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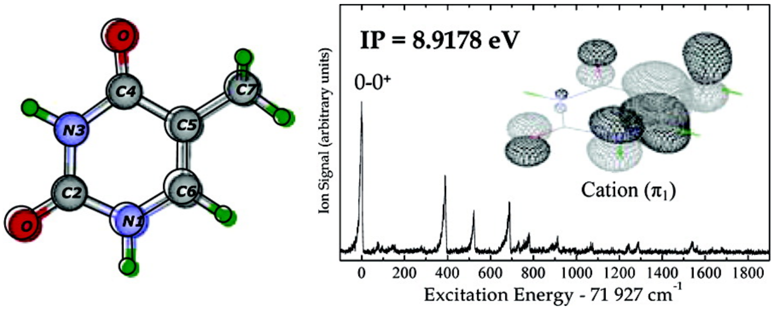

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Ionization Spectroscopy of a DNA Base: Vacuum-Ultraviolet Mass-Analyzed Threshold Ionization Spectroscopy of Jet-Cooled Thymine

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Here, we provide the first report of the high-resolution vacuum-ultraviolet (VUV) ionization spectroscopic analysis of thymine. Ionization of nucleic acid bases is the first step in DNA damage/mutation caused by exposure to ionizing radiation.[1−8] After the initial ionization of a nucleic acid base, the hole trapped in that base migrates along the DNA helix through hopping and/or tunneling mechanisms, resulting in various types of damages, such as tautomerization via proton transfer and breaks in the strands of bases comprising the double helix. This oxidative degradation of nucleic acids is ubiquitous in the evolutionary and carcinogenic processes in living organisms.[7] Naturally, scientists have had a keen interest in this subject since the discovery of the DNA double-helix structure by Watson and Crick.[1−6,9−12] More recently, the conducting properties of DNA have received much attention due to the potential for developing DNA-based molecular devices.

According to the hopping mechanism, charge migration in DNA occurs through hole/electron hopping among the highest-occupied molecular orbital (HOMO) levels of the constituent DNA bases through the $\pi-\pi$ interaction between adjacent stacked bases.[13,14] The relative HOMO energy levels of individual DNA bases are thus fundamental properties that are crucial to achieving a molecular-level understanding of charge transfer in DNA.[9,10] Knowledge of the geometrical changes in DNA bases upon ionization is also very important to our understanding of these systems since the vibrational motion of the base cation acting as a charge carrier is predicted to either interrupt or accelerate the charge hopping process.[14] Accordingly, a number of experimental and theoretical studies have focused on this subject in recent decades.[15−20] However, compared to the many high-level calculations, experimental work on DNA base ionization remains at a primitive level. The experimental ionization potentials reported to date are scattered over a wide range and contain large uncertainties.[1−6] The lack of exact experimental data has precluded stringent testing of recent high-level theoretical calculations.[11,12] Furthermore, no data are currently available on the vibrational structures of DNA base cations. Modern state-of-the-art experimental tools should be able to provide much more accurate information on these important physical properties of DNA bases.[21] This information would allow us to develop more quantitative explanations for various phenomena associated with the DNA base ionization and future molecular electronic devices. In the present study, we used mass-analyzed threshold ionization (MATI) spectroscopy to determine the ionization potential and cationic vibrational structure of the DNA base, thymine.

Recent extensive studies on DNA bases in the gas phase have established that most DNA and RNA bases have ultrashort lifetimes in their excited states and that the associated vibronic structures of some bases are not unambiguously assigned, particularly for thymine and uracil.[15−18,22] The more conventional two-color MATI spectroscopy using the resonant vibronic state as an intermediate state, therefore, turns out to be ill-suited to the analysis of DNA bases. Here, we adopt a VUV nanosecond laser pulse with a resolution of ~0.8 cm^{-1} as a direct soft ionization source. The VUV laser pulse in the 135−140 nm range was generated via a four-wave mixing process in a Kr cell (1−3 Torr) using a fixed 212.552 nm UV laser pulse for the two-photon Kr $5p[1/2]_0-4p^6$ transition and a tunable visible laser pulse in the 449−495 nm range. The resulting VUV laser pulse ($\Delta t \sim 5$ ns) was then separated from the UV and visible fundamentals using the edge of a collimating CaF_2 lens and was overlapped with the molecular beam of thymine seeded in the He carrier gas. The supersonic jet was formed from a nozzle (General valve, 0.2 mm diameter orifice) heated to 260−280 °C. The long-lived high-lying Rydberg states reached by the VUV photon were pulsed-field ionized after a delay time of 20 μs following the VUV laser pulse to give the MATI spectrum in Figure 1.

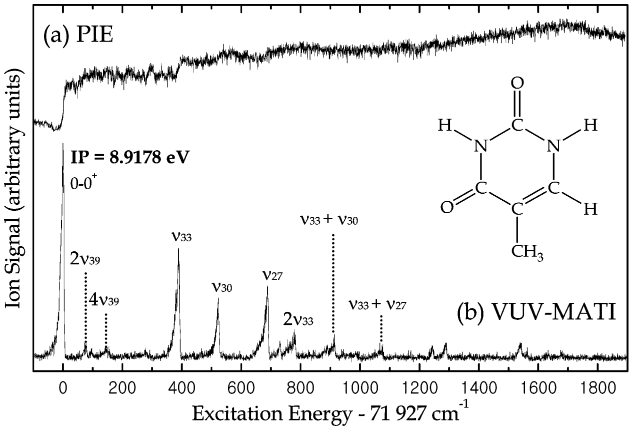

Figure 1. (a) Photoionization efficiency (PIE) and (b) VUV-MATI spectrum of thymine. See Supporting Information for the normal mode description of the observed vibrational bands.

A strong $0-0^+$ band is observed at the VUV photon energy of 71 927 cm^{-1}, which corresponds to the adiabatic ionization energy of thymine. The position of this origin band coincides with a sharp rise in the photoionization efficiency spectrum, which monitors directly formed ions as a function of energy, confirming that this is the real adiabatic ionization potential. After correcting for the field effect on the true ionization potential,[21] the accurate ionization potential of thymine is determined to be 8.9178 ± 0.0010 eV. This value is 0.1103 or 0.18 eV higher than theoretical values of 8.8075 or 8.74 eV from DFT (UB3LYP/6-311+G(d,p))[23] and PMP2 calculations,[12] respectively. The ionization potential measured in this work is compared with previously reported experimental values scattered in the range of 8.82−9.18 eV.[1−6] Initial thermal energy and relatively poor resolution of the methods employed in previous measurements should be responsible for any discrepancy in Table 1.

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Table 1. Experimental Ionization Potentials of Thymine

IP (eV)	method	ref/year
8.9178 ± 0.0010	VUV-MATI	this work
8.82 ± 0.03	photoionization mass spectrometry (PIMS)	6/2005
9.15 ± 0.15	electron ionization	5/1996
9.18	photoelectron spectroscopy (PES) (vertical)	4/1989
8.87 ± 0.05	PIMS	2/1976
9.14 ± 0.03	PES (vertical)	1/1975

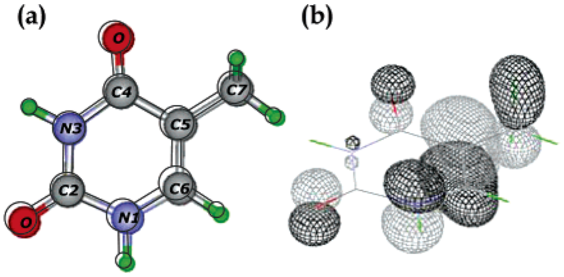

Figure 2. Minimum energy structures of thymine in (a) the neutral (circle and rod) and cationic ground states (ball-and-stick). (b) The shape of HOMO (π_1) calculated using DFT ((U)B3LYP/6-311+G(d,p)).[23]

The most stable tautomer of thymine in the gas phase is known to adopt a diketo form from infrared[24] and microwave[25] studies. The energy of the most stable enolic tautomer has recently been calculated to be 9.28 kcal/mol higher than that of the diketo tautomer.[26] The MATI spectrum in Figure 1 showing no spectral complexity due to other species, therefore, is ascribed to that of the diketo thymine. The MATI spectrum of thymine is amazingly simple considering that there are 39 normal modes for this molecule. The spectral simplicity indicates that only a few vibrational modes are Franck−Condon active in the ionization process. Consistent with this, the $0-0^+$ origin band is the strongest feature in the MATI spectrum (Figure 1), indicating that the molecular structure of the thymine cation is not dramatically different from that of the neutral ground state. According to ab initio calculations,[23] the removal of an electron from the HOMO of thymine significantly changes the ring structure adjacent to the CH_3 moiety. This structural change mainly takes the form of an elongation of the C5−C6 bond from 1.35 Å in the neutral molecule to 1.41 Å in the cation, as depicted in Figure 2.

Therefore, particular vibrational modes associated with the in-plane ring-distortion are expected to be active in the MATI spectrum. Accordingly, low-frequency bands observed at 389, 523, 688, and 730 cm^{-1} are assigned as in-plane ring distortion modes of the thymine cation from the corresponding not-scaled ab initio frequencies of 392 (C═O symmetric deformation), 580 (C═O antisymmetric deformation), 692 (ring breathing), and 765 cm^{-1} (ring deformation + C5−C7 stretching), respectively.[23]

The band of lowest vibrational frequency observed at 77 cm^{-1} should correspond to the torsional mode of the CH_3 moiety of the ion. This frequency is much lower than the CH_3 torsional frequencies of 173 or 182 cm^{-1} measured previously for ground-state neutral thymine in neutron inelastic and Raman scattering experiments, respectively.[19] This disparity indicates that the ionization process significantly decreases the CH_3 torsional barrier height.[20] The vibrational structure of the thymine cation reflected in the MATI spectrum indicates that, compared to the neutral molecule, the thymine ring is asymmetrically distorted and that the CH_3 torsion is floppier. This structural change of thymine upon ionization should be taken into account when modeling the hole/electron-transfer mechanism in DNA.

Ionization potentials and cationic vibrational structures of DNA bases are fundamental physical properties that are essential for the understanding of electron/hole transfer processes in DNA and RNA. Nonetheless, these properties have not yet been fully scrutinized experimentally. Here, we have presented for the first time the highly resolved ionization spectrum of the DNA base, thymine. In particular, we have accurately determined the ionization potential of thymine to 8.9178 eV. In addition, our spectral data reveal the geometrical change that thymine undergoes upon ionization, with the associated vibrational frequencies. Given the biological importance of the ionization of DNA bases, the present work on thymine should be extended to other DNA bases as well as DNA base pairs and solvated DNA bases. The results of such experimental studies will stimulate more rigorous theoretical calculations in this important field.

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Supporting Information Available: High-resolution VUV-MATI spectrum, vibrational frequencies with normal mode descriptions, and the complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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