

Structural Distortion of Pyridazine in the $^1(n, \pi^*)$ Excited State: Evidence for Local Excitation

Kyo-Won Choi,^[a] Doo-Sik Ahn,^[b] Sungyul Lee,^{*,[b]} Heechol Choi,^[c] Kyoung-Koo Baeck,^{*,[c]} Seong-Ung Heo,^[a] Sun Jong Baek,^[d] Young S. Choi,^{*,[d]} and Sang Kyu Kim^{*,[a]}

Orbital interaction is fundamentally important in understanding molecular structure, reaction mechanism, and chemical reactivity. The extent of orbital interaction is, however, hardly known quantitatively, and resulting molecular properties have often been inferred from general conceptual rules of thumb which cannot be validated.^[1] One way to find out the extent of orbital interactions is to induce local perturbation via the external field. That is, as the orbital interaction gets stronger, electronic delocalization would be more efficient after the local perturbation is set to work. In this sense, molecular structures in the excited or ionic states are quite informative since localization of electrons would result in structural distortion. Diazabenzene has received a lot of attention as model systems for this situation.^[2–7] There has long been a well-conceived idea about the extents of orbital interactions and their effects on the properties of diazabenzene. Among these diazabenzene, the electronic delocalization in the excited pyridazine is considered to be relatively weak, and thus many authors have suggested that structural distortion occurs in the S_1 state due to the local $^1(n, \pi^*)$ excitation,^[4,7] though its through-bond interaction is known to be significant.^[1] According to Hoffmann's suggestions,^[1] and judging from relative values for the electronic excitation and ionization energies,^[2] the orbital interaction in pyridazine is considered to be much stronger than that of pyridazine or pyrimidine. Therefore, the geometrical distortion in the excited state has been considered hardly to occur, because

the two closely spaced lone-pairs of nitrogen atoms interact so strongly in pyridazine to give efficient electronic delocalization. This latter conjecture, taken for granted for a long time by most experimentalists, has essentially blocked the investigation of photophysics and photochemistry of pyridazine for the last several decades. As a result, even the vibronic assignments still remain controversial, despite a number of spectroscopic studies on the S_1 state of pyridazine.^[2,5,7–13]

Two nonbonding orbitals of pyridazine generate two mixed orbitals, n_+ and n_- , of which the latter is higher in energy. The lowest singlet transition is therefore the $^1(n_-, \pi^*)$ transition, giving the B_1 symmetry for the S_1 state in C_{2v} . The resonance-

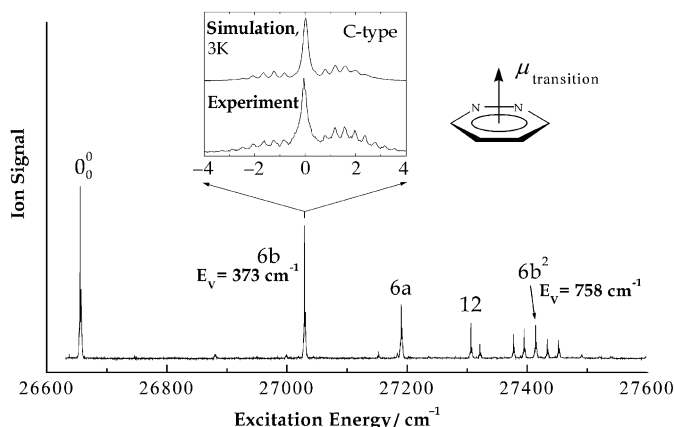


Figure 1. The S_1 - S_0 excitation spectrum of pyridazine. Inset: Experimental and simulated rotational contours.

enhanced two-photon ionization (R2PI) spectrum of pyridazine shows the S_1 origin at 26656 cm^{-1} , Figure 1. Difficulties in further assignment of vibronic bands originate from a strong band located at 373 cm^{-1} above the S_1 origin, the nature of which has been under controversy for a long time.^[5] The issue has been whether this band belongs to a nearby S_2 state, $^1(n_+, \pi^*)$ or $^1(n_-, \pi^*(2))$ ($\pi^*(2)$ denotes the higher-lying π^* state). Both states give A_2 (C_{2v}) electronic symmetry, which suggests that transitions to those states are electronically forbidden. Rotational contour analysis for the 373 cm^{-1} band, Figure 1, shows that the transition dipole moment is along the molecular c axis, which indicates that the total symmetry of the excited state associated with the 373 cm^{-1} band must be B_1 , which is also the case for the origin transition. Accordingly, if the 373 cm^{-1} band is due to excitations of the S_2 (A_2) state, then its vibrational symmetry should be b_2 . This indicates that the 373 cm^{-1} band is not the origin of the S_2 state, which implies that the origin of this state would be even below that of S_1 . The other possible assignment is that the 373 cm^{-1} band is the vibronic band associated with S_1 (B_1). In this case, the vibrational mode symmetry should be a_1 . However, problems then arise as no feasible a_1 vibrational mode with such a low frequency as 373 cm^{-1} can be found. In addition to these two scenarios, many other conjectures about the S_1 state of pyridazine have been suggested in a number of theoretical and experimental papers.^[5] This long-term controversy on the vibron-

[a] K.-W. Choi, S.-U. Heo, Prof. S. K. Kim

Department of Chemistry and School of Molecular Sciences (BK21)
Korea Advanced Institute of Science and Technology (KAIST)
Daejeon 301-750 (Korea)
Fax: (+82) 42-869-2810
E-mail: sangkyukim@kaist.ac.kr

[b] D.-S. Ahn, Prof. S. Lee

School of Environmental Science and Applied Chemistry (BK 21)
Kyunghee University, Kyungki-Do 449-701 (Korea)
Fax: (+82) 31-202-7337
E-mail: sylee@khu.ac.kr

[c] H. Choi, Prof. K.-K. Baeck

Department of Chemistry, Kangnung University
Gangwon-Do 210-702 (Korea)
Fax: (+82) 33-647-1183
E-mail: baeck@kangnung.ac.kr

[d] S. J. Baek, Prof. Y. S. Choi

Department of Chemistry, Inha University, Incheon 402-751 (Korea)
Fax: (+82) 32-867-5604
E-mail: yschoi@inha.ac.kr

ic structure of the excited pyridazine results from the fact that the interpretations in previous publications were mostly based on the assumption that the symmetry of the excited pyridazine remains as C_{2v} . Theoretical studies aiming to inspect this concept had to provide not only vertical excitation energies but also the stationary structure and vibration frequencies of the excited state. No previous theoretical work provided such a full set of information, and the lack of such reliable theoretical results was one of the main obstacles preventing complete analysis of the absorption spectrum of pyridazine. Our combined work of both state-of-the-art high-level theoretical and experimental methods shows an unambiguous interpretation of the spectrum and suggests a challenge to the concept of orbital interaction in determining the molecular geometry of an excited-state.

Herein, we report mass-analyzed threshold ionization (MATI) spectra^[14] to give highly resolved vibronic features of pyridazine in the D_0 state, Figure 2. Each MATI spectrum is taken via a specific S_1 intermediate state. According to the Franck-Condon principle, the strongest MATI band represents a vibrational mode associated with the S_1 intermediate state employed for the corresponding MATI spectrum. In Figure 2, it is quite clear that the 373 cm^{-1} band in the S_1 state correlates to the strong band located at a surprisingly high frequency of 537 cm^{-1} above the D_0 origin at 70242 cm^{-1} . This band can be unambiguously assigned to the $6b^+$ mode with b_2 symmetry in C_{2v} , since it matches so well with the ab initio (Ub3 lyp-DFT/6-311 g(d,p); Gaussian 98^[18]) vibrational frequency of 565 cm^{-1} . The 373 cm^{-1} band is not the S_2 origin, because then it would be expected that the origin band is more intense in the MATI spectrum in Figure 2b than the $6b^+$ band. Thus, this experimental finding indicates that the 373 cm^{-1} S_1 band is associated with the $6b$ vibrational mode. If the symmetry of the S_1 pyridazine were C_{2v} , however, the transition would be forbidden because the vibrational symmetry of $6b$ is b_2 . This is strong evidence that the geometrical distortion along the $6b$ mode, breaking the C_2 symmetry, reduces the symmetry of the S_1 pyridazine to the planar C_s symmetry. That is, the symmetry species of the 373 cm^{-1} band is reduced to A'' in C_s , and the transition from the ground state becomes allowed since the B_1 symmetry of the transition dipole moment is isomorphic to A'' in C_s .

It is also found that the 758 cm^{-1} band in the S_1 - S_0 excitation spectrum, Figure 1, corresponds to the first overtone of $6b$ in the S_1 state, giving the $6b^{2+}$ frequency of 1078 cm^{-1} in

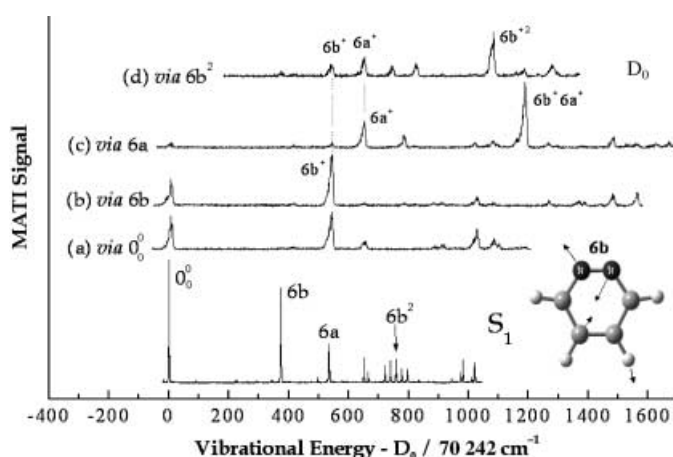


Figure 2. MATI spectra taken via various S_1 intermediate states. The atomic displacement description for the $6b$ normal mode is also shown.

the MATI spectrum in Figure 2. While the $6b^{2+}$ frequency is very close to 1074 cm^{-1} (double the $6b^+$ fundamental frequency), the $6b^2$ frequency of S_1 (758) is much higher than double the $6b$ fundamental frequency (746). This negative anharmonicity for $6b$ in the S_1 state indicates that the potential energy surface along the $6b$ mode becomes steeper as the vibrational quantum number increases, which suggests the existence of a barrier with the peak corresponding to a C_{2v} geometrical conformation. This experimental finding also confirms that the minimum energy structure of the S_1 pyridazine is distorted either along the C_2 axis or within the C_5 plane. Assignments for other bands in R2PI and MATI spectra are then straightforward, and are listed in Table 1.

Table 1. Vibrational frequencies of pyridazine cation (D_0) and mode assignments from various MATI spectra.

Origin	Pyridazine cation; Δ [cm^{-1}] ^[a]						Cal. ^[b]	Assignment
	+373 (6b) ^[c]	+534 (6a)	+650 (12)	+721 (8b)	+739 (15)	+758 (6b ²)		
0	0		369			369	385	Origin
	410						418	16b ⁺
537	537	537			537	537	565	6b ⁺
648	648	648				648	662	6a ⁺
		781				739		16b ⁺
			818			818		16b ⁺ 16a ⁺
			879				899	16a ⁺
1020	1020	1017		1016	1016			12 ⁺
1080		1079				1078		1 ⁺ or 16b ⁺ 6a ⁺
			1090	1090	1091		1106	6b ⁺
				1167	1167		1173	8b ⁺
		1183				1180		15 ⁺
	1263	1263			1263		1292	6b ⁺ 6a ⁺
						1272		9b ⁺
	1363							16b ⁺ 6b ⁺
	1476	1477						
	1557							6b ⁺ 1 ⁺

[a] Shifts from the ionization threshold (70242 cm^{-1}). [b] DFT (Ub3 lyp/6-311 g(d,p)) calculations for the D_0 state. [c] Assignments for the S_1 vibronic states in the corresponding row.

Because the interpretations in previous publications were mostly based on the assumption that the symmetry of the excited pyridazine remains as C_{2v} , the geometry of the S_1 pyridazine in a B_1 electronic state is optimized within the C_{2v} symmetry. The coupled-cluster singles and doubles (CCSD) method^[15] and the equation-of-motion coupled-cluster single and double (EOM-CCSD)^[16] method with binary basis sets (6–31+G* on N and C, 6–31G on H) were used for the ground and excited electronic states, respectively. The calculated vibrational frequencies give two imaginary frequencies for 6b ($590 i \text{ cm}^{-1}$) and 16a ($184 i \text{ cm}^{-1}$), which indicates that the minimum energy geometry of pyridazine in the S_1 state is distorted along both the unsymmetrical in-plane (6b) and out-of-plane (16a) modes. Further optimization of the stationary geometry of the S_1 (B_1 electronic state) along the out-of-plane mode, maintaining the C_2 -axis symmetry, ended up with a very slightly twisted geometry (of electronic state B). The other imaginary frequency mode breaks the C_2 symmetry, producing a virtually planar C_5 symmetry that would control the actual selection rule for transition. The geometry of the nearest excited state (A_2 state), which was computed to be 4135 cm^{-1} above the B_1 state at C_{2v} geometry,^[5,8] was also optimized.

It is important to note that the A_2 and the B_1 electronic states in the C_{2v} planar structure correspond to the A'' and A' electronic state, respectively, in a C_5 symmetry structure in which the symmetry plane bisects the molecular plane. However, as the molecule is distorted within the molecular plane along the 6b vibration mode and the molecular plane is the symmetry plane of C_5 symmetry, these two states reduce to the same A'' electronic state. The optimization of the stationary geometry of the S_1 , both the B_1 and A_2 , along the unsymmetrical in-plane (6b) mode results in the same distorted planar structure (the A'' electronic state), and its energy is 2647 cm^{-1} below that of the planar A_2 state. The EOM-CCSD adiabatic excitation energy of the A'' is 27553 cm^{-1} , which is very close to the experimental value 26656 cm^{-1} . The lowest three in-plane (a' mode) vibrational frequencies of the optimized A'' state are computed to be 335, 605, and 728 cm^{-1} , which are comparable to the experimentally observed values 373, 534, and 650 cm^{-1} , respectively.

Our optimized geometry, energy, and vibrational frequencies of the S_1 , are all in accordance with the experimental observations. It is now clear that the S_1 pyridazine of A'' electronic state has an in-plane distorted C_5 -symmetric structure, and the lowest in-plane vibrations are clearly shown in the MATI spectroscopy. The confusion^[2–13] regarding the two nearby electronic states, the $S_1(B_1)$ and the $S_2(A_2)$, are now resolved; both A_2 and B_1 correspond to the same S_1 state. Our computation also confirms that the true S_2 electronic state is located about 0.5 eV above the S_1 state, as mentioned earlier.^[5,8]

In conclusion, the conventional concept that strong orbital interactions of pyridazine guarantee complete electronic delocalization even in the excited state is found to be misleading. MATI spectroscopy^[14] turns out to be an extremely useful technique to identify clearly the nature of intermediate S_1 or S_2 vibronic states. Generalization of the concept regarding orbital

interaction is now subject to rigorous experimental and theoretical tests.

Experimental Section

Experimental setup and conditions have been described in detail elsewhere.^[17] Briefly, pyridazine (Aldrich) was heated to 80°C , mixed with a carrier Ar gas, and expanded into a vacuum through a 0.5 mm diameter nozzle orifice. The supersonically cooled molecular jet was skimmed through a 1 mm diameter skimmer before it was overlapped with two independently tunable laser pulses. For R2PI spectra, the wavelength of one laser pulse was scanned through S_1 resonant states, while that of the other laser pulse was fixed for ionization of the excited pyridazine. Meanwhile, in MATI spectroscopy, the wavelength of one laser pulse was fixed for a specific S_1 state excitation while that of the other laser pulse was scanned through various cationic D_0 states.

Acknowledgements

This work was supported by Korea Research Foundation Grant No. KRF-2002-070-C00046. We sincerely thank Dr. T. Suzuki (RIKEN, Japan) for the help in initiating this project and helpful discussion.

Keywords: ab initio calculations • excited states • laser spectroscopy • mass spectrometry • orbital interactions • pyridazine

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Received: February 9, 2004 [200400053]