# High-Resolution Laser-Induced Fluorescence Spectra of 7-Azaindole−Water Complexes and 7-Azaindole Dimer

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*Received: May 17, 1996; In Final Form: July 29, 1996*⊗

The geometric structures of 7-azaindole−water complexes, (7-AzI)-$(H_2O)_n$ ($n = 1-3$), and 7-AzI dimer were investigated by laser-induced fluorescence (LIF) spectroscopy with high resolution (∼0.01 $cm^{-1}$). For the 7-AzI−$(H_2O)_n$ complexes ($n = 1-3$), the LIF spectra show partially resolved rotational structure, which has been analyzed in combination with theoretical calculations. This analysis yields the rotational constants and characterizes the structures. In 7-AzI−$(H_2O)_{1,}$ the $H_2O$ molecule is located in the molecular plane, forming a six-membered ring with two hydrogen bonds. Analyses for 7-AzI−$(H_2O)_2$ and −$(H_2O)_3$ show, furthermore, that both the second and the third $H_2O$ are located in the molecular plane of 7-AzI, forming a network ring of hydrogen bonds. For the 7-AzI dimer, the LIF spectrum shows an unresolved rotational envelope. The rotational contour has been analyzed, and we discuss the dimer's likely structure.

## 1. Introduction

Proton-transfer reactions (PTR) in electronic excited states are fundamentally important reactions playing a crucial role in a large variety of photochemical and biological processes.[1−3] Among many molecules undergoing this type of photoreaction, the dimer of 7-azaindole (7-AzI) deserves special attention, because it exhibits a particularly well-documented example of cooperative double PTR in its excited state.[4−15] However, there has been no quantitative study of the structures of the 7-AzI complexes even in the gas phase. The recent development of tunable, ultraviolet, high-resolution dye lasers has opened up a new region of the spectrum to high-resolution studies.[16,17] Using such techniques we have obtained the high-resolution spectrum of the 7-AzI dimer which gives information about its geometric structure. In related work, Held et al.[18] and Berden et al.[19] have investigated recently the geometric structures of complexes between aromatic molecule and waters with fully resolved rotational spectroscopy.

The 7-AzI−$H_2O$ complexes intrigue us from the viewpoint of their geometric structure because of the capability of making a network of hydrogen bonds. Since 7-AzI has both donor and acceptor sites for hydrogen bonding, the geometric arrangements can lead to the formation of cyclic structures and/or open chain structures. In $H_2O$ solution, the tautomerization of 7-AzI has been reported; the visible emission from the tautomer is observed upon the UV excitation of the 7-AzI molecule in $H_2O$ solution.[9,20−26] However, there has been no observation of the tautomerization of the 7-AzI−$H_2O$ complex in the gas phase. In order to elucidate this difference between the bulk and the isolated system, we measured the high-resolution laser-induced fluorescence (LIF) spectra of the 7-AzI−$(H_2O)_n$ complexes ($n = 1-3$) and analyzed their partially resolved rotational structures to determine their geometric structures with the guidance of theoretical calculations.

Moreover, we have determined the absolute direction of the transition dipole moment in the $S_1-S_0$ excitation of 7-AzI. The rotational selection rules are determined by the direction of the transition moment with respect to the inertial axes. For example, certain rotational transitions may be allowed when the transition moment coincides with one of the inertial axes and forbidden when the transition moment is perpendicular to that axis. In an asymmetric molecule like 7-AzI, the transition dipole moment of the $S_1-S_0$ transition is expressed by a mixed A + B type transition,[27] which is believed to be in the plane of the molecule. In our previous work,[28] we have determined the direction of the transition dipole moment of the 7-AzI monomer as tilted by 16° with respect to the *a* axis, but there is still an ambiguity in its direction. In the analysis of the 7-AzI−$H_2O$ complexes, the inertial axes are shifted by the addition of the $H_2O$ molecules, while the direction of the transition dipole moment is unchanged for the localized excitation on the 7-AzI molecule. These observations allow us to determine the direction of the transition dipole moment by comparing its projections along the shifted axes of the complexes.

In this paper, we determined the geometries of the 7-AzI−$(H_2O)_n$ complexes ($n = 1-3$) and the absolute direction of the transition dipole moment of 7-AzI itself. In addition the results for the nonreactive dimer are also presented although there are still some problems with its complete assignment.

## 2. Experimental Section

The supersonic jet apparatus and the laser system used in the present study were similar to those reported previously.[29] The sample of 7-AzI seeded in a He carrier gas (60−100 psi) was expanded into a vacuum chamber through a pulsed valve having a 1 mm diameter orifice. The jet-cooled 7-AzI−$(H_2O)_n$

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.

S1089-5639(96)01441-7 CCC: $14.00

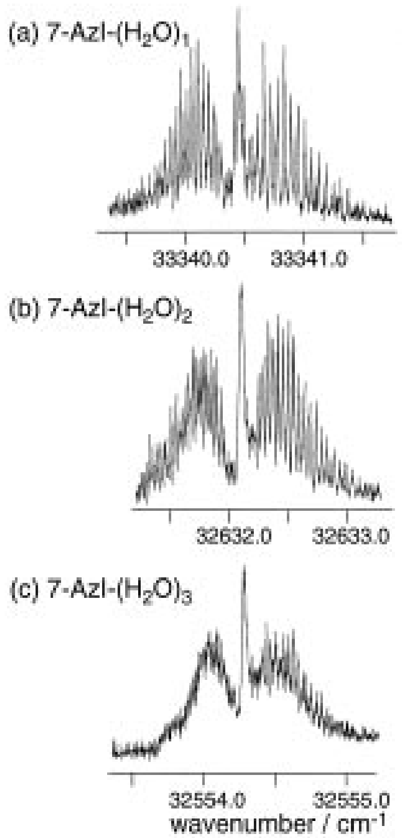


**Figure 1.** Rotationally resolved LIF spectra of the 0−0 band for 7-AzI−$(H_2O)_n$ ($n$ = 1−3) complexes: (a) 7-AzI−$(H_2O)_1$, (b) 7-AzI−$(H_2O)_2$, and (c) 7-AzI−$(H_2O)_3$. The transitions for 7-AzI−$(H_2O)_n$ are red-shifted by 1288, 1997, and 2075 cm$^{-1}$ from the bare 7-AzI 0−0 band, respectively. The spectral line width is about 300 MHz.

complexes and 7-AzI dimer were probed at a point 15−25 mm downstream from the nozzle. The LIF signal was detected with an EMI9659QB photomultiplier tube (PMT). An optical slit was affixed to the front of the PMT so that only fluorescence from the center of the free jet expansion was viewed. This was done to eliminate detection of fluorescence from molecules with off-axis velocity components and thus reduce the Doppler width of the spectral lines.

The probe laser system is a pulse-amplified CW ring dye laser. The dye laser (Coherent 699) was pumped with an argon ion laser (Coherent Innova 200) and operated with either Kiton-Red or R-640 laser dye. The pulse amplifier (Lambda Physik FL 2003) was pumped by the XeCl (308 nm) output of a Lambda Physik EMG 103 MSC excimer laser. The pulse-amplified light was then frequency doubled in a KDP crystal to generate the necessary UV radiation (line width ~300 MHz). Frequency calibration was accomplished with a pulsed wavemeter (Burleigh WA-4500) while an iodine spectrum was simultaneously recorded.

## 3. Computational Methods

The geometrical structures of 7-AzI−$H_2O$ complexes in their ground electronic states were studied by *ab initio* molecular orbital calculations using the self-consistent field (SCF) method, with a 6-31G basis set. The programs used were Gaussian 92[30] and Gaussian 94.[31] All of the computations were carried out on the YHP735 computers of our laboratory and of the computer center in the Institute for Molecular Science (IMS). The geometries of all the complexes were optimized by using the energy gradient method. The details of the calculations will be published elsewhere.[32]

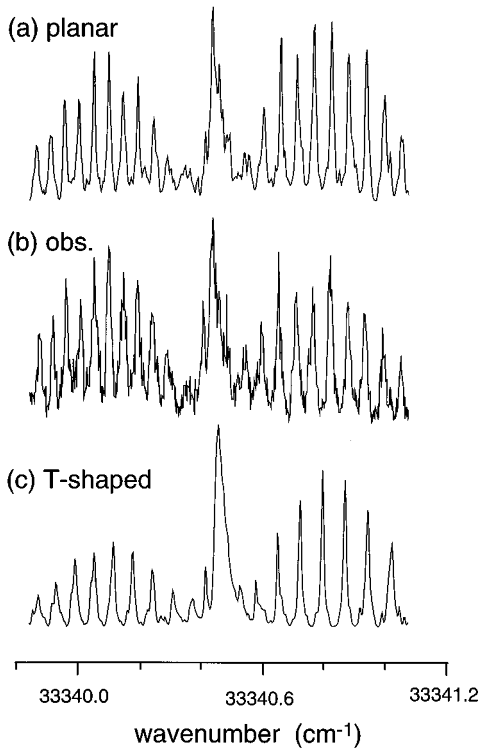
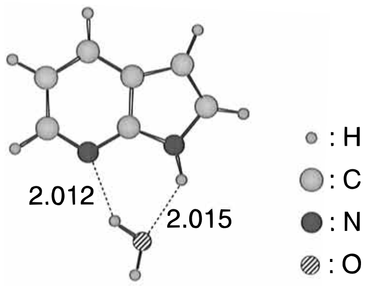


**Figure 2.** Rotationally resolved LIF spectrum of the 7-AzI−$(H_2O)_1$ complex: (a) simulation assuming a planar structure, (b) observed spectrum, and (c) simulation assuming a T-shaped structure. The assumed structures are shown in Figure 3. The observed spectrum was reproduced only by the planar structure, and the rotational constants used for the simulation are listed in Table 1.

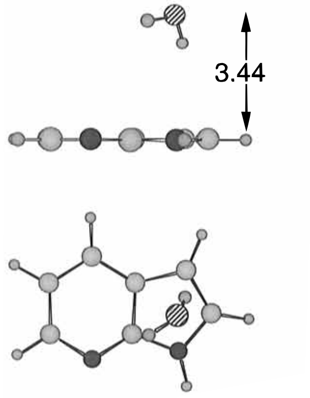
## 4. Results and Discussion

*4.1. 7-AzI−$(H_2O)_n$ Complexes.* Figure 1 shows the rotationally resolved LIF spectra of the 0−0 band for 7-AzI−$(H_2O)_n$ ($n$ = 1−3). Since the probe laser resolution of ~0.01 cm$^{-1}$ was insufficient to obtain the fully resolved rotational structure, the peaks observed in the spectra are different K subbands and progressions having different *J* values remain unresolved. The 0−0 band of 7-AzI−$(H_2O)_1$ is located at 33 340.4 cm$^{-1}$ in vacuum, red-shifted by 1288 cm$^{-1}$ from the 0−0 transition of bare 7-AzI, as reported previously.[11,33] As shown in the figure, the 0−0 band of 7-AzI−$(H_2O)_2$, located at 32 632.1 cm$^{-1}$ in vacuum, is further red-shifted by 708 cm$^{-1}$ compared to that of 7-AzI−$(H_2O)_1$. However, the 0−0 band of 7-AzI−$(H_2O)_3$, located at 32 554.3 cm$^{-1}$ in vacuum, is only red-shifted by 78 cm$^{-1}$ compared to that of 7-AzI−$(H_2O)_2$. The red shifts of the 0−0 bands of the complexes should be rationalized through the characteristics of their geometries. Presumably both the first and the second $H_2O$ are each attached to a sensitive site to induce a considerable red shift of the electronic transition, whereas the third $H_2O$ is not attached to such a site, giving a relatively small red shift.

*4.1.a. 7-AzI−$(H_2O)_1$.* Figure 2 shows the rotationally resolved LIF spectrum of the 7-AzI−$(H_2O)_1$ complex: (a) simulation assuming a planar structure, (b) observed spectrum, and (c) simulation assuming a T-shaped structure. In the simulation, the structure of 7-AzI was reasonably assumed to be the same as that obtained for the bare 7-AzI. Since higher rotational quantum levels are slightly overpopulated, as is often observed in the supersonic free jet expansion experiments, the rotational distributions were reproduced by a double-Boltzmann distribution. Two rotational temperatures employed were 1.8 ± 0.3 K and 3.0 ± 1 K, with the relative weights of the components being 0.8 and 0.2, respectively. Motivated in part



(a) planar



(b) T–shaped

**Figure 3.** Optimized geometries of the 7-AzI−$(H_2O)_1$ complex in the ground state from an *ab initio* calculation (basis set 6-31G): (a) a planar structure and (b) a T-shaped structure with side and top views. The planar structure of (a) is 40 kJ/mol more stable than the T-shaped one. The lengths of the hydrogen bonds are shown in angstroms.

**TABLE 1: Rotational Constants of 7-Azaindole−$(H_2O)_n$ ($n$ = 0−3) in $cm^{-1}$ (See Text for Details of the Fits)**

| | ground state ($S_0$) | | excited state ($S_1$) |
|---|---|---|---|
| | expt[a] | calcd[b] | expt[c] |
| | (a) 7-AzI monomer[d] | | |
| A | 0.13082(5) | 0.13149 | 0.12468(5) |
| B | 0.05677(2) | 0.05611 | 0.05675(2) |
| C | 0.03970(1) | 0.03933 | 0.03911(1) |
| | (b) 7-AzI−$(H_2O)_1$ [d] | | |
| A | 0.0596(1) | 0.05961 | 0.06051(2) |
| B | 0.0452(2) | 0.04523 | 0.04621(2) |
| C | 0.02572(5) | 0.02572 | 0.02595(1) |
| | (c) 7-AzI−$(H_2O)_2$ [d] | | |
| A | 0.0477(1) | 0.04779 | 0.04822(2) |
| B | 0.0279(2) | 0.02789 | 0.02881(2) |
| C | 0.0177(1) | 0.01770 | 0.01810(1) |
| | (d) 7-AzI−$(H_2O)_3$ [d] | | |
| A | 0.0385(2) | 0.0385 | 0.0388(5) |
| B | 0.0181(3) | 0.0181 | 0.0184(7) |
| C | 0.0126(1) | 0.0126 | 0.0129(4) |

[a] The rotational constants in the ground state for 7-AzI−$(H_2O)_n$ ($n$ = 1−3) were fixed at the *ab initio* values to determine the rotational constants in the excited state [b] The rotational constants derived from the theoretical calculation with a SCF/6-31G basis set. [c] For 7-AzI−$(H_2O)_n$ ($n$ = 1−3), the rotational constants of the excited state were derived from the simulation by fixing the rotational constants in the ground state at the values obtained from the *ab initio* calculation. [d] The mixing ratios between A- and B-type transitions are A:B = 78(5):22(5) for 7-AzI, 59(5):41(5) for 7-AzI−$(H_2O)_1$, 54(5):46(5) for 7-AzI−$(H_2O)_2$, and 50(4):50(4) for 7-AzI−$(H_2O)_3$.

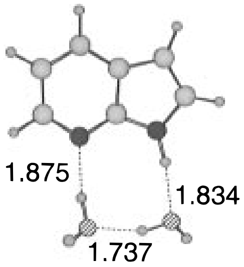
by the previous studies, we have considered the two structures shown in Figure 3. Since 7-AzI possesses both proton donor (N−H bond) and proton acceptor (N atom) sites, the planar structure is formed via two hydrogen bonds: one is between the N−H of 7-AzI and the O atom of $H_2O$, and the other is between the N atom of 7-AzI and the H−O of $H_2O$. A structure similar to this has been reported in a study of phenol−$H_2O$ complexes.[34,35] In the phenol−$H_2O$ complexes, the hydrogen bonding network is crucial for their formation. The T-shaped structure, on the other hand, is formed by the interaction between the H atom in $H_2O$ and a $\pi$ electron in the aromatic ring of 7-AzI. A similar structure has been reported in a study of benzene−$H_2O$.[36]

As shown in the simulation, the simulated spectrum of the T-shaped structure has a much wider spacing of the peaks compared to the observed spectrum, and the observed spectrum was best reproduced by the planar structure. However, the position of the $H_2O$ was somewhat ambiguous within an uncertainty of 0.2 Å, because the rotational structure was only partially resolved with a line width of ~300 MHz, and because it is possible to reproduce the observed spectrum by the adjustment of the other three rotational constants in the electronic excited state.

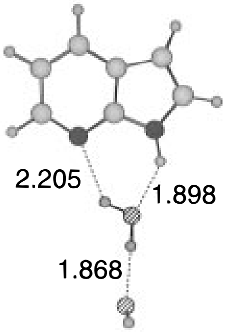
In order to substantiate the planar structure, *ab initio* calculations were performed. Figure 3 shows the optimized structures for 7-AzI−$(H_2O)_1$. Two structures are calculated to be stable isomers: the planar structure, having two hydrogen bonds, is 40 kJ/mol more stable than the T-shaped structure. Since the optimized planar structure is in good agreement with the structure from the rotational analysis, the ground state structure for 7-AzI−$(H_2O)_1$ was fixed at the *ab initio* values to determine the rotational constants in the excited state, which are listed in Table 1. By comparing the rotational constants of the ground and excited states, it can be seen that the $H_2O$ is closer to the 7-AzI molecule by ~0.1 Å in the excited state. In fact, hydrogen bonds usually become stronger in electronically excited states; the hydrogen bond length becomes shorter upon the electronic excitation by 0.08−0.1 Å in 2-pyridone−$H_2O$ [18] and by 0.04 Å in phenol−$H_2O$.[19]

The PTR has been observed and extensively studied in bulk solution: the visible emission, observed upon the UV excitation of the 7-AzI in $H_2O$ solution, is ascribed to the tautomer.[9,20−26] In these studies a 1 to 1 complex has been proposed to be responsible for the tautomerization, because it seems unlikely that multiple PTRs take place simultaneously in the 7-AzI−$(H_2O)_n$ ($n \geq 2$) complexes. In the gas phase, there has been no direct observation of the PTR. On the basis of the structure of the 7-AzI−$(H_2O)_1$ complex (Figure 3a), the PTR seemingly requires considerable rearrangement of the nuclei around the $H_2O$ molecule, because the shape of the $H_2O$ resulting from the tautomerization would become very strained without such a rearrangement. Therefore, this work on the structure of the 7-AzI−$(H_2O)_1$ complex suggests that the complex in solution takes a slightly different structure, stabilized by surrounding $H_2O$ molecules, resulting in the lowering of the activation energy for the PTR.

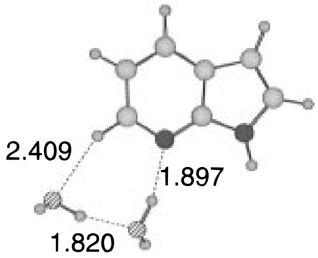
*4.1.b. 7-AzI−$(H_2O)_2$.* Before performing the spectral simulation for 7-AzI−$(H_2O)_2$, a theoretical calculation was done to pick some candidates for the most stable structure. Figure 4 shows optimized geometries for the 7-AzI−$(H_2O)_2$ complex in the ground state from an *ab initio* calculation (SCF/6-31G): (a) planar eight-membered ring structure, (b) planar six-membered ring structure, and (c) planar seven-membered ring structure. In the structure of Figure 4a, one $H_2O$ molecule is attached to the proton donor (N−H) and the other to the proton acceptor



(a) planar 8-membered ring



(b) planar 6-membered ring



(c) planar 7-membered ring

**Figure 4.** Optimized geometries of the 7-AzI−$(H_2O)_2$ complex in the ground state from an *ab initio* calculation (basis set 6-31G): (a) a planar eight-membered ring, (b) a planar six-membered ring, and (c) a planar seven-membered ring. Among the isomers, the complex of (a) having the eight-membered ring is the most stable by 33 kJ/mol. The lengths of the hydrogen bonds are shown in angstroms.

(N atom) sites. Structure b consists of the stable 7-AzI−$(H_2O)_1$ and another $H_2O$ molecule. The second $H_2O$ extends the molecular plane longitudinally so that the rotational constants of (b) are quite different from those of the other two isomers (a) and (c) which are nearly indistinguishable experimentally. Among the isomers, the complex having the eight-membered ring of (a) is calculated to be the most stable, 33 kJ/mol below the others.

Figure 5 shows the rotationally resolved LIF spectrum of the 7-AzI−$(H_2O)_2$ complex (Figure 5b), in addition to two calculated spectra, assuming (a) the planar eight-membered ring structure and (c) the planar six-membered ring structure. The observed spectrum was reasonably reproduced by the planar eight-membered ring structure of Figure 5a. Rotational constants used for the simulation are listed in Table 1. All of the rotational constants in the electronic excited state increase compared to those of the ground state, and the change in the rotational constants indicates that the $H_2O$ molecules move closer to the 7-AzI molecule upon electronic excitation due to the increase in hydrogen bond strength, similar to 7-AzI−$(H_2O)_1$.

*4.1.c. The Direction of the Transition Dipole Moment.* The rotational structures of 7-AzI−$(H_2O)_1$ and 7-AzI−$(H_2O)_2$, measured with high resolution, enable us to determine the direction of the transition dipole moment. The transition dipole moment of 7-AzI, lying in the molecular plane, gives rise to a mixed A- and B-type transition because it is an asymmetric molecule. As reported previously, the transition dipole moment has been determined to be 16 ± 5° with respect to the *a* axis, but the sign of the angle was not given by the analysis on the monomer. There is an ambiguity between the directions indicated by the **P** and **Q** vectors shown in Figure 6a.[28]

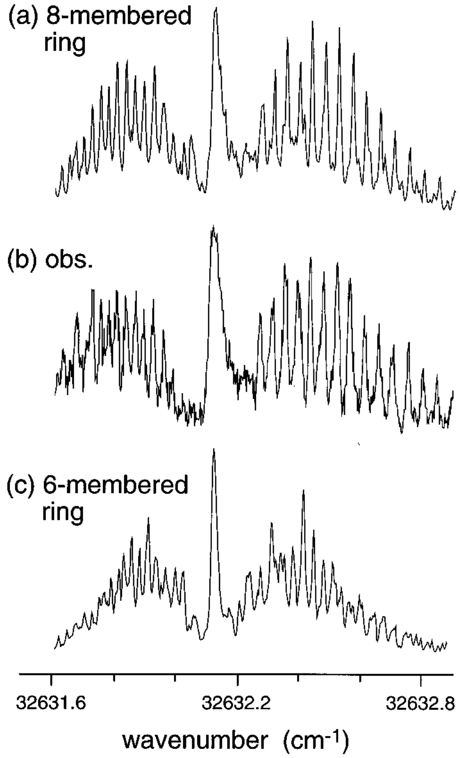
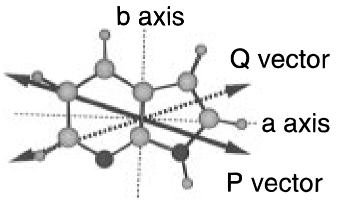


**Figure 5.** Rotationally resolved LIF spectrum of 7-AzI−$(H_2O)_2$ complex: (a) simulation assuming a planar eight-membered ring structure, (b) observed spectrum, and (c) simulation assuming a planar six-membered ring structure. The assumed structures are shown in Figure 4, and the observed spectrum was reasonably well reproduced by the planar eight-membered ring structure. Rotational constants used for the simulation are listed in Table 1.

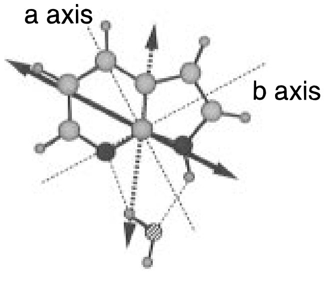
However, the sign of the angle can be determined by the analysis of the rotational structure of 7-AzI−$H_2O$ complexes. Although the inertial axes vary with the $H_2O$ addition to the 7-AzI molecule, the direction of the transition dipole moment is expected to be unchanged with respect to the 7-AzI molecule, because the electronic transition of the 7-AzI−$H_2O$ complex is a local excitation in the 7-AzI molecule. Figure 6 shows the two directions of the transition dipole moment given by the mixing ratio of A- and B-type transitions in the simulation for 7-AzI−$(H_2O)_n$ ($n$ = 0−2): A:B = 59(5):41(5) for 7-AzI−$(H_2O)_1$ and A:B = 54(5):46(5) for 7-AzI−$(H_2O)_2$. Comparing the results, the direction is reasonably determined as that indicated by the **P** vector because its orientation is essentially unshifted for all three molecules.

*4.1.d. 7-AzI−$(H_2O)_3$.* Figure 7 shows optimized geometries for the 7-AzI−$(H_2O)_3$ complex in the ground state from *ab initio* calculation (SCF/6-31G): (a) a planar ten-membered ring structure, (b) a planar eight-membered and seven-membered ring structure, and (c) a planar eight-membered ring structure. Among the isomers, the complex having the 10-membered ring of (a) is the most stable compared to (b) and (c). The isomers of 7b and 7c are 14.1 and 24.6 kJ/mol in energy above 7a, respectively.

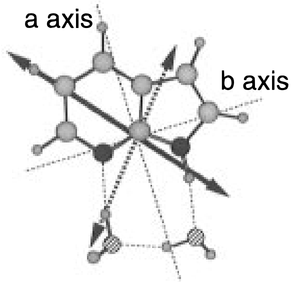
Figure 8 shows (a) a rotationally resolved LIF spectrum of the 7-AzI−$(H_2O)_3$ complex along with (b) the simulated



(a) 7-AzI



(b) 7-AzI-$(H_2O)_1$



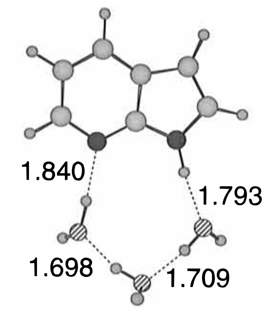
(c) 7-AzI-$(H_2O)_2$

**Figure 6.** Two directions of the transition dipole moment given by the mixing ratio of A- and B-type transitions in the simulation for 7-AzI−$(H_2O)_n$ ($n = 0-2$). Although two possibilities for the direction are allowed for each case, the direction is determined to be that of the **P** vector because the direction of the transition dipole moment in the local excitation should be unchanged with respect to the 7-AzI molecule.

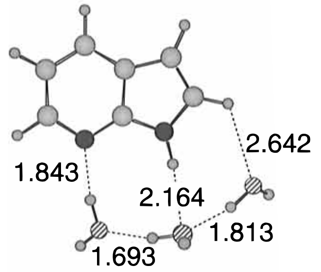
spectrum assuming the most stable planar 10-membered ring structure. Although the simulation of the observed LIF spectrum does not definitely exclude the possibilities of another structure, the observed spectrum is reasonably well reproduced by the planar 10-membered ring structure. Rotational constants used for the simulation are listed in Table 1. As observed in a recent IR depletion spectroscopy experiment on 7-AzI−$(H_2O)_3$,[37] there are no absorption bands from 3400 to 3700 cm$^{-1}$, the so-called "window region" of the O−H stretch in $H_2O$.[34] This would suggest that all of the $H_2O$ molecules are bonded, forming one network ring of hydrogen bonds.

As mentioned in the preceding section, the amount of red shift in the electronic transition is sensitive to the geometry. These results indicate that the third $H_2O$ molecule is attached to neither the proton donor nor the acceptor sites of 7-AzI, as shown in Figure 7a. Since the electronic transition is attributed to the local excitation of the 7-AzI molecule, it is natural that the origin band of 7-AzI−$(H_2O)_3$ should be close to that of 7-AzI−$(H_2O)_2$. The shifts of the origin bands of 7-AzI−$(H_2O)_n$ complexes can be rationalized in this way.

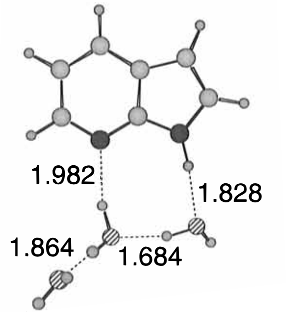
*4.2. 7-AzI Nonreactive Dimer.* As reported previously, there are two isomers of the 7-AzI dimer: a reactive dimer and a nonreactive dimer.[11,12] The reactive dimer has two equivalent hydrogen bonds, exhibiting a tautomerization reaction with a PTR through electronic excitation. In contrast, the nonreactive 7-AzI dimer does not exhibit the PTR, in other words, it does not undergo the tautomerization reaction even after the electronic excitation. Although the structure of the reactive dimer is clear from several investigations, that of the nonreactive dimer is still unclear. In previous work,[28] the rotational envelope (from the LIF spectrum with a low resolution of ~0.6 cm$^{-1}$) of what was reported as the nonreactive dimer's 0−0 band was qualitatively analyzed, and three candidates for the structure of the nonreactive dimer were proposed: single bonded, T-shaped, and nonplanar.



(a) 10-membered ring



(b) 7-8-membered ring



(c) 8-membered ring

**Figure 7.** Optimized geometries of the 7-AzI−$(H_2O)_3$ complex in the ground state from an *ab initio* calculation (basis set 6-31G): (a) a planar ten-membered ring, (b) planar eight-membered and seven-membered rings, and (c) a planar eight-membered ring. Among the isomers, the complex of (a) having the 10-membered ring is the most stable. The lengths of the hydrogen bonds are shown in angstroms.

Figure 9 shows the LIF spectrum obtained in the present study with a higher resolution of ~0.01 cm$^{-1}$. The 0−0 band is located at 32 290.8 cm$^{-1}$ in vacuum, which is consistent with our previous work. Now, if it is assumed that the carrier of the spectrum is a simple 7-AzI dimer, simulations of the proposed structures can be compared to the LIF spectrum. Although the rotational structure remains very congested even with the laser resolution of ~0.01 cm$^{-1}$, the more detailed rotational contour enables us to deduce the structure more clearly than before. Among the three candidates the T-shaped structure gives the best match to the features in the observed spectrum. A simulation, assuming the T-shaped geometry, is also shown in Figure 9. In the simulation, the direction of the transition dipole moment was fixed in one 7-AzI molecule of the dimer, and the mixing ratio of A-type, B-type, and C-type transition was

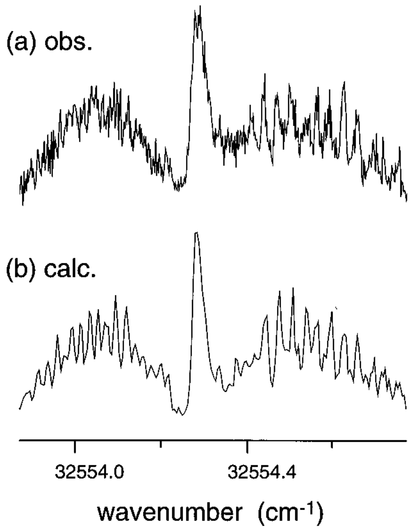


**Figure 8.** Rotationally resolved LIF spectrum of 7-AzI−$(H_2O)_3$ complex: (a) observed spectrum and (b) simulation assuming a planar 10-membered ring structure. The observed spectrum was reasonably well reproduced by the planar 10-membered ring structure. Rotational constants used for the simulation are listed in Table 1.

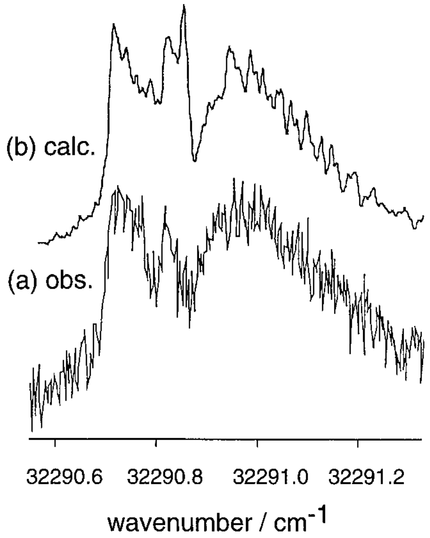


**Figure 9.** LIF spectrum of 7-AzI dimer: (a) observed spectrum and (b) simulation assuming a T-shaped structure.

obtained from its projections upon the inertial axes. This is justified because the electronic excitation can be understood as being localized on a single molecule.

Despite the reasonable agreement between the simulation assuming a T-shaped dimer geometry and the observed rotational contour, there is still some uncertainty, for several reasons, as to the actual carrier of the spectrum. Experimentally, the very hygroscopic nature of the parent 7-AzI means the $H_2O$ can never be totally excluded from the sample. Indeed our reported spectra of $n = 1$ and 2 $H_2O$ clusters were obtained without the further addition of water while the $n = 3$ cluster required it. There is also the question of why the red shift of the nonreactive dimer ($\sim$2300 $cm^{-1}$) is almost the same as that of the reactive dimer having two equivalent hydrogen bonds. In very recent work,[37] the infrared (IR) absorption of what is thought to be the nonreactive 7-AzI dimer by IR depletion spectroscopy demonstrated there was a strong absorption at 3704.7 $cm^{-1}$. In the IR depletion experiment, the mass-selected ion current corresponding to 7-AzI dimer cation was monitored. Prior to the photoionization event, an IR probe laser irradiated the sample. The resulting IR absorption, which is quite near the window region of the O−H stretch in $H_2O$, indicates that the species may contain an $H_2O$ molecule. However, this experiment is also consistent with an $H_2O$-containing species dissociating into the dimer cation in the ionization process with little excess energy while the dimer cation is inaccessible directly from the corresponding neutral due to Franck−Condon considerations. Our LIF spectrum cannot rule out the possibility that the species contains $H_2O$ because of the congestion of the spectrum.

## 5. Conclusions

The electronic spectra of the 7-AzI−$(H_2O)_n$, $n = 1-3$, complexes and the nonreactive 7-AzI dimer have been observed with high-resolution electronic spectroscopy. Rotational analysis of each of these spectra have been performed as well as *ab initio* calculations for several possible ground state structures. The complex 7-AzI−$(H_2O)_1$ is found to have a planar structure, which however is incompatible with a PTR without considerable nuclear rearrangement. The 7-AzI−$(H_2O)_n$ complexes for both $n = 2$ and 3 likewise have planar structures, with water and the 7-AzI forming eight- and ten-membered ring structures, respectively. The analysis of the 7-AzI−$(H_2O)_n$ spectra also allows the determination of the direction of the transition dipole moment of 7-AzI itself as shown in Figure 6. The analysis of the spectrum of the nonreactive dimer of 7-AzI is not so definitive as those for the water complexes. Although the obtained spectrum of the nonreactive dimer can seemingly be reproduced assuming T-shaped geometry, the species may contain an $H_2O$ molecule as indicated by the IR absorption. Clearly further experiments are necessary to fully elucidate the composition of this species.

**Acknowledgment.** We are very grateful to Prof. Suehiro Iwata (Institute for Molecular Science) for fruitful discussion. We are also grateful to Prof. M. Fujii and Mr. T. Omi (Waseda University) for providing data on IR absorption of the 7-AzI complexes prior to publication. One of the authors (H.W.) wishes to thank the Japan Society for the Promotion of Science for Young Scientists for providing the research fellowships. This work is partially supported by a grant-in-aid for scientific research on priority areas from the Ministry of Education, Science and Culture. The work at Ohio State has been supported by the National Science Foundation via Grant 9320909.

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