Structure of Gas Phase Radical Cation of 1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}] Dodecane Determined from Zero Kinetic Energy Photoelectron Spectroscopy

Yonggang He,[†] Chengyin Wu,[†] Wei Kong,*,[†] Kevin P. Schultz,[‡] and Stephen F. Nelsen[‡]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003, and Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706-1396

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We report gas-phase vibrational spectroscopy of the ground-state cation of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]-dodecane (TTD) using two-color two-photon zero kinetic energy photoelectron spectroscopy. From the distribution of active vibrational modes and comparisons between the experiment and theoretical simulation, we offer proof that the cationic state and the first electronically excited state have the same D_{2d} symmetry.

The present study concerns 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]-dodecane (TTD), which is designated [1^4.2^2]adz in the "cage adamanzane" nomenclature system introduced by Springborg and co-workers[1] for tricyclic tetraamines having saturated bridging carbon chains. Current interests in cage adamanzanes

TTD   **D$_{2d}$**   **S$_4$**
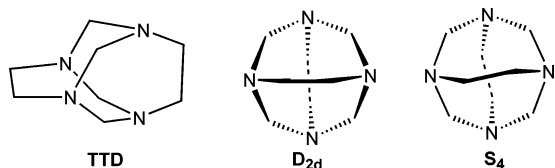
center upon their importance in biochemistry and coordination chemistry.[2−9] From a fundamental point of view, the basicity and strain energy of these compounds are particularly interesting.[10−13] TTD was prepared by Bichoff in 1898,[14] but its structure was presumed to contain 1,3-diazacyclopentane. A low-temperature proton NMR study later discovered the mistake in the structural assignment.[15] The X-ray diffraction pattern of TTD verified the structure as shown, and the symmetry of the ground state was believed to be D_{2d}.[16] TTD is one of the very few saturated amines that gives a radical cation persistent enough to show a reversible cyclic voltammogram.[17] Recent gas-phase studies based on fluorescence excitation and dispersed emission spectroscopy under supersonic jet expansion conditions concluded that TTD is twisted at its NCCN bonds, so it has static S_4 symmetry, but dynamic D_{2d} symmetry, and the tunneling barrier is only about 0.3 kcal/mol between NCCN twists of opposite sign.[18] The same study also showed that the first excited electronic state (S$_1$, the 3s Rydberg state) should be of D_{2d} symmetry.

Our interest in TTD stems from the discussion on the symmetry of the radical cation since the 1970s, particularly regarding the effect of solvent. Nelsen and Buschek first recorded the electron spin resonance spectrum of TTD$^{•+}$ in the condensed phase.[19] Later, based on semiempirical quantum mechanical calculations, Nelsen, et al. proposed unequal NCH$_2$CH$_2$N distances caused by a three-electron σ-bond,[20] similar to the type demonstrated by Alder in some bicyclic diamine radical cations.[21] With more advanced technology, including electron−nuclear double resonance (ENDOR) spectroscopy and a variety of deuterated compounds, the most recent work by Zwier et al. concluded that there was a single energy minimum with D_{2d} symmetry.[22]

So far all the reports on the symmetry of TTD$^{•+}$ were based on indirect evidence:[18,22] the gas-phase experiment relied on the similarity between a low Rydberg state (3s) and the ground cationic state,[18] while the ENDOR experiment was performed in the solution phase.[22] The issue of solvent effects on the symmetry of TTD$^{•+}$ has not been fully investigated. Moreover, the limited time resolution of the ENDOR experiment can only provide a time-averaged "effective" symmetry. In this work, we report gas-phase studies of TTD$^{•+}$ using two-color two-photon zero kinetic energy (ZEKE) photoelectron spectroscopy.[23] From the distribution of active vibrational modes and comparisons between the experiment and theoretical simulation, we offer further proof that the D$_0$ state and the S$_1$ state do have the same D_{2d} symmetry.

The experimental apparatus is a standard molecular beam machine with a time-of-flight mass spectrometer and a pulsed valve heated to ∼100 °C.[24] The sample was synthesized in Madison, Wisconsin, using the literature method.[14] Two counter propagating laser beams were used: one for resonant excitation to the different vibrational levels of the S$_1$ state, and the other for further ionization. By fixing the ionization laser at 328 nm and scanning the resonant laser, we recorded a two-color 1+1′ resonantly enhanced multiphoton ionization spectrum. Our result is in excellent agreement with that of Zwier et al.,[18] and the spectrum is provided as part of the Supporting Information for reference. By fixing the resonant laser at one of the vibrational levels of the S$_1$ state, scanning the ionization laser, and detecting only the ZEKE electrons, vibrational spectroscopy of the cation was obtained.

Figure 1 shows the ZEKE spectra of TTD taken via the origin band and eight different levels of mode 20 of the S$_1$ state. This

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* Corresponding author. E-mail: Wei.kong@oregonstate.edu
† Oregon State University.
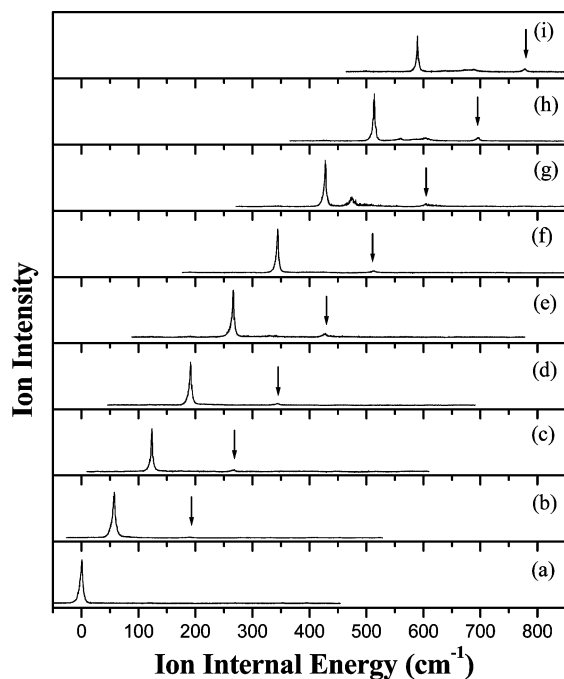‡ University of Wisconsin.

Figure 1. ZEKE spectra of TTD taken via the $v = 0-8$ levels of mode 20 $(a-i)$ of the S_1 state. The arrows indicate transitions with $\Delta v = 2$. The abscissa is in reference to the adiabatic ionization energy at 56343 cm^{-1}.

TABLE 1: Observed Vibrational Levels of Mode 20 of TTD$^{\bullet+}$ (cm^{-1})

v	0	1	2	3	4	5	6	7	8
E_v	0	57	123	191	266	344	428	513	590
ΔE		57	66	68	75	78	84	85	77

mode corresponds to rotation of the NR$_3$ units in opposite directions about the NCH$_2$CH$_2$N axes, and its symmetry species is a in the S_4 point group and a_2 in both the D_{2d} and C_{2v} point groups.[25] The most remarkable feature of Figure 1 is the dominance of a single transition, and this phenomenon has been documented as a propensity of $\Delta v = 0$,[26] while Δv is the change in the vibrational quantum number between the S_1 and D_0 states. The features marked by arrows correspond to transitions with $\Delta v = 2$, and the rest of the weak features correspond to other vibrational modes of the cation, and they are not addressed in this letter. Trace a taken via the origin of the S_1 state results in an adiabatic ionization energy of 56343 $\pm$ 3 cm^{-1} (6.9856 $\pm$ 0.0004 eV), including a correction due to the detection field.[23] This value is lower than 7.39 eV determined from vertical ionization.[19] Traces $b-i$ provide the energies for the different vibrational levels of mode 20, and the results are listed in Table 1.

To decipher the symmetry of the D_0 state from Figure 1, we attempted to reproduce the experimental observation from a series of calculations. With the Gaussian 03 suite,[27] the S_1 state was calculated at the CIS level using the 6-31G basis set. The D_0 state was calculated using the density functional theory (DFT) with the Becke 3LYP functional and the 6-31+G(d) basis set. Similar to the reports by Zwier et al.[22] and Nelsen et al.,[20] our geometry optimization for the radical cation of TTD resulted in two stable structures belonging to D_{2d} and C_{2v}, with the D_{2d} structure more stable by 18.7 kcal/mol. Using the vibrational frequencies and the displacement vectors thus obtained, we then calculated the Franck–Condon (FC) factors from the S_1 to the D_0 state,[25] and the results are displayed in Figure 2. The dark gray columns represent intensities obtained by assuming D_{2d}
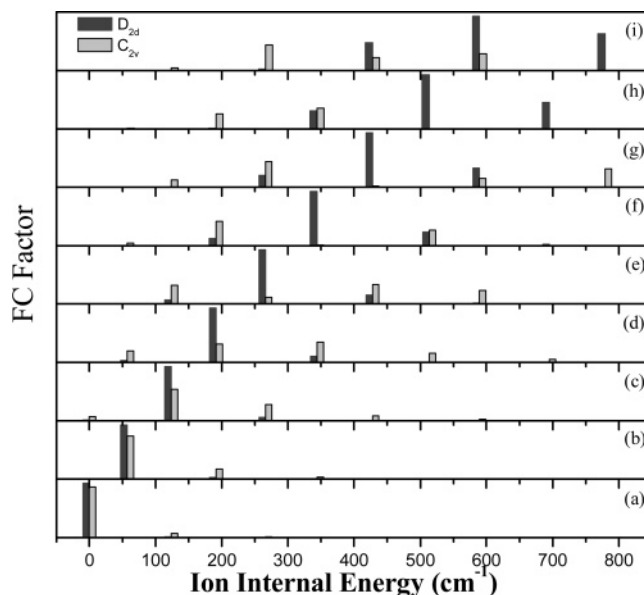

Figure 2. Franck–Condon factors from the S_1 to the D_0 state of TTD. The vibrational levels of the S_1 state are $v = 0(a) - 8(i)$. The dark (or light) gray columns were obtained by assuming D_{2d} (or C_{2v}) symmetry for the D_0 state.

symmetry for the D_0 state, and the light gray columns represent those from C_{2v} symmetry. It is important to note that although the displacement vectors for the S_1 and the D_0 states were obtained from different calculations, the displacement vectors for the D_{2d} and C_{2v} structures were obtained using the same method with the same basis set. Moreover, calculations based on results using different basis sets yielded the same distribution of FC factors. The comparison in Figure 2 should therefore be of considerable credence.

From Figure 2, the vibrational distribution obtained based on the D_{2d} symmetry is a far better representation of that in Figure 1, and the symmetry of the D_0 state is thus better described to be D_{2d} than C_{2v}. Although for transitions from the low vibrational levels of the S_1 state, the difference between the two symmetry groups is not obvious, transitions from higher levels are remarkably sensitive to the symmetry assumption of the D_0 state. This result is reasonable since the larger the amplitude of vibration, the broader the space explored by the molecular frame.

The strong propensity of $\Delta v = 0$ demonstrated from both the experiment and the calculation is a natural result of similarity between the S_1 and the D_0 states. The normal modes of the two states have essentially the same displacement vectors, and the vibrational wave functions of the two states are almost identical. This result also provides evidence for the assumption that the S_1 state is representative of the D_0 state,[18] even though it is the lowest member of the Rydberg series.

The anharmonicity demonstrated in Table 1 is interesting. The energy gap between adjacent vibrational levels increases with the vibrational quantum number. This result is also consistent with the D_{2d} symmetry of the cation. Since the ground state of the neutral molecule is considered to tunnel between two equivalent S_4 structures, it is therefore natural that the diminished tunneling barrier would result in a flat and wide bottom for the S_1 and the D_0 states. The potential surface of mode 20 thus resembles more to a square well than to a parabola, leading to an increased energy gap for higher vibrational levels.

In summary, from the vibrational spectroscopy of the cation in the gas phase, we offer direct evidence for the D_{2d} symmetry

Letters

J. Phys. Chem. A, Vol. 109, No. 6, 2005 **961**

of the ground cationic state of TTD. The previous assumptions regarding the Rydberg nature of the S_1 state and the negligible effect of the solvent on the geometry of the cation are validated.

Supporting Information Available: A: Two-color two-photon resonantly enhanced multiphoton ionization spectrum of TTD. B: Geometry of TTD in the S_1 state calculated at the CIS level using the 6-31G basis set. C. Geometry of TTD in the D_0 state with a D_{2d} symmetry calculated using the Becke 3LYP functional with the 6-31+G(d) basis set. D. Geometry of TTD in the D_0 state with a C_{2v} symmetry calculated using the Becke 3LYP functional with the 6-31+G(d) basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

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