduced rotational constant increases on going from the monomer to the neon complex. On the other hand, an increase of the barrier height and decrease of the reduced rotational constant were observed on going from the neon complex to the argon complex and from the argon complex to the krypton complex. These results suggest that the torsional potential is deformed on complex formation mainly by electronic interaction, but not by steric hindrance. If steric hindrance is the main origin of the change, the barrier height and the reduced rotational constant are expected to change monotonically from the monomer to the krypton complex according to the size of the counterpart.

In present study, the change of torsional potential of *m*-tolunitrile in the S_1 state on the 1:1 complex formation with H_2O or N_2O is investigated in detail by the LIF-excitation and hole-burning spectroscopies. Interaction of H_2O and N_2O with *m*-tolunitrile is expected to be different from that of rare gas atoms. H_2O and N_2O associate to *m*-tolunitrile from the side more strongly than rare gas atoms do; rare gas atoms associate weakly on the aromatic ring.

Experimental Section

Two sets of nanosecond pulsed-laser systems were used for spectral measurements; the second-harmonic outputs of dye lasers pumped by the second harmonic of a Nd:YAG laser (Continuum, Powerlite 7000, ND6000, UVX and UVT; ∼1 mJ/pulse, line width ∼ 0.2 cm^{-1}) and a XeCl excimer laser (Lumonics, HE−420-SM-B and Lambda Physik, FL3002; 100∼500 μJ/pulse, line width < 0.2 cm^{-1}). In hole-burning measurements, the former with higher power was used for the pump laser, whereas the latter with narrower line width was used for the probe laser. Delay between the pump and probe pulses was set to 1 μs in the hole-burning measurements.

A photomultiplier (Hamamatsu, R955) was used for the fluorescence detector. A shortcut optical filter (HOYA, UV28

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or UV30) was used in front of the detector to eliminate laser scattering. Wavelengths of the laser outputs were calibrated with a seethrough hollow cathode lamp (Hamamatsu, GALVATRON L2783).

In measurements of the monomer, helium (Taiyo Toyo Sanso Co., 99.9999%) passing through a reservoir containing *m*-tolunitrile (Tokyo Kasei, reagent grade) cooled at −25∼0 °C in a thermostating water-bath was expanded into a vacuum chamber through a pulsed valve with an orifice diameter of 0.8 mm. The background pressure in the chamber was held below 10^{-2} Pa throughout measurements. In measurements of the water complex, several drops of either water (homemade distilled water) or water-d_2 (Merck, Uvasol, 99.8%) were added into the reservoir. Helium gas containing 0.5∼3% of N_2O (Showadenko, 4N grade, 99.99%) was prepared in a tank with 12 l in volume, and was used for N_2O-complex experiments.

Stagnation pressure was varied in the range of 1∼3 atm to change the degree of cooling of jets. All measurements were performed at 20 mm downstream from the pulsed valve.

Analyses and Calculations. The observed torsional frequencies were analyzed by assuming the following torsional potential $V(\phi)$

$$V(\phi) = \frac{1}{2}\{V_3[1 - \cos(3\phi)] + V_6[1 - \cos(6\phi)]\} \tag{1}$$

where ϕ is the torsional angle, and V_3 and V_6 are heights of the 3- and 6-fold barriers, respectively. Using the parameters V_3, V_6, and B (the reduced rotational constant for the methyl group), torsional frequencies can be calculated with the procedure found in the literature.[12,13] Values of the parameters were determined by adjusting the calculated frequencies to the observed ones.

Optimized geometries and energies of the monomer and complexes were calculated with molecular orbital calculations (GAUSSIAN 98),[14] where HF/6-31G** and CIS/6-31G** were, respectively, used for the ground electronic (S_0) and S_1 states calculations.

Results and Discussion

The conventional notation is used for the levels of internal rotation.[15,16] The vibronic states due to the methyl torsion are denoted by $0a_1$, 1e, 2e, $3a_1$, $3a_2$, 4e, and so on, using a combination of the rotational quantum number in a one-dimensional free rotor and the symmetry species. Primes and double primes on the quantum numbers are used to distinguish levels in the S_1 and S_0 states, respectively.

A. *m*-Tolunitrile-H_2O Complex. (1) *LIF-Excitation Spectra.* Figure 1 shows the LIF-excitation spectra of *m*-tolunitrile in a supersonic jet. The concentration of water was increased on going from (a) to (c) by adding small amount of water into the sample reservoir. The peaks observed at 35 813.3 and 35 812.0 cm^{-1} are due to the $0'a_1 \leftarrow 0''a_1$ and $1'e \leftarrow 1''e$ transitions of the monomer, respectively. The progression marked with **m** starting from the doublet and extending toward the higher frequency is due to methyl torsional motion of the monomer. The 35 712.7 cm^{-1} band marked with * was assigned to the *m*-tolunitrile dimer by examining the dependence of its relative signal intensity to those of monomer bands on the *m*-tolunitrile concentration.

The spectra shown in Figure 1 are scaled so as to show the bands due to the $0'a_1 \leftarrow 0''a_1$ and $1'e \leftarrow 1''e$ transitions of the monomer nearly constant. Most of the bands observed at the lower frequency side of the doublet are assignable to complexes containing *m*-tolunitrile and water; their relative intensities increase as the water concentration increases. The bands observed below 35 680 cm^{-1} are assignable to the 1:2 complex of *m*-tolunitrile and water, since the intensities of the bands depend more greatly on the water concentration than those of the bands observed in the 35 680−35 810 cm^{-1} region.

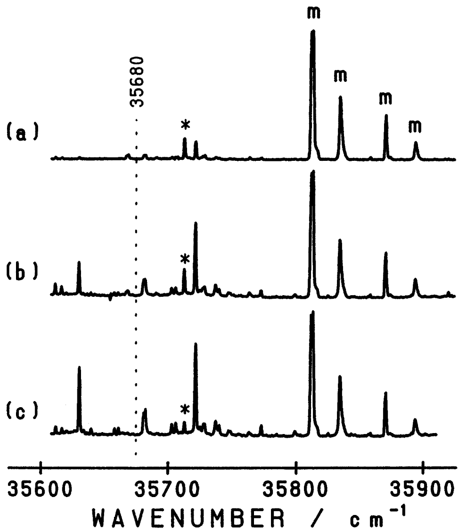

Figure 1. LIF-excitation spectra of *m*-tolunitrile diluted by helium containing small amount of water. Concentration of water increases from (a) to (c). In spectrum (a), bands marked with **m** are due to the monomer. Band marked with * is due to the *m*-tolunitrile dimer.

Many bands were observed in the 35 680−35 810 cm^{-1} region of the LIF-excitation spectrum when water was added to the sample gas. They are assumed to be torsional and intermolecular modes of the 1:1 complex of *m*-tolunitrile and H_2O, where the spectrum is so complicated that assignment of the bands is difficult without further information. The bands in the region should be assigned to plural species, i.e., isomers of the 1:1 complex, because more bands than expected for a single complex are observed. To observe transitions due to a specific species from a specific state selectively, hole-burning spectra were measured by setting the probe frequency to one of the bands with appreciable intensity in the region.

(2) *Hole-Burning Spectra.* Figure 2 shows the results of LIF-excitation and hole-burning measurements. The top trace is the expanded spectrum of Figure 1(c). The traces **A**, **B** and **C_1∼C_4** show the hole-burning spectra measured by probing bands marked with **A**, **B** and **C_1∼C_4** in the LIF-excitation spectrum, respectively.

In the LIF-excitation spectrum, the doublet bands **A** and **B** were assumed to be assigned to the $1'e \leftarrow 1''e$ and $0'a_1 \leftarrow 0''a_1$ transitions of a *m*-tolunitrile-H_2O complex. Because transitions from the $0''a_1$ and $1''e$ states to the a_1 and e states in S_1, respectively, are allowed, the dips assignable to the $2'e \leftarrow 1''e$ and $4'e \leftarrow 1''e$ transitions were observed in the hole-burning spectrum **A** as well as the dip due to the $1'e \leftarrow 1''e$ transition, whereas the dips assignable to the $0'a_1 \leftarrow 0''a_1$ and $3'a_1 \leftarrow 0''a_1$ transitions were observed in the hole-burning spectrum **B**.

In each region for the $2'e \leftarrow 1''e$ and $4'e \leftarrow 1''e$ transitions in the hole-burning spectrum **A**, two dips marked with crosses that can be assigned to the torsional mode were observed; one of the dips would be due to an intermolecular mode. In each case, it is difficult to judge only from the experimental results for *m*-tolunitrile-H_2O which dip corresponds to the torsional motion. To distinguish the dips due to torsion and intermolecular vibrations, a similar experiment using D_2O (heavy water) was carried out because it is expected that the isotope substitution of water would significantly affect intermolecular vibrational frequencies but have little effect on methyl torsional frequencies.

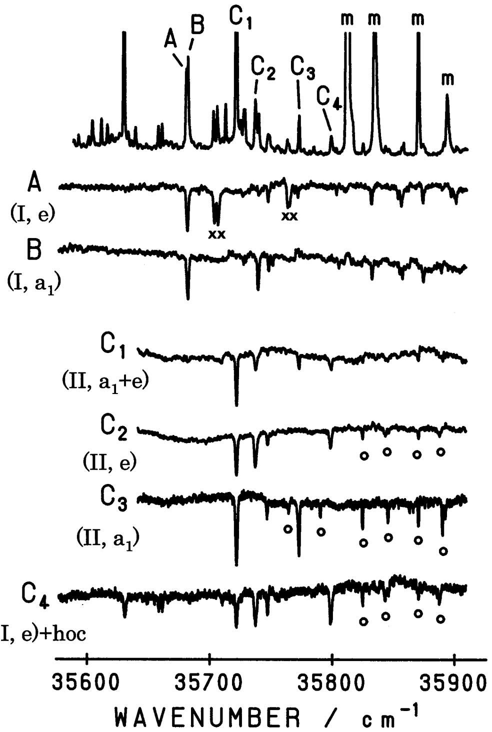

Figure 2. LIF-excitation spectrum in Figure 1(c) is shown in an expanded vertical scale (top trace). Bands marked with **m** are bands due to the monomer. Hole-burning spectra measured by probing, respectively, bands **A**, **B** and **C**$_1$~**C**$_4$ in the LIF-excitation spectrum (traces **A**, **B** and **C**$_1$~**C**$_4$). In parentheses are shown the number of probed complex, I or II, and the symmetry of probed mode, a_1 or e. "hoc" represents a higher order complex. For dips marked with crosses or circles, see text.

However, no detectable shift by the isotope substitution was observed for any of the dips; no information for the assignment was obtained. Here, transitions with lower frequencies were assumed to be the torsional modes. This assignment is supported by the analysis of spectra for *m*-tolunitrile-N_2O complex described later. The alternative interpretation that neither bands are due to intermolecular modes but that 2e degeneracy is being split seems less probable; such splitting of the degenerated e mode has not been observed yet for any molecules and molecular complexes with a methyl group as far as we know.

In the hole-burning spectra **A** and **B**, no dip corresponding to the **C**$_1$ band in the LIF-excitation spectrum was observed. This fact indicates that species giving the **C**$_1$ band is different from that giving bands **A** and **B**. Because all of the **A**, **B**, and **C**$_1$ bands are due to the 1:1 complex of *m*-tolunitrile and H_2O as judged from the water concentration dependence on their intensities, species giving bands **A** and **B**, and species giving band **C**$_1$ are considered to be isomers of the 1:1 complex. The former and the latter are called, respectively, H_2O Complex (I) and H_2O Complex (II) hereafter.

In the hole-burning spectrum **C**$_1$, the dips due to H_2O Complex (I) observed in spectra **A** and **B** were not observed, whereas the dips assignable to the $2'e \leftarrow 1''e$, $3'a_1 \leftarrow 0''a_1$ and $4'e \leftarrow 1''e$ transitions of H_2O complex (II) were observed. We assumed that the bands due to the $0'a_1 \leftarrow 0''a_1$ and $1'e \leftarrow 1''e$ transitions of H_2O complex (II) overlap at the **C**$_1$ band. To confirm this assignment, hole-burning spectra were measured by probing the bands assigned to the $2'e \leftarrow 1''e$ and $3'a_1 \leftarrow 0''a_1$ transitions (spectra **C**$_2$ and **C**$_3$, respectively). Dips assignable to the $1'e \leftarrow 1''e$, $2'e \leftarrow 1''e$ and $4'e \leftarrow 1''e$ transitions were observed in the hole-burning spectrum **C**$_2$, while dips assignable to the $0'a_1 \leftarrow 0''a_1$ and $3'a_1 \leftarrow 0''a_1$ transitions were observed in the hole-burning spectrum **C**$_3$. These experimental results support our assignment. All of the bands observed in spectra **C**$_2$ and **C**$_3$ were observed in spectrum **C**$_1$. In spectra **C**$_2$ and **C**$_3$, some additional dips marked with open circles were observed. These dips are presumably caused by the more intense pump pulses used for the measurements of spectra **C**$_2$ and **C**$_3$, which emphasized bands observed weakly in spectrum **C**$_1$. Assignments of the bands, which form a peculiar progression, will be discussed in a separate paper.

TABLE 1: Observed Torsional Frequencies (in cm^{-1})[a]

	$3'a_1$	$2'e$	$4'e$
monomer	57.1	22.0	81.9
H_2O complex (I)	57.6	22.1 or *25.1*[b]	82.1 or *83.4*[b]
H_2O complex (II)	51.1	15.4	77.2
N_2O complex (I)	56.9	22.6	82.1
N_2O complex (II)	52.4 or *57.0*[c]	17.6 or *19.4*[c]	79.2

[a] Frequencies for $3'a_1$ are measured from the $0'a_1$ states. Frequencies for $2'e$ and $3'e$ are measured from the $1'e$ states. [b] Two bands assignable to each of the $2'e$ and $4'e$ bands were observed for H_2O Complex (I). Here, frequencies shown by roman type are adopted by the analogy of the results for N_2O Complex (I). [c] Two bands assignable to each of the $3'a_1$ and $1'e$ bands were observed for N_2O Complex (II). Here, frequencies shown by roman type are adopted by the analogy of the results for H_2O Complex (II).

TABLE 2: Parameter for Torsional Potential (in cm^{-1})[a]

	B	V_3	V_6
monomer	5.04	38.0	−24.0
H_2O complex (II)	5.09	7.0	−19.5
N_2O complex (II)	5.13	19.5	−18.0

[a] Observed torsional frequencies for H_2O Complex (I) and N_2O Complex (I) are reproduced using the values for monomer.

Trace **C**$_4$ in Figure 2 is the hole-burning spectrum measured by probing the $4'e \leftarrow 1''e$ transition of H_2O complex (II), which should coincide with spectrum **C**$_2$ obtained by probing the $2'e \leftarrow 1''e$ transition. Although all the dips observed in spectrum **C**$_2$ were observed in spectrum **C**$_4$, some additional dips were observed in the lower frequency region of spectrum **C**$_4$. The additional dips are assignable to a *m*-tolunitrile-$(H_2O)_2$ complex; they were observed, presumably because the $4'e \leftarrow 1''e$ transition of H_2O complex (II) and one of the transitions of the *m*-tolunitrile-$(H_2O)_2$ complex overlap at the **C**$_4$ band.

(3) *Comparison of Torsional Potentials.* The observed torsional frequencies of *m*-tolunitrile in H_2O Complexes (I) and (II) are summarized in Table 1. The torsional frequencies in H_2O Complex (I) are nearly equal to those in the monomer within 0.5 cm^{-1}. Thus, the torsional potential in H_2O Complex (I) was concluded to be similar to that in the monomer.

On the other hand, torsional frequencies in H_2O complex (II) are different appreciably from those in the monomer. The potential parameters obtained by the analysis of experimental data are shown in Table 2. The torsional potentials for the monomer and complexes are schematically drawn in Figure 3. For the potential of H_2O complex (II), the height of 3-fold barrier is much lower than that for the monomer, while the height of 6-fold barrier is only a little lower than that for the monomer. Consequently, the torsional potential in H_2O complex (II) looks like to have 6-fold symmetry.

Two types of effects of complex formation on the torsional potentials are considered; one is the steric hindrance and the other is the electrostatic effect. The present result suggests that the latter is the major effect in the case of the H_2O complex (II); if the former is the main effect, then an increase of the

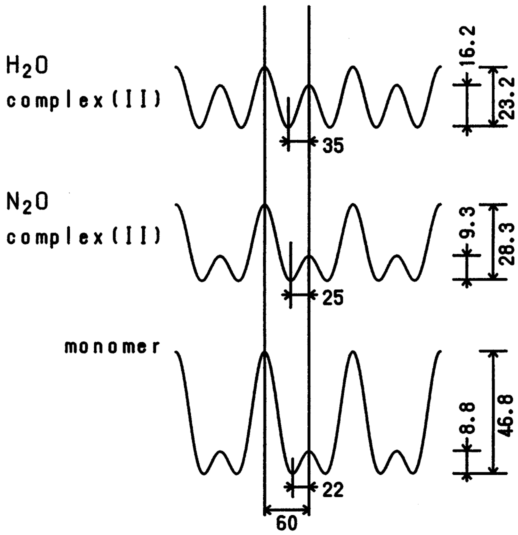

Figure 3. Torsional potential of methyl group in (a) the *m*-tolunitrile monomer, (b) N_2O Complex (II), and (c) H_2O Complex (II). Horizontal and vertical axes show the torsional angle (degree) and the energy (cm^{-1}), respectively.

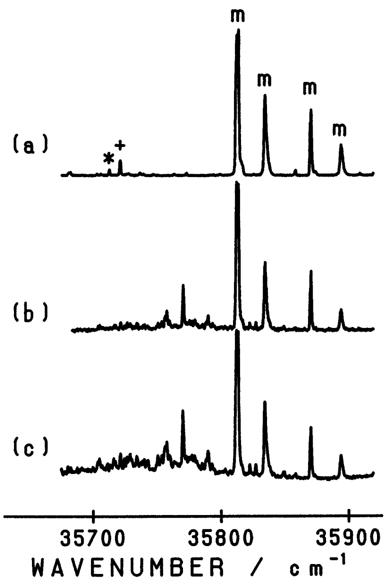

Figure 4. LIF-excitation spectra of *m*-tolunitrile diluted by helium containing N_2O at the concentrations of (a) 0%; (b) 1%; and (c) 2%. In spectrum (a), bands marked with **m** are due to the monomer. Bands marked with * and + are, respectively, due to the *m*-tolunitrile dimmer and H_2O complex (II).

barrier height at least with some extent by the complex formation is expected, and 6-fold symmetry of the torsional potential in H_2O complex (II) seems improbable. On the other hand, if the torsional potential is determined by the charge distribution on *m*-tolunitrile which is affected by the intermolecular electrostatic interaction, then the torsional potential proposed for H_2O complex (II) seems acceptable.

B. *m*-Tolunitrile-N_2O Complex. (1) *LIF-Excitation Spectra.* LIF-excitation spectra of *m*-tolunitrile diluted with helium containing N_2O at concentrations of (a) 0%, (b) 1%, and (c) 2% are shown in Figure 4. Bands marked with **m**, * and + are background bands, respectively, due to *m*-tolunitrile monomer, dimer and *m*-tolunitrile-H_2O complex. The spectra are scaled so as to show the doublet band due to the $0'a_1 \leftarrow 0''a_1$ and $1'e \leftarrow 1''e$ transitions of monomer nearly constant.

Many new bands and a broad background appeared by adding N_2O into the diluent gas. The broad background is due to higher order clusters containing a *m*-tolunitrile and some N_2O molecules because large clusters of N_2O are formed efficiently in supersonic jets.[17] Intensities of the sharp bands observed in the 35 760−35 800 cm^{-1} region were found to be nearly proportional to the concentration of N_2O, indicating that they are assignable to the 1:1 complexes of *m*-tolunitrile and N_2O. On the other hand, intensities of the bands appearing in the 35 700−35 760 cm^{-1} region, which show higher dependence on N_2O concentration than the bands in the 35 760−35 800 cm^{-1} region, are possibly assignable to the 1:2 complex of *m*-tolunitrile and N_2O.

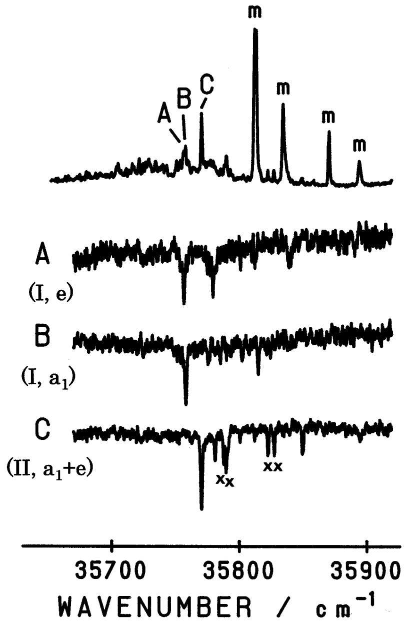

Figure 5. LIF-excitation spectrum in Figure 4(c) is shown in an expanded vertical scale (top trace). Bands marked with **m** are due to the monomer. Hole-burning spectra measured by probing, respectively, bands **A**, **B**, and **C** in the LIF-excitation spectrum (traces **A**, **B**, and **C**). In parentheses are shown the number of probed complex, I or II, and the symmetry of probed mode, a_1 or e. For dips marked with crosses, see text.

(2) *Hole-Burning Spectra.* The bands for *m*-tolunitrile-N_2O complex observed in the 35 760−35 800 cm^{-1} region of the LIF-excitation spectrum display features similar to those for *m*-tolunitrile-H_2O complex. Because the corresponding isomers are expected for both the N_2O complexes and the H_2O complexes, hole-burning spectra were measured to get the spectrum of each isomer separately. Experimental results are shown in Figure 5, where top trace is the expanded LIF-excitation spectrum of Figure 4(c), whereas the traces **A**, **B**, and **C** are hole-burning spectra measured by probing bands marked with **A**, **B**, and **C** in the LIF-excitation spectrum, respectively. Signal-to-noise ratios of the hole-burning spectra for the N_2O complexes are lower than those for the H_2O complexes. This is presumably caused by weaker signal intensity and also background emission due to higher order complexes.

Hole-burning measurements indicate that there exist two isomers for *m*-tolunitrile-H_2O complex. One isomer gives bands **A** and **B** in the LIF-excitation spectrum which were assumed to be assigned as the $1'e \leftarrow 1''e$ and $0'a_1 \leftarrow 0''a_1$ transitions, respectively. In the hole-burning spectrum **A**, dips assignable to the $2'e \leftarrow 1''e$ and $4'e \leftarrow 1''e$ transitions were observed in addition to the $1'e \leftarrow 1''e$ transition, while dips assignable to the $0'a_1 \leftarrow 0''a_1$ and $3'a_1 \leftarrow 0''a_1$ transitions were observed in the hole-burning spectrum **B**. Transitions observed in the hole-burning spectra **A** and **B** were not observed in the hole-burning spectrum **C**, indicating that band **C** in the LIF-excitation spectrum is due to the other isomer. Since the dips assignable to the transitions from the $0''a_1$ and $1''e$ states were observed together in the hole-burning spectrum **C**, the $1'e \leftarrow 1''e$ and $0'a_1 \leftarrow 0''a_1$ transitions should overlap at band **C** in the LIF-excitation spectrum. In the similar way as the H_2O complexes, two isomers of *m*-tolunitrile-N_2O complex are called N_2O Complex (I) and N_2O Complex (II) hereafter. N_2O Complex (I) gives bands **A** and **B**, whereas N_2O Complex (II) gives band **C** in the LIF-excitation spectrum.

Two dips were observed for N_2O Complex (II) in each region for the $2'e \leftarrow 1''e$ and $3'a_1 \leftarrow 0''a_1$ transitions, which are marked with crosses in the hole-burning spectrum **C**. Although it is difficult to judge only from the experimental results for *m*-tolunitrile-N_2O complex which dip corresponds to torsional motion, transitions with lower frequencies are assumed to be the torsional modes. This assignment is supported by the analysis for H_2O Complex (II); in the assignment, shifts of torsional frequencies on complex formation for N_2O Complex (II) are similar to those for H_2O Complex (II).

(3) *Comparison of Torsional Potentials.* Observed torsional frequencies of *m*-tolunitrile in N_2O complexes are summarized in Table 1. Torsional frequencies for N_2O Complex (I) are nearly equal to those for the monomer and H_2O Complex (I) within 0.6 cm^{-1}. Thus, torsional potential in N_2O Complex (I) was concluded to be similar to those in the monomer and H_2O Complex (I).

On the other hand, torsional frequencies in N_2O Complex (II) are different appreciably from those in the monomer. Parameters for the torsional potential of N_2O Complex (II) obtained by analyzing the observed frequencies are shown in Table 2. The torsional potential is schematically drawn in Figure 3. The barrier height in N_2O Complex (II) is lower than that of the monomer, although the change of potential on complex formation with N_2O is not so large as that on the complex formation with H_2O.

C. Change of Torsional Potential on Complex Formation. Because the behavior of *m*-tolunitrile-H_2O and *m*-tolunitrile-N_2O complexes is similar, the H_2O complex is mainly discussed below. H_2O Complexes (I) and (II) were found to coexist in the supersonic jet. The torsional potential in H_2O Complex (I) is similar to that in monomer, whereas that in H_2O Complex (II) is different appreciably from that in monomer. Structures of the isomers were surveyed with the help of molecular-orbital calculations, for the structural information on the complexes is strongly needed for detailed discussion.

It has been reported that H_2O in a benzonitrile-H_2O complex stays beside the cyano group of benzonitrile.[18,19] The structure was proposed based on the analysis of rotational contour in high-resolution LIF-excitation spectra[18] and on the analysis of infrared absorption spectra of the complex with the help of molecular-orbital calculations.[19] In the latter case, the observed vibrational frequencies of H_2O in the complex was analyzed. In the proposed structure, the oxygen atom and one of the two hydrogen atoms of H_2O lie on the plane of aromatic ring, whereas it was not elucidated whether the other hydrogen atom stays on the aromatic plane or not. Recently, three isomers of 4-aminobenzonitrile-H_2O complex have been determined by the analyses of infrared spectra.[20] In two of the three isomers, H_2O associates to 4-aminobenzonitrile at the cyano group; H_2O in one isomer stays beside the cyano group, while H_2O stays at the end of the cyano group in the other isomer.

On the analogy of benzonitrile-H_2O and 4-aminobenzonitrile-H_2O complexes, three geometries of *m*-tolunitrile-H_2O complex were considered. Since the two sides of the cyano group of *m*-tolunitrile are not identical, two isomers are possible when H_2O stays at the side of the cyano group; i.e., isomers with H_2O at the same and opposite sides of the methyl group. In the third isomer, H_2O stays at the end of the cyano group.

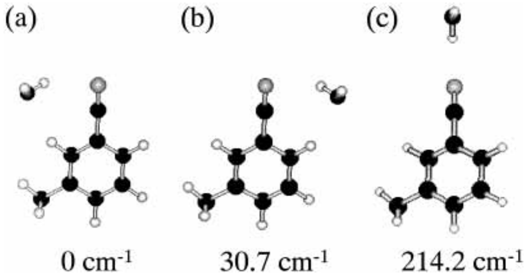

Figure 6. Optimized geometries and their relative energies of the *m*-tolunitrile-H_2O complexes in their S_0 states obtained by the HF/6-31G** method.

These three geometries in their S_0 states were optimized with HF/6-31G** method. The results are shown in Figure 6, where optimized geometries of (a) isomer with H_2O beside cyano group at the same side of the methyl group, (b) isomer with H_2O beside cyano group at the opposite side of the methyl group, and (c) isomer with H_2O at the end of the cyano group are shown with their relative energies. Optimized geometries similar to those shown in Figure 6 were also obtained with the B3LYP/6-31G** and MP2/6-31G* methods, although the relative energies of isomers calculated with these methods differ a little. A geometry in which H_2O stays on the aromatic ring could not be optimized.

Only the isomers with similar stabilities are expected to be observed in the LIF-excitation spectra, since relative intensities of all the bands for the 1:1 complexes do not change by changing the stagnation pressure in the range of 1−3 atm. Therefore, observed complexes are assignable to isomers (a) and (b) in Figure 6, which have comparable energies. Only small amount of Isomer (c) with the appreciably higher energy than isomers (a) and (b) can exist in the supersonic jet.

Correspondence between H_2O complexes (I) and (II), and Isomers (a) and (b) should be discussed next. H_2O Complex (I) and (II) should be assigned to Isomers (b) and (a), since the effect of the complex formation on the methyl torsional potential is assumed to be more serious as the distance between the methyl group and H_2O becomes smaller whether the effect is of steric hindrance or electrostatic. H_2O stays at the opposite side of the methyl group in Complex (I) [Isomer (b)], resulting in a torsional potential similar to that in the monomer. On the other hand, H_2O staying at the near side of the methyl group perturbs and deforms the torsional potential appreciably in Complex (II) [Isomer (a)].

Relative stabilities for the optimized geometries of *m*-tolunitrile-H_2O complexes (I) and (II) in S_1 calculated by CIS/6-31G** method were found to be reversed; Isomer (a) is more stable in S_0, while Isomer (b) is more stable in S_1. The results of calculations indicate that the origin band of isomer (b) appears at lower frequency than that of Isomer (a), and support the assignments of Isomers (b) and (a) to Complexes (I) and (II), respectively, although calculations of geometries and energies of the molecular complexes in their excited electronic states with the simple CIS method are not so reliable as in the ground electronic states.

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