

# Experimental observation of guanine tautomers with VUV photoionization

Jia Zhou, Oleg Kostko, Christophe Nicolas, Xiaonan Tang, Leonid Belau, Mattanjah S. de Vries,<sup>1</sup> and Musahid Ahmed.\*

*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

<sup>1</sup> *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*

## Abstract

Two methods of preparing guanine in the gas phase, thermal vaporization and laser desorption, have been investigated. The guanine generated by each method is entrained in a molecular beam, single photon ionized with tunable VUV synchrotron radiation, and analyzed using reflectron mass spectrometry. The recorded photoionization efficiency (PIE) curves show a dramatic difference for experiments performed via thermal vaporization compared to laser desorption. The calculated vertical and adiabatic ionization energies for the eight lowest lying tautomers of guanine suggest the experimental observations arise from different tautomers being populated in the two different experimental methods.

\* MS: 6R-2100, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA-94720, USA. Phone: (510) 486-6355; fax: (510) 486-5311; e-mail: MAhmed@lbl.gov

Determinations of ionization energies and other properties of the DNA bases in the gas phase are not trivial.<sup>1,2</sup> The challenge stems from the fact that transporting these non-volatile and in most cases very fragile molecules to the gas-phase leads to extensive fragmentation, making it difficult to generate intact parent molecules. This is further compounded by the possibility of forming different conformers, rotamers and tautomers during the vaporization process.<sup>3</sup> For instance, the guanine molecule has four labile hydrogen atoms which can bind to 7 possible electronegative binding sites, giving rise to a large number of possible tautomers (Figure 1). According to calculations,<sup>4</sup> the four lowest energy tautomers are within 0.1 eV of each other, of which the keto-N9H form (structure shown in Figure 1) is the most stable. The next low energy tautomer is approximately 0.2 eV higher in energy, and three more forms are in the 0.26-0.28 eV range; the rest of the tautomers lie above 0.5 eV. The 8 lowest lying tautomers and their calculated energies are listed in table 1.

Traditionally, resonant two photon ionization (R2PI) and optical double resonance spectroscopies<sup>5-7 8,9</sup> have been used to study the guanine tautomers produced via laser desorption. However, Choi and Miller<sup>10</sup> showed that the tautomer distribution observed by IR spectroscopy of guanine formed by thermal vaporization with subsequent entrainment in ultra cold helium droplets differs from that observed in laser desorption probed by R2PI. This led to a flurry of experimental<sup>9</sup> and theoretical<sup>11,12</sup> efforts to reassign the tautomer populations that are formed in the laser desorption process. The proposed explanation for the discrepancy is that the lowest energy keto tautomers (as well as tautomer 4) have short lived (picosecond or less) excited states and therefore cannot be detected by nanosecond pulsed R2PI. These tautomers do show up in the helium droplet experiment because it is essentially a ground state absorption

measurement. Thus it seems that in laser desorption experiments, tautomers 1-8 are populated in the molecular beam, but of these only tautomers 3 and 5-7 can be observed by R2PI. In thermal vaporization experiments, where the cooling condition is better, only tautomers 1-4 are populated, all of which are observed in He droplets. However, as pointed out in a recent review,<sup>3</sup> comparison of these results is difficult because different experimental detection techniques have been used to assign the tautomer distribution and structure of guanine generated via different gas-phase approaches. Therefore it is desirable to use a universal detection scheme to directly compare the different vaporization techniques.

Among the four naturally occurring DNA bases, extensive experimental and theoretical studies have shown that guanine in the gas phase has the lowest ionization energy.<sup>13,14</sup> However, previous SPI studies of guanine have all been conducted utilizing the thermal vaporization method. Hush and Cheung<sup>15</sup> using photoelectron spectroscopy (PES) reported a vertical ionization energy (VIE) of 8.24 eV. Orlov *et al.*<sup>16</sup> reported an adiabatic ionization energy (AIE) of 7.77 eV in a photoionization mass spectrometry measurement. Another PES measurement by Lin *et al.*<sup>17</sup> of guanine vaporized at 317 °C reported a VIE of 8.28 eV with an onset at 7.8 eV, in agreement with the earlier results. A recent photoionization mass spectrometry measurement by Belau *et al.*<sup>18</sup> of thermally vaporized guanine in a molecular beam in a microhydrated environment reported an appearance energy of  $8.1 \pm 0.1$  eV. Plekan *et al.*<sup>19</sup> performed photofragmentation studies using fixed wavelength VUV radiation and attempted to explain the fragmentation patterns by relating them to published photoelectron spectra.

Cauet *et al.*<sup>13,20</sup> and Roca-Sanjuan *et al.*<sup>14</sup> discussed various ab-initio methods used in calculating the ionization energies for DNA bases with particular emphasis on guanine; they are good reference points for the numerous calculations that have been performed on the photoionization of DNA bases. Cauet *et al.*<sup>13</sup> calculated the AIE and VIE of the canonical form of guanine to be 7.82 eV and 8.27 eV at the MP2/6-311++G(d,p) level of theory while Roca-Sanjuan *et al.*<sup>14</sup> reported them as 7.65 eV and 8.09 eV, respectively, using CASPT2 level of theory. Recently, Shukla and Leszczynski<sup>21</sup> using B3LYP/6-311++G(d,p) level of theory calculated the VIE's for the eight lowest energy tautomers of guanine, while Marian<sup>11</sup> used restricted Kohn-Sham level (B3-LYP functional) to calculate VIE's for the same eight tautomers. Elshakre<sup>22</sup> and Dolgounitcheva *et al.*<sup>23</sup> calculated VIE's for the five lowest energy tautomers of guanine.

Differences in ionization energies and shape of the onset for the various tautomers should be accessible with tunable VUV radiation. To this end we employed single photon ionization (SPI) to directly probe the tautomer distribution of guanine formed both via thermal vaporization and via laser desorption with subsequent entrainment in a molecular beam. This method would detect the various tautomers of guanine on an equal footing, allowing for the desired comparison between the two production methods. SPI with tunable VUV radiation, where absorption to intermediate levels is not required, provides a convenient and reliable method to measure ionization energies of fragile biological molecules.<sup>24</sup> Specifically, threshold photoionization deposits minimal excess energy into a molecule, thereby reducing the fragmentation produced by multiphoton absorption.

The experiments were performed on a molecular beam apparatus coupled to a 3 meter VUV monochromator on the Chemical Dynamics Beamline at the Advanced Light Source. An in-line gas filter removes higher order harmonics before the monochromator.<sup>25</sup> The thermal vaporization<sup>18</sup> source has been described recently in a publication detailing the microhydration of DNA bases. In the current experiments the backing pressure was 5.8 psi of Ar through a 100  $\mu\text{m}$  diameter nozzle. For the laser desorption experiments, a source that was used to produce carbon clusters<sup>26</sup> was adapted, for which guanine was pressed with graphite powder to produce a 3/8" rod that was then mounted on the ablation apparatus. A Nd-YLF laser operating at 527 nm with a repetition rate of 500 Hz was telescoped with a two lens (1 m and 0.3 m plano-convex) combination onto the graphite rod. Backing pressures behind the nozzle were 90 psi (He) or 100 psi (N<sub>2</sub>) and the pulsed valve was operated at 500 Hz to synchronize with the laser. Time-of flight spectra were recorded for the photoionization energy range between 7.5 and 10.5 eV. The typical step size for the PIE scans is 100 meV and the dwell time was 120 s for the laser desorption experiments, and 50 meV and 62.5 s for thermal vaporization.

Figure 2 shows the PIE curves for guanine acquired with thermal vaporization at three different temperatures (300, 325, and 395 °C) (Figure 2A) and laser desorption where the carrier gas was either N<sub>2</sub> or He (Figure 2B). The PIE curves from thermal vaporization experiments are very different in shape compared to those from laser desorption experiments. As will be discussed below, different wavelength dependences of the photoionization efficiency for different tautomers are expected. Therefore the different shapes of the photoionization curves can be correlated with different tautomer distributions. The thermal vaporization PIE curves shows a very gentle curvature with an

onset at  $7.75 \pm 0.05$  eV, while the laser desorption experiments show a dramatic rise in intensity at 8.2 eV. The error in the energy scale for the laser desorption experiment is  $\pm 0.1$  eV. The higher signal to noise ratio of the thermal vaporization experiments, especially at higher vaporization temperatures (325 and 395 °C), is due to the higher guanine density in the supersonic molecular beam together with higher detection repetition rate, 8 KHz, as opposed to 0.5 KHz of the laser desorption experiments. There are also the mechanical complications of a rotating and translating rod coupled to a pulsed valve and laser. Shown in the inset of Figure 2A is a PIE curve derived from integrating the photoelectron (PE) spectrum reported by Lin *et al.*<sup>17</sup> It is in agreement with our PIE curves up to 9 eV for the two thermal vaporization data sets recorded at 395 °C with Kr in the gas filter. When Ar is used in the gas filter, 2<sup>nd</sup> harmonic radiation is transmitted along with the fundamental below 7.8 eV, complicating the determination of ionization onsets. With Kr in the gas filter, the onset for the thermal vaporization PIE curves measured in this work is  $7.75 \pm 0.05$  eV, a remarkable agreement with the onset for the PE spectrum at 7.8 eV.

A comparison with the PE spectrum reported by Lin *et al.*<sup>17</sup> also shows that only the ground electronic state is accessed below 9 eV in the PIE curves. Theoretical work by Dolgounitcheva *et al.*<sup>23</sup> confirms that this is at least the case for tautomers 1-5. Therefore the shapes of the PIE curves up to 9 eV depend mostly on the Franck-Condon overlap of the neutral and cation ground electronic states, which differ for the different tautomers. To aid the interpretation of the PIE spectra, we performed ab-initio calculations of the VIE's and AIE's for the eight lowest lying tautomers of guanine at the B3LYP level with the 6-311+G(d,p) basis set using Gaussian 03,<sup>27</sup> the results are shown in Table 1. Geometry optimizations were carried out for the neutral and cation ground

states of each tautomer, and AIE's are obtained from the differences in the ground state energies. Zero point energy (ZPE) corrections showed minimal change ( $< 0.012$  eV) in the AIE's. The VIE's were obtained by single-point energy calculations of cations with neutral ground state geometries. For simplicity, the tautomers are numerically labeled in accordance to their energetic ordering in the neutral state. However, it must be noted that the order for the two lowest energy tautomers are switched in this calculation compared to other levels of theory.<sup>3</sup> Given the small energy difference between the two tautomers, 0.015 eV with ZPE correction (0.019 eV without), this switching of energetic ordering between different levels of theory is not too surprising. Also shown in Table 1 are the calculated VIE's of Shukla and Leszczynski<sup>21</sup> and Marian;<sup>11</sup> our VIE's are in complete agreement with the former, and 0.11-0.12 eV higher compared to the latter.

The four tautomers that were identified in the He droplet experiments are tautomers 1-4. The calculated AIE's for these tautomers are 7.80, 7.68, 7.70 and 7.75 eV, respectively. The measured onset in the PIE curves for the thermal vaporization experiments is 7.75 eV, and assuming this onset is adiabatic in nature, then the measured AIE is 7.75 eV for thermal vaporized guanine. This is consistent with the presence of the four lowest energy tautomers (which lie within 0.1 eV of each other) in our experiment, in agreement with the thermal vaporization He droplet experiments.<sup>10</sup> The vaporization temperatures in the current experiments are in the range of 300-395 °C while the He droplet experiments were performed at 350 °C. In addition to the four tautomers seen in the helium droplet experiments, tautomer 5, which lies 0.19 eV above tautomer 1 with a calculated AIE of 7.76 eV, could also be populated in the thermal experiments. The VIE's calculated for tautomers 1-5 are 8.16, 8.02, 8.00, 8.02 and 8.04 eV, respectively,



which gives a difference of 0.36, 0.34, 0.30, 0.27 and 0.28 eV from the calculated AIE's. This difference in the ionization energies, especially for the two lowest energy tautomers, has been observed before in theoretical calculations<sup>13,14,20</sup> and has been commented upon. It suggests a poor Frank-Condon overlap between the neutral and cation potential energy surfaces which would lead to a gentle curve in the PIE as opposed to a sharp onset. This is indeed observed in the experimental PIE for the thermal vaporization experiments. The neutral and cation geometries of three representative tautomers are shown in Figure 3. It is readily apparent that the NH<sub>2</sub> (amino) moiety undergoes a significant geometry change when it is ionized, becoming coplanar with the ring for the five lowest energy tautomers. This change in geometry would give rise to the gentle curvature observed in the PIE curves.

Now we turn our attention to the three tautomers that lie approximately 0.25 eV above tautomer 1 which were observed in the previously published laser desorption molecular beam experiments in addition to tautomer 3.<sup>3</sup> The PIE curves shown in Figure 2B for the laser desorbed guanine are very different from the thermal case. There is a sharp rise in signal at 8.2 eV. This onset in ionization within the large error limits ( $\pm 0.1$ ) agrees well with the AIE's calculated for tautomer 6 and 7, which are 8.04 and 8.12 eV, respectively. Furthermore, with the absence of the amino moiety in these two tautomers, there is only minor geometry change upon ionization which is reflected in the calculated VIE's, 8.18 and 8.25 eV, being very similar to the calculated AIE's. The difference between the VIE and AIE for these tautomers is 0.13 and 0.14 eV, respectively, which is half of that for the lower energy tautomers 1-5. Therefore the Franck-Condon overlap between the neutral and cation ground state potential energy surfaces should be considerably better, resulting in a relatively sharp rise in the PIE, consistent with the experimental observation.

Tautomer 8 could also be populated in the laser desorption experiments with calculated AIE and VIE's of 8.17 and 8.44, respectively. However, with poor Frank-Condon overlap comparable to the low lying tautomers, its PIE signature would be hidden by the more dominant tautomers 6 and 7.

The picture that emerges from the comparison of PIE curves from thermally vaporized and laser desorbed guanine is a difference in the tautomer distributions between the two experimental methods. The different tautomers of guanine are likely to have similar ionization cross sections but their Franck-Condon overlaps differ significantly; this is particularly relevant below 9 eV, where only the ground electronic state of the cation should be accessed. Therefore it seems that in thermal desorption experiments, only tautomers 1-4, and perhaps 5, are populated, producing gentle PIE onsets due to poor FC overlap associated with a large difference between AIE and VIE. On the other hand, in laser desorption experiments, tautomers 6 and 7 are also present and because of their better FC overlap these tautomers dominate the PI signal with a sharp onset. This result would explain why tautomers 6 and 7 are absent in the He droplet data and present in the laser desorption data. The fact that the lower energy keto tautomers were not observed in the R2PI data could still be due to the dynamics of the excited neutral states.

An unequivocal experimental determination of the ionization energies of each guanine tautomer will require more sophisticated spectroscopic approaches. Two such methods are being implemented in our group. The first involves utilizing Mass Analysed Threshold Ionization (MATI), demonstrated elegantly by Choi et al.<sup>28</sup> for the DNA base Thymine, and the second is an IR-VUV 2-color photoionization scheme<sup>29</sup> which follows in the spirit

of the work performed by De Vries<sup>1</sup> and Mons.<sup>3</sup> With both of these schemes and utilizing VUV ionization, it will be possible to bypass the intermediate excited states of the neutral guanine molecule and to directly probe their photoionization dynamics.

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**Table 1: Computed  $\Delta E$ , VIE, and AIE for guanine tautomers. All energies in eV.**

N	Tautomer	This Work <sup>a</sup>			Previous Work	
		$\Delta E$	AIE	VIE	VIE <sup>b</sup>	VIE <sup>c</sup>
1	Keto-N7H	0.000	7.80	8.16	8.16	8.04
2	Keto-N9H	0.015	7.68	8.02	8.02	7.91
3	Enol-N9H	0.070	7.70	8.00	8.00	7.89
4	Enol-N9H- <i>trans</i>	0.098	7.75	8.02	8.02	7.90
5	Enol-N7H	0.190	7.76	8.04	8.05	7.93
6	Keto-N7H-imino	0.256	8.04	8.18	8.18	8.07
7	Keto-N7H-imino- <i>cis</i>	0.267	8.12	8.25	8.25	8.13
8	Keto-N7H-N3H	0.276	8.17	8.44	8.44	8.33

N refers to tautomer numbering scheme used in this work in increasing relative energy. AIE and VIE represent adiabatic and vertical ionization energy, with no ZPE correction.  $\Delta E$  is relative energy including ZPE correction, with respect to Keto-N7H tautomer. (a) this work, calculated using B3LYP/6-311+G(d,p); (b) B3LYP/6-311++G(d,p)<sup>21</sup>; (c) Restricted Kohn-Sham (B3-LYP functional)/TZVP<sup>11</sup>.

## Figure Captions

Figure 1. Geometry of the Keto-N9H guanine tautomer, which is typically considered the ground state structure. The four labile hydrogen atoms are indicated, and the seven binding sites for them are the five nitrogen atoms and the oxygen atom. To form enol structures, an H atom migrates from an NH group to the O atom.

Figure 2. PIE curves of guanine prepared by thermal vaporization (panel A) and laser desorption (panel B). The thermal vaporization experiments in a molecular beam seeded in Ar are performed at 300 °C (○), 325 °C (□), and 395 °C (△) with Ar in the gas filter; signal below 7.8 eV arise from 2<sup>nd</sup> harmonic light being transmitted through the gas filter. The three thermal vaporization PIE's are normalized to each other at 10.5 eV. The inset in panel A shows thermal vaporization data (▽, -) at 395 °C with Kr in the gas filter, together with integrated photoelectron spectrum (solid black line) reported by Lin *et al.* (317 °C vaporization cell).<sup>17</sup> The laser desorption experiments in a molecular beam seeded in He (8) and N<sub>2</sub> (▲) with Ar in the gas filter are normalized to each other at 8.8 eV. The eight lowest lying tautomers of guanine are denoted by the numbers in energetic order. The grey solid lines represent AIE's and (B) represent VIE's calculated in this work and reported in Table 1.

Figure 3. Guanine tautomers 1, 3, and 6, representing the geometry change upon ionization for each class of tautomers. Notice that for the tautomers without a



NH<sub>2</sub> group, the molecular structures are essentially planar in both neutral and cation ground states, whereas for the tautomers with a NH<sub>2</sub> group, the hydrogen atoms of the NH<sub>2</sub> group are out of plane in the neutral ground state.

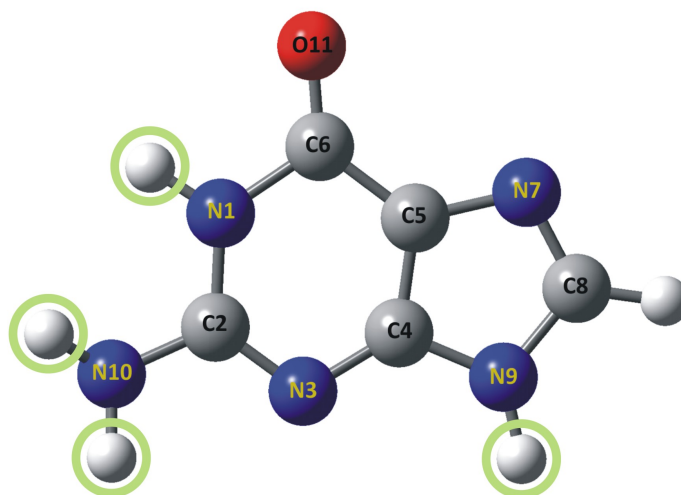


Figure 1

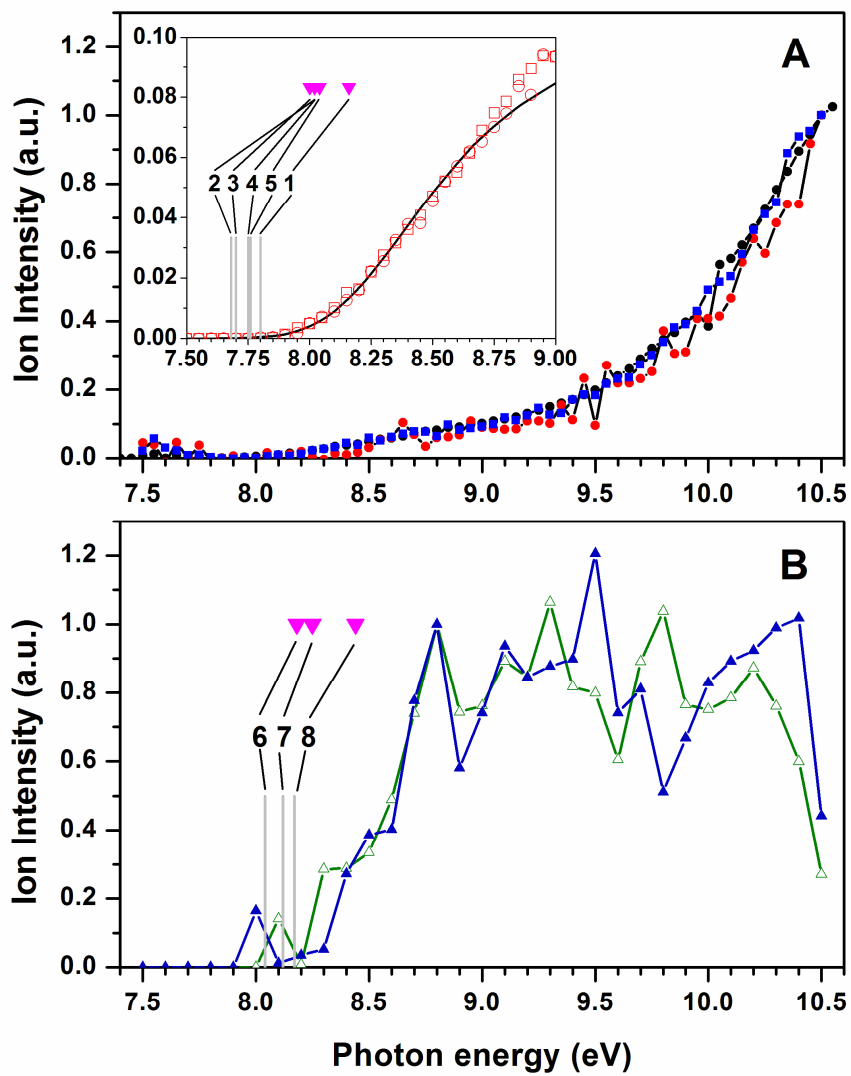


Figure 2

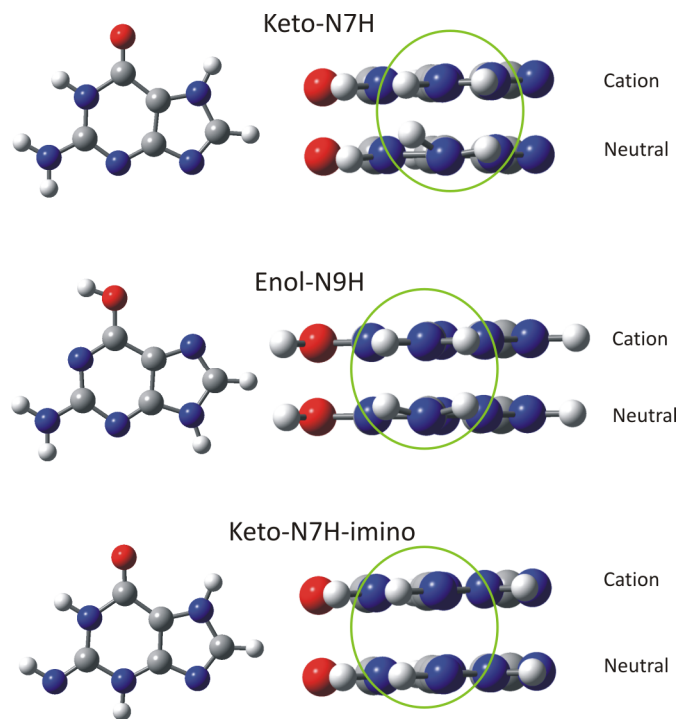


Figure 3

FIGURE FOR TOC

