SPECTROSCOPIC STUDY OF HYDROGEN BONDED 7-AZAINDOLE CLUSTERS

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The geometric structures of 7-azaindole (7-AzI) and its dimer were investigated by laser-induced fluorescence (LIF). The rotationally resolved LIF spectrum (resolution: $\sim 0.00003\text{ cm}^{-1}$ of 7-AzI monomer shows that (i) rotational constants are $A'' = 0.13082(5)$, $B'' = 0.05677(2)$, $C'' = 0.03970(1)$, $A' = 0.12468(5)$, $B' = 0.056752(2)$, and $C' = 0.03911(1)$, and (ii) the transition dipole moment direction is tilted at an angle of $\pm 21(5)$ degrees with respect to a axis. The LIF spectrum (resolution: $\sim 0.06\text{ cm}^{-1}$) of the non-reactive 7-AzI dimer suggests there are three possibilities for the geometric structure, having "single bonded", "T-shaped", and "non-planar" structures.

The ionization energy of 7-AzI was determined to be $8.1171(5)\text{ eV}$ by using pulsed-field ionization photoelectron spectroscopy (PFI-PES). Several vibronic bands of 7-AzI cation were observed and compared with those of neutral 7-AzI in the S_0 and S_1 states. The electron binding energies of 7-AzI cluster anions ($2 \leq n \leq 5$) were determined by photoelectron spectroscopy.

KEY WORDS: Laser-induced fluorescence, Rotational constant, Pulsed-field ionization, Photoelectron spectroscopy, 7-azaindole, 7-azaindole cluster

1. INTRODUCTION

Proton-transfer reactions (PTR) are fundamentally important reactions playing a crucial role in a large variety of chemical and biological processes.¹⁻³ Among many molecules undergoing this type of photoreaction, a dimer of 7-azaindole (7-AzI) deserves particular attention, because it exhibits a particularly well-documented example of cooperative double PTR in its excited state.⁴⁻¹² However, there has been no quantitative study about the structure of 7-AzI and its dimer in the gas phase. The recent development of tunable, ultraviolet, high resolution dye lasers that are

commercially available has opened up a new region of the spectrum to high resolution studies.^{13,14}

The rotational structure measured with a high-resolution dye laser enables us to determine the direction of the transition dipole moment and rotational constants giving information about geometric structure. 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 7-AzI the transition dipole moment of S_1 - S_0 transition is believed to be in the plane of the molecule, and therefore the transition of interest is a mixed A + B type transition.¹⁵ If the A-type features can be separated from the B-type features, their relative intensity provides a measure of the direction of the transition dipole moment.

7-AzI clusters, furthermore, intrigue us from the viewpoint of their geometric structure because it is capable of self-associating through 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 this paper we report the structures of 7-AzI and its dimer and the vibronic structure of its cation. We observed and analyzed the rotational structure in the cold gas phase spectrum of 7-AzI to obtain accurate rotational constants and the orientation of the transition dipole moment. Moreover, we measured the rotational contours of non-reactive 7-AzI dimer with a resolution of ~ 0.06 cm⁻¹ in order to determine the structure of the dimer which does not exhibit the PTR in the electronic excitation. In addition to these studies, we measured the ionization energy (E_i) of 7-AzI and the vibronic structures in its cation by using a pulsed field ionization ZEKE method.¹⁶⁻²⁰ Furthermore, photoelectron spectroscopy of 7-AzI cluster anions was also performed to investigate geometries of large 7-AzI clusters.

2. EXPERIMENTAL

2.1. LIF Spectrum Measurement

The supersonic jet apparatus used in the present study was similar to that reported previously.^{11,21} The sample seeded in a He carrier gas was expanded into a vacuum chamber. The jet cooled molecules were probed at a point of 10–15 mm downstream from the nozzle by laser-induced fluorescence (LIF). The output of a pulsed dye laser pumped by a XeCl excimer laser (Lambda Physik FL3002E/LPX105i) was frequency-doubled to obtain ~ 300 nm radiation and the dye used was R-610. The line widths were 0.3 cm⁻¹ and 0.06 cm⁻¹ without and with an intra-cavity etalon. The fluorescence, collected through a lens, was detected by a photomultiplier (Hamamatsu R562). The signal from the photomultiplier was fed into a preamplifier and processed by a boxcar integrator (Stanford Research Systems, SR250).

For the measurement of a rotationally resolved LIF spectrum of the 7-AzI monomer, a single-mode tunable dye laser (Coherent 699-29, linewidth 1 MHz) was used with R6G dye, and its second harmonics was obtained in a KDP crystal.²² The

excitation laser light was crossed at right angles to the pulsed molecular beam. The fluorescence was collected by lenses and a concave mirror, and detected by a photomultiplier (Hamamatsu, R943-02). The photocurrent was amplified and counted by a photon counter (Hamamatsu C767) with a ~ 2 ms gate duration, and processed with a microcomputer. The ambient pressure was 1×10^{-5} Torr and the repetition rate was typically 25 Hz.

2.2. Pulsed Field Ionization ZEKE Measurements

Figure 1 shows a schematic diagram of the apparatus, consisting of a pulsed beam source and an ionization chamber equipped with electron optics.²³ The sample seeded in He carrier gas was expanded into the vacuum chamber from a pulsed valve (General Valve, 400 μm diameter). The jet-cooled molecule was introduced into the second chamber through a skimmer, and was excited to a vibronic level in the S_1 state by the second harmonics of the output of a dye laser excited by a Nd³⁺:YAG laser (Quanta-Ray, GCR-12 & PDL-2). Subsequently, the molecule in the S_1 state was excited to a Rydberg state by a second dye laser pumped by a Nd³⁺:YAG laser (Quanta-Ray, GCR-3 & PDL-3). At 2 μs after the laser excitation, negative voltage was applied to a repeller plate to generate an electric field of ~ 1 V/cm. Thus, the molecules in the high Rydberg state were ionized by field ionization, and the ejected photoelectrons were accelerated towards the electron optics. The photoelectrons were

Figure 1 A schematic diagram of the apparatus, consisting of a pulsed beam source and an ionization chamber equipped with electron optics

detected by a microchannel plate (Hamamatsu, F2221-21S). The electron optics consist of a series of electron lenses and an einzel lens to condense the electron trajectory, and provided a signal intensity increment of a factor of ~ 30 .²³ The signal from the microchannel plate was fed into a preamplifier and processed by a boxcar integrator (Stanford Research Systems, SR250). The intensity was measured against the wavelength of the exciting dye laser to the Rydberg states and was recorded in a microcomputer (NEC, PC-9801DA) via a computer interface module (Stanford Research Systems, SR245).

2.3. Photoelectron Spectroscopy of Anions

The details of the experimental setup have been provided elsewhere.²⁴ Briefly, the apparatus consists of a pulsed cluster anion source, a time-of-flight (TOF) mass spectrometer, and a magnetic bottle TOF spectrometer. 7-AzI cluster anions were formed by injecting electrons into a supersonic jet of 7-AzI, where the total stagnation pressure is ~ 10 atmospheres. The electrons were produced by focusing the second harmonics of a Nd³⁺:YAG laser (Quanta-Ray, GCR-12) gently onto a Y₂O₃ disk surface located at ~ 4 mm downstream from a pulsed valve (400 μ m diameter). Molecules in the beam were translationally cooled down to at least ~ 30 K, estimated by multi-photon ionization for other aromatic molecules.²⁵ The cluster anions were coaxially extracted by applying a pulsed electric field (~ 900 eV). After a 1.5-m flight path, the cluster anions were mass-selected by their TOF and the target cluster anion was selected by pulsed deflection plates, and was decelerated to an energy of 20–50 eV by a potential elevator located in front of the magnetic bottle TOF spectrometer. The decelerated cluster anion was allowed to enter a photodetachment region, and the kinetic energy of electrons photo-detached by the fourth harmonics (532 nm, 2.33 eV) of the other Nd³⁺:YAG laser (Quanta-Ray, GCR-3) was analyzed by their TOF. The photoelectrons were created in a strong inhomogeneous field (~ 1000 G), which was generated by a small cylindrical permanent magnet, and were guided by weak magnetic fields (~ 10 G) through a 70-cm drift tube. The photoelectrons were detected by a dual micro-channel plate (Hamamatsu) and the signal was accumulated into a multi-channel scaler/averager (Stanford Research Systems, SR430) after amplification. Energy calibration was performed by measuring the photoelectron spectra of monomer anions of noble metals. The obtained energy resolution was ~ 80 meV (fwhm) at 1-eV electron energy. Each spectrum was accumulated for 10000–20000 laser shots.

3. RESULTS & DISCUSSION

3.1. The structure of 7-AzI monomer

Figure 2 shows the rotationally resolved LIF spectrum of 7-AzI monomer, with the calculated A-type and B-type spectra. Although the cooling in a supersonic expansion greatly simplifies the rotational structure compared to the static gas at ambient temperature, the rotational structure is still quite complicated due to a large molecule

Figure 2. The rotationally resolved LIF spectrum of 7-AzI monomer, in addition to calculated (2) A-type and (3) B-type spectra. Rotational constants used for the simulation are listed in table 1.

of 7-AzI. The analysis of the spectrum presents some difficulties, because the rotational structure depends on many parameters: six rotational constants (three for each electronic state involved in the transition), the rotational population distribution, frequently described by dual temperatures, the direction of the transition dipole moment with respect to the inertial axes, and the line width.

At first, the rotational constants, A'' , B'' , and C'' , in the ground state were approximately obtained from the geometry of 7-AzI optimized with *ab initio* SCF MO method. The program used is GAMESS (North Dakota State University version) and the computers are KUBOTA MIPS-RS3330, where the basis set is STO-6G. With the energy-gradient technique for the closed shell SCF wavefunction, the geometry of 7-AzI is fully optimized without any symmetry constraint. Next, approximate values of $((B' + C' - (B'' + C'')))$ and $(A' - A'')$ were obtained from the analysis of the spectral features; (i) Q branch has red-shaded structures with both J and K values, and (ii) an interval in the progressions of P branch becomes large with J values, while that in the progressions of R branch becomes small. On the basis of these approximate values, rotational constants both in the ground and excited states were determined by least square fit procedure for asymmetric top molecules. The obtained rotational constants (A, B, C) in the ground and excited states are tabulated in Table I. As listed in the table, all of the rotational constants decrease by going from S_0 to S_1 . This implicates that the six- and five-membered rings of 7-AzI in S_1 are slightly expanded compared to that in S_0 . These conclusions are expected ones from the typical π - π^* excitation of benzene derivatives, and probably correspond to a general loosening of the electronic structure on excitation, reflecting the anti-bonding character of the π^* orbitals.²⁶

Table I Calculated and experimental rotational constants of 7-azaindole in cm^{-1} . The other parameters in the calculation were two temperatures of 2 ± 0.3 K and 5 ± 1 K, where the former component was $85 \pm 3\%$.

	Ground state (S_0)		Excited state (S_1)
	cal. ^{a)}	exp.	exp.
A	0.12846	0.13082(5)	0.12468(5)
B	0.05297	0.05677(2)	0.05675(2)
C	0.03750	0.03970(1)	0.03911(1)

a) calculated rotational constants were derived from the geometry of 7-AzI optimized and *ab initio* SCF MO method, where the basis set is STO-6G.

The transition moment was assumed to lie in the plane of the 7-AzI giving rise to a mixed A- and B-type transition. Figure 3 shows an expanded view of the spectrum in the region from 0 to $+0.25 \text{ cm}^{-1}$, because the relative intensities of the Q branch region to the low frequency region of the R branch are sensitive to the mixture of A- and B-type transitions. As shown in fig. 3, the main features consist of A-type transition, but weak components attributed to B-type transition exist, as being labelled by asterisks. From the relative intensities in the spectrum, the mag-

Figure 3 An expanded view of the spectra in the range from 0 to +0.25 cm^{-1} ; (1) observed, (2) calculated A-type, and (3) calculated B-type spectra. Rotational constants used for the simulation are listed in table I. Although the main features consist of A-type transition, several rotational lines attributed to B-type transition also exist. Some of them are labelled by asterisks (*).

nitude of the A- and B-components of the transition moment was determined. This gives the angle of the transition dipole moment with respect to the a axis, but not the sign of the angle. As shown in fig. 4, the transition dipole moment was determined to be 21 ± 5 degrees with respect to the a axis, giving 78(5)% A-type and 22(5)% B-type, although there are two choices of transition moment direction (P and Q vectors). J. Catalan and P. Perez have calculated the direction of the transition dipole moment by using a CNDO/S method,¹⁵ and they have concluded that the transition moment is 7.5 degrees with respect to the a axis and is tilted to the side of the Q vector.

3.2. The structure of 7-AzI dimer

As reported previously, there are two isomers of the 7-AzI dimer: a reactive dimer and a non-reactive dimer (see figure 5).¹² The reactive 7-AzI dimer has two hydrogen

Figure 4 Two possible transition moments in 7-azaindole. The transition dipole moment was determined to be 21 ± 5 degrees with respect to the *a* axis and there are two choices of transition dipole moment direction (P and Q vectors).

bonds (fig. 5a), forming a tautomer with a proton transfer by electronic excitation. On the other hand, the non-reactive 7-AzI dimer does not exhibit the proton transfer reaction, in other words, does not form the tautomer even after electronic excitation. The structure of the non-reactive dimer has been suggested; stacked (fig. 5b-1),²⁷ single-bonded (fig. 5b-2), T-shaped (fig. 5b-3), and non-planar structure (fig. 5b-4).

Figure 6 shows the LIF spectrum of the non-reactive 7-AzI dimer with resolution of ~ 0.06 cm^{-1} , together with simulated spectra. Even though the resolution was insufficient to resolve rotational structure in the band, a simulation for the experimental envelope gives qualitative information. When we tried to simulate the experimental envelope by assuming the stacked structure (fig. 5b-1), the sharp rise in the red side could not be reproduced. The envelope was almost reproduced by assuming a B-type transition in the other three structures, as shown in fig. 6. Thus the structure of the non-reactive dimer can be figured out as one of three possible structures (figs. 5b-2, 5b-3, and 5b-4). The measurement of the high-resolution LIF spectrum of the non-reactive dimer is in progress.

3.3. The vibronic structure of 7-AzI cation

Figure 7a and 7b show the PFI spectra of jet-cooled 7-AzI via two different vibronic states in the S_1 state; (a) via vibrational ground state and (b) via $+276$ cm^{-1} state.

(a) reactive dimer

(b) non-reactive dimer

(b-1) stacked structure

(b3) single-bonded structure

(b-2) T-shaped structure

(b-4) non-planar structure

Figure 5 The structure of 7-AzI dimer; (a) reactive dimer and (b) non-reactive dimer. There are several possible structures as the non-reactive dimer; (1) stacked, (2) single-bonded, (3) T-shaped, and (4) non-planar structures.

The first prominent peak is located at the total energy of $65468(4)\text{ cm}^{-1}$ ($8.1171(5)\text{ eV}$), corresponding to the adiabatic ionization energy (E_i) of 7-AzI. This value is consistent with the E_i value measured by MPI-photoelectron spectroscopy as $8.11(1)\text{ eV}$.²⁸ Several subsequent vibronic bands in the D_0 state are visible in the spectra. Comparing the two spectra of figs. 7a and 7b, the intensity of $+537\text{ cm}^{-1}$ vibronic band drastically changed, which is attributed to the difference in the Franck-Condon factor from each intermediate state.

Figure 6 LIF spectrum of the non-reactive 7-AzI dimer with resolution of $\sim 0.06 \text{ cm}^{-1}$ (bottom), in addition to simulated envelopes assuming (a) single bonded, (b) T-shaped, and (c) non-planar structures.

In fig. 7a, a dispersed fluorescence spectrum of 7-AzI from the vibrational ground state in the S_1 state is also shown; the bands in the spectrum corresponds to vibronic structure in the S_0 state.¹¹ Comparing the dispersed fluorescence spectrum with the PFI spectrum via the vibrational ground state in the S_1 state (fig. 7a), both band positions and their intensities in two spectra are found to be similar each other. This reflects the similarity of geometric structures between S_0 and D_0 , implying that a loss of one π electron does not lead to any drastic change of the geometric structure of 7-AzI.

Figure 7 PFI spectra of jet-cooled 7-AzI via two different vibronic levels in the S₁ state excited by the first laser ν₁; (a) via vibrational ground state and (b) via +276 cm⁻¹ state. An inserted figure into (a) is a dispersed fluorescence spectrum of 7-AzI from the vibrational ground state in the S₁ state.

3.4. Photoelectron spectroscopy of 7-AzI cluster anions

Figure 8 shows photoelectron spectra of (7-AzI)_n⁻ (n = 2–5) detached by 532-nm (2.66 eV) photons. In the spectra, the horizontal axis corresponds to the electron binding energy, E_b, defined as E_b = hν – E_k, where E_k is the kinetic energy of the photoelectron. It was ascertained with several species (benzonitrile, yttrium, etc.) that an anion can be produced in our source when its electron affinity (EA) of species is positive. In this work, the 7-AzI monomer anion could not be produced, and

Figure 8 Photoelectron spectra of $(7\text{-Azl})_n^-$ cluster anions ($n = 2-5$). 7-Azl monomer anion cannot be produced because the EA of 7-Azl is negative. The positions of E_T and VDE (see text) are indicated by downward and upward arrows, respectively.

therefore it suggests that the EA of 7-AzI is negative. For 7-AzI cluster anions, all the spectra exhibit similar bell-shaped envelopes without any reproducible fine structure. From these spectra, we derived the threshold binding energies, E_T s, and vertical detachment energies (VDEs) from the onset and the maximum of each spectrum, respectively. These values are listed in Table II together with the peak width (fwhm) of each spectrum. The E_T gives an estimate of the upper limits of adiabatic EAs [23, 24], although the E_T almost coincides with the adiabatic EA when the anion and neutral geometries are similar.

Table II Cluster size dependence of the threshold electron energy (E_T), vertical detachment energy (VDE), and peak widths (fwhm) of 7-AzI cluster anions (units: eV)

cluster size, n	E_T	VDE	fwhm
1	≤ 0	≤ 0	—
2	0.81(4)	1.34(3)	0.43(8)
3	1.01(5)	1.60(4)	0.41(6)
4	0.90(5)	1.64(7)	0.51(8)
5	1.03(4)	1.76(3)	0.43(6)

Numbers in parentheses indicate uncertainties in derived quantities; 0.81(4) represents 0.81 ± 0.04 .

The spectra of cluster anions ($n = 2-5$) are essentially identical in shape, but being shifted by 0.1–0.2 eV in the electron binding energy with an additional 7-AzI. The shifts of E_T s are monotonic except for $n = 4$. The increase of the electron binding energy is attributed to the stabilization of the solvation. At $n = 4$, the peak width becomes large compared to other cluster-sizes. The anomaly at $n = 4$ corresponds to either electronic or geometric change; the most plausible explanation for it is the coexistence of geometric isomers. A main force in the clustering process is reasonably assumed to be hydrogen-bonding forces. Then, the geometries of the most stable cluster ($3 \leq n \leq 5$) is figured out as shown in fig. 9. At $n = 4$, two structures are possible; a planar, open chain (fig. 9b-1) and a cyclic chain (fig. 9b-2),²⁹ though clusters never exhibit the cyclic chain structure at odd n . In the cyclic chain structure, the cluster can be stabilized not only by hydrogen bonds but also by the overlap of π electron clouds. The overlap of π electron clouds can stabilize the neutral cluster, but never the cluster anion, because an excess electron of the cluster anion is likely to occupy π^* orbital. Therefore, it is reasonable that the E_T of the cyclic anion becomes small compared to that of the planar anion, leading to both the decrease of E_T and the increase of the peak width at $n = 4$.

4. CONCLUSIONS

A high resolution LIF spectrum of 7-AzI enables us to determine the rotational constants and the direction of the transition dipole moment precisely. The E_i of 7-AzI was also determined to be 8.1171(5) eV by using a PFI-ZEKE method. On the basis

Figure 9 The plausible structure of 7-AzI clusters on the assumption of clustering by a hydrogen-bond force; (a) $n = 3$, (b) $n = 4$, and (c) $n = 5$. At $n = 4$, two structures are possible; a planar, open chain (b-1) and a cyclic chain (b-2).

of the spectroscopic constants, the possible structures of its dimer were discussed by a low resolution LIF spectrum, though a higher resolution study is needed. For larger 7-AzI clusters, photoelectron spectroscopy for cluster anions was performed to discuss their stability instead of the LIF method; an anomaly at $n = 4$ was revealed, which was attributed to the coexistence of geometric isomers.

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