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# Hydrogen bonds in the nucleobase-gold complexes: Photoelectron spectroscopy and density functional calculations

Guo-Jin Cao, Hong-Guang Xu, Ren-Zhong Li, and Weijun Zheng<sup>a)</sup>

*Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

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The nucleobase-gold complexes were studied with anion photoelectron spectroscopy and density functional calculations. The vertical detachment energies of uracil-Au<sup>-</sup>, thymine-Au<sup>-</sup>, cytosine-Au<sup>-</sup>, adenine-Au<sup>-</sup>, and guanine-Au<sup>-</sup> were estimated to be  $3.37 \pm 0.08$  eV,  $3.40 \pm 0.08$  eV,  $3.23 \pm 0.08$  eV,  $3.28 \pm 0.08$  eV, and  $3.43 \pm 0.08$  eV, respectively, based on their photoelectron spectra. The combination of photoelectron spectroscopy experiments and density functional calculations reveals the presence of two or more isomers for these nucleobase-gold complexes. The major isomers detected in the experiments probably are formed by Au anion with the canonical tautomers of the nucleobases. The gold anion essentially interacts with the nucleobases through N-H...Au hydrogen bonds. © 2012 American Institute of Physics. [doi:10.1063/1.3671945]

## I. INTRODUCTION

The interactions between gold clusters and DNA have attracted tremendous attentions because of their importance in nanotechnology and biotechnology. It has been reported that DNA can be used as templates to assemble gold nanoparticles into macroscopic functional materials.<sup>1-3</sup> In addition, it has been suggested that gold nanoparticles modified with single-stranded oligonucleotides can be used as probes for DNA sequencing and disease diagnosis,<sup>4-6</sup> or can be used to mediate gene transfer.<sup>7</sup> It is crucial to investigate the gold-nucleobase interactions in detail in order to get insight into the interactions of gold with DNA. Although most of the DNA molecules used for gold nanoparticle assembling are thiolated and the thiol-gold interaction is dominant, the nucleobase-gold interactions cannot be ignored.<sup>8</sup> Moreover, better understanding of the nucleobase-gold interactions might be helpful for people to design special DNA molecules for gold nanoparticle assembling without using thiol linkers.<sup>9</sup> Many experiments have been conducted to study the interactions of nucleobase with gold surfaces and gold nanoparticles. The self-assembly and chemisorption of DNA bases on Au(111) surface were investigated with scanning tunneling microscopy.<sup>10-12</sup> The DNA nucleosides bound to gold nanoparticles in aqueous solution were studied with surface-enhanced Raman scattering.<sup>13</sup> The temperature-programmed desorption experiments show that the heat of desorption of DNA bases from gold thin film decreases in the order of  $G > A > C > T$ .<sup>8</sup> The base-dependent competitive adsorption of single-stranded DNA on polycrystalline Au films indicates that the adsorption affinity to gold surface decreases in the order of  $A > C \geq G > T$ .<sup>14</sup> On the other hand, the isothermal titration calorimetry studies on the binding of DNA bases to gold nanoparticles show that the strength of nucleobase-gold interaction decreases in the

order of  $C > G > A > T$ .<sup>9</sup> While these experiments all agree that the interaction between thymine and gold is relatively weak, it is unclear why different experiments got different orders for guanine, adenine, and cytosine. That could be due to the effects of complex environments in the condensed phases. It is very necessary to investigate the nucleobase-gold interactions in more isolated systems in the gas phase in order to exclude the effects of the environments.

Interactions of nucleobases with many metal ions or atoms have been investigated in the gas phase with a number of experimental techniques. Cerda and Wesdemiotis determined the bond energies between nucleobases and alkali metal ions ( $M = \text{Li}^+, \text{Na}^+, \text{and K}^+$ ) using collisionally activated dissociation experiments.<sup>15</sup> Rodgers and Armentrout investigated the non-covalent interactions of nucleobases with alkali metal ions and the first-row transition metal ions ( $M = \text{Li}, \text{Na}, \text{K}, \text{and Sc-Zn}$ ) using threshold collision-induced dissociation method.<sup>16,17</sup> They suggested that the interactions with adenine's amino group are strong enough to disrupt hydrogen bonding in A-T (A-U) base pairs for  $\text{Li}^+, \text{Na}^+, \text{and transition metal ions}$ . Elimination of purine and HCN from  $M^+$ -adenine complexes ( $M = \text{Sc}, \text{Ti}, \text{and V}$ ) has also been detected.<sup>17</sup> Pederson *et al.* investigated the photoinduced dehydrogenation processes in the Al-cytosine, Al-guanine, and Mn-guanine complexes.<sup>18-20</sup> Liu *et al.* and Sun *et al.* studied the photodissociation of  $\text{Mg}^+$ -uracil,  $\text{Mg}^+$ -thymine, and  $\text{Mg}^+$ -cytosine complexes and found that the site of bond rupture is at the carbonyl group bound to  $\text{Mg}^+$ .<sup>21,22</sup> Gillis *et al.* studied the structures of hydrated  $\text{Li}^+$ -cytosine and  $\text{Li}^+$ -thymine complexes with infrared multiple photon dissociation and showed that the  $\text{Li}^+$  ion bonds to the  $\text{O}_4$  site in both cytosine and thymine.<sup>23</sup> Krasnokutski *et al.* have investigated Al-uracil, Al-thymine, Li-uracil, Li-thymine, and Li-adenine complexes with zero kinetic energy electron spectroscopy.<sup>24-26</sup> They found that Al and Li atoms prefer to bind to the  $\text{O}_4$  atom of uracil and thymine. There is no report of gas-phase experimental studies on nucleobase-Au complexes although there are many

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: zhengwj@iccas.ac.cn. Tel.: +86 10 62635054. Fax: +86 10 62563167.

experiments on the interactions of nucleobases with gold films and nanoparticles.

There have been numerous theoretical investigations on the complexes of nucleobases and gold clusters.<sup>27–40</sup> Kryachko and Remacle<sup>29</sup> conducted theoretical studies on the interactions of Au<sub>3</sub> and Au<sub>4</sub> clusters with DNA bases. They found that the most stable planar complexes were formed via N-H...Au or O-H...Au bonds. They termed these bonds nonconventional hydrogen bonds. In fact, non-conventional hydrogen bonds in the form of X-H...M (M = transition metal) have been introduced previously by Brammer *et al.*<sup>41–45</sup> and have also been investigated experimentally and theoretically by a number of research groups.<sup>46–52</sup> According to the criteria of X-H...M hydrogen bond suggested by Brammer *et al.*,<sup>44</sup> the bridging hydrogen atom should be bonded to an electronegative element (X) and the metal atom (M) involved should be electron-rich. Gold is a late transition metal with a filled *d* shell. It is highly electronegative,<sup>53</sup> somewhat similar to the halogens such as Br and I. Therefore, it has been proposed by theoreticians that gold and gold clusters are able to participate in the formation of X-H...M hydrogen bonds in a number of systems, such as Au<sub>n</sub>-nucleobase,<sup>27–40</sup> Au<sub>n</sub>-(HF)<sub>m</sub>,<sup>54</sup> Au<sub>n</sub>-(H<sub>2</sub>O)<sub>m</sub>,<sup>55</sup> and Au<sub>n</sub>-(NH<sub>3</sub>)<sub>m</sub> complexes.<sup>56,57</sup> Recently, Nuss and Jansen<sup>58</sup> provided the first crystallographic characterization of N-H...Au hydrogen bonds in [Rb([18]crown-6)(NH<sub>3</sub>)<sub>3</sub>]Au·NH<sub>3</sub>. Despite the abundance of theoretical calculations on Au<sub>n</sub>-nucleobase complexes, it is yet to be confirmed by experiments whether the nucleobases and gold can really form X-H...Au hydrogen bonds.

In order to help the understanding of the nucleobase-gold interactions, here we conducted a joint photoelectron spectroscopy and theoretical study on the structures and electronic properties of the nucleobase-Au complexes.

## II. EXPERIMENTAL AND THEORETICAL METHODS

### A. Experimental

The experiments were conducted on a home-built apparatus consisting of a time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer, which has been described in Ref. 59. The nucleobase-Au complexes were produced by laser vaporization of rotating and translating disk targets with the second harmonic (532 nm) of a nanosecond Nd:YAG laser (Continuum Surelite II-10). Each disk target was prepared by pressing a powder mixture of gold (99.99%) and nucleobase (uracil, Alfa Aesar, 99+%; thymine, Alfa Aesar, 97%; cytosine, Sigma-Aldrich, 99%; adenine, Sigma-Aldrich, 99%; guanine, Alfa Aesar, 98+%) at a molar ratio of 1:2. Helium gas with 5.5 atm backing pressure was delivered through a pulsed valve into the laser ablation source to cool the formed nucleobase-Au complexes. The nucleobase-Au cluster anions were mass-selected and photodetached with 266 nm or 193 nm photons. The resultant electrons were energy-analyzed with the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated using the known spectrum of Cu<sup>-</sup> and Au<sup>-</sup>. The resolution of the photoelectron spectrometer was ~40 meV at 1eV kinetic energy.

### B. Theoretical

We investigated the structures of the nucleobase-Au complexes with density functional calculations using B3LYP functional incorporated in the GAUSSIAN 09 program package.<sup>60</sup> The 6-31++G(*d,p*) basis set was used for the C, H, N, and O atoms, and the LanL2DZ basis set containing an effective core potential was used for gold. All the 13 keto/enol tautomers of uracil,<sup>61–63</sup> 13 keto/enol tautomers of thymine,<sup>64–66</sup> 14 amino/imino/keto/enol tautomers of cytosine,<sup>67,68</sup> 14 amino/imino tautomers of adenine,<sup>69,70</sup> and 36 different tautomers of guanine<sup>71–73</sup> were taken into account in the search of low-energy isomers of these complexes.

No symmetry constraint was imposed during the geometry optimizations. The vibrational frequencies were calculated to confirm that the structures are real local minima. The natural bond orbital analyses<sup>74,75</sup> were performed to gain insights into the charge distributions and the bonding properties of the nucleobase-Au complexes. The corrections of zero-point vibrational energy were considered in the calculations of relative energies.

### III. EXPERIMENTAL RESULTS

Figure 1 shows the photoelectron spectra of nucleobase-Au anions obtained with 266 and 193 nm photons. The vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) of nucleobase-Au anions estimated from their photoelectron spectra are listed in Table I. The spectra

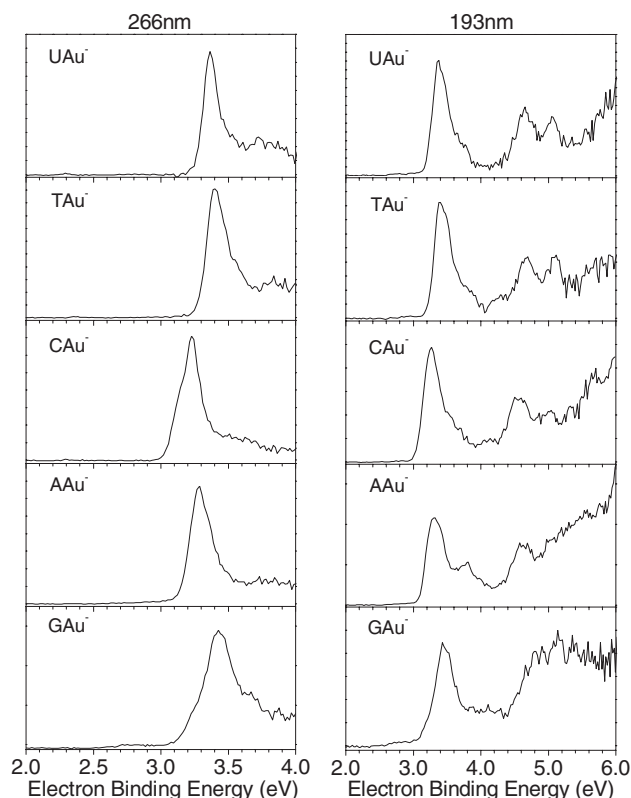


FIG. 1. Photoelectron spectra of nucleobase-Au anions recorded with 266 nm and 193 nm photons.

TABLE I. Experimentally observed VDEs and ADEs from the photoelectron spectra of nucleobase-Au<sup>-</sup> complexes.

	VDE (eV)	ADE (eV)
UAu <sup>-</sup>	3.37(8) <sup>a</sup>	3.27(8)
TAu <sup>-</sup>	3.40(8)	3.29(8)
CAu <sup>-</sup>	3.23(8)	3.06(8)
AAu <sup>-</sup>	3.28(8)	3.15(8)
GAu <sup>-</sup>	3.43(8)	3.20(8)

<sup>a</sup>The numbers in parentheses indicate the uncertainties in the last digit.

taken with 266 nm photons are dominated by a single, intense, and relatively sharp peak, and those taken with 193 nm photons show more features at higher binding energy. Uracil-Au<sup>-</sup> (UAu<sup>-</sup>) has three major features centered at 3.37 eV, 4.65 eV, and 5.05 eV, respectively. Similarly, thymine-Au<sup>-</sup> (TAu<sup>-</sup>) has three major features centered at 3.40 eV, 4.69 eV, and 5.12 eV; cytosine-Au<sup>-</sup> (CAu<sup>-</sup>) has three major features centered at 3.23 eV, 4.58 eV, and 5.04 eV, respectively. The spectra of UAu<sup>-</sup>, TAu<sup>-</sup>, and CAu<sup>-</sup> also have a broad feature above 5.5 eV. Adenine-Au<sup>-</sup> (AAu<sup>-</sup>) has two resolved major features centered at 3.28 and 4.62 eV, and an unresolved broad feature between 4.9 and 6.0 eV. In addition, a small shoulder in the range of 3.5–4.0 eV is very obvious in the AAu<sup>-</sup> spectrum taken with 193 nm photons. Guanine-Au<sup>-</sup> (GAu<sup>-</sup>) has a low-binding feature centered at 3.43 eV and an unresolved broad feature above 4.5 eV. For all the spectra of nucleobase-Au anions, small shoulders can be observed behind the first main peaks. These shoulders are more likely due to the existence of low-lying isomers as the intensities of the shoulders varied with the source conditions. The change of source conditions can change the relative populations of the low-lying isomers. More isomers are formed under “hot” source condition. If the source conditions are controlled very well, the numbers of these isomers can be minimized. As can be seen in the spectra of AAu<sup>-</sup>, the shoulder at 193 nm is more intense than that at 266 nm, probably due to the deterioration of source conditions at 193 nm.

It is interesting to compare the photoelectron spectra of nucleobase-Au<sup>-</sup> complexes (Figure 1, 193 nm) with that of gold anion (Au<sup>-</sup>). As it has been measured previously, Au<sup>-</sup> has photoelectron peaks at 2.31, 3.45, and 4.97 eV.<sup>76</sup> Thus, the first peak of UAu<sup>-</sup> shifts to higher binding energy by ~1.06 eV relative to the first peak of Au<sup>-</sup>, the second peak shifts by ~1.20 eV relative to that of Au<sup>-</sup>, but the third peak of UAu<sup>-</sup> shifts by only 0.08 eV relative to that of Au<sup>-</sup>. The spectra of TAu<sup>-</sup> and CAu<sup>-</sup> display similar shifts relative to that of Au<sup>-</sup>. For AAu<sup>-</sup>, the first and second peaks shift by 0.97 and 1.17 eV, respectively. The first peak of GAu<sup>-</sup> shifts by ~1.12 eV. The high-binding features of AAu<sup>-</sup> and GAu<sup>-</sup> are relatively broader. Therefore, we cannot estimate the exact shifts for their third peaks. But, we can discern that their spectra follow the same pattern as those of UAu<sup>-</sup>, TAu<sup>-</sup> and CAu<sup>-</sup>. The large shifts of the first and second peaks and the small shift of the third peak imply that only the first two orbitals of Au<sup>-</sup> are affected significantly by the nucleobases.

#### IV. THEORETICAL RESULTS AND DISCUSSION

The structures of TAU<sup>-</sup>, CAu<sup>-</sup>, AAu<sup>-</sup>, and GAu<sup>-</sup> have been calculated previously by Kryachko,<sup>37</sup> and those of UAU<sup>-</sup> and AAu<sup>-</sup> have been computed by Valdespino-Saenz and Martinez.<sup>33,38</sup> These earlier works were focused on the complexes formed by Au<sup>-</sup> and the predominant forms of tautomers of the nucleobases. However, the nucleobases in the gas phase or in the condensed phases may have various tautomers. In this work, in the search of low-energy isomers of nucleobase-Au<sup>-</sup> complexes, we considered the complexes formed by Au<sup>-</sup> and all possible tautomers of the nucleobases reported in the literature and optimized their full geometric structures without any symmetry restriction. The structures of the typical low-lying isomers of UAU<sup>-</sup>, TAu<sup>-</sup>, and CAu<sup>-</sup> are shown in Figure 2, and those of AAu<sup>-</sup> and GAu<sup>-</sup> are

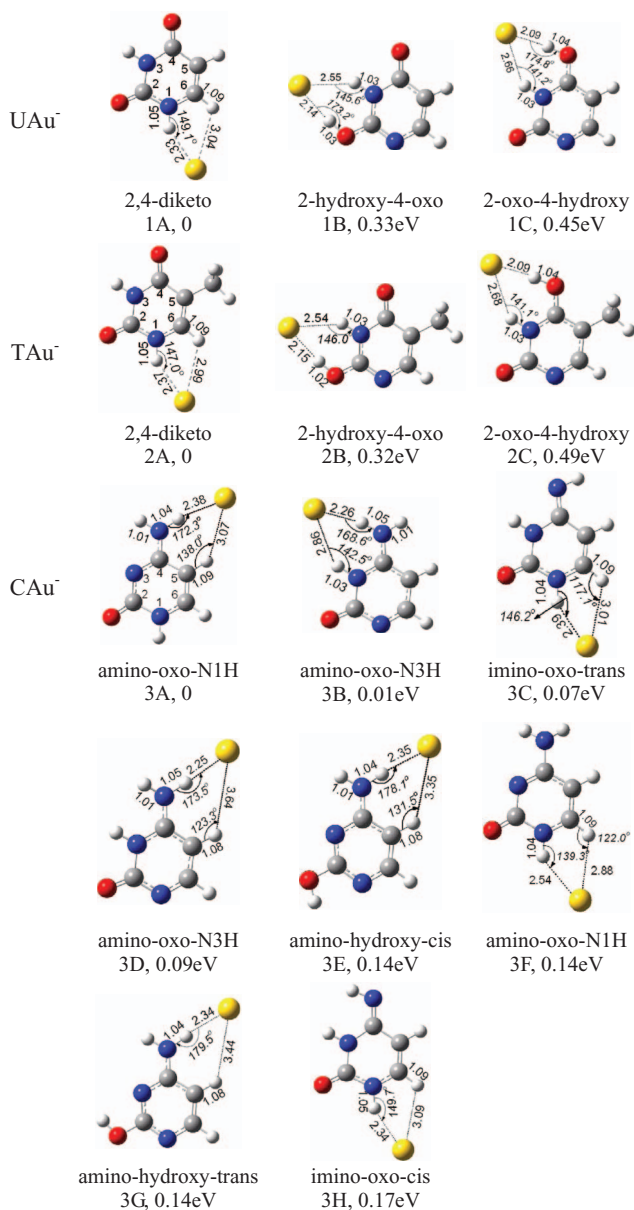


FIG. 2. Structures and relative energies of the low-lying isomers of uracil-Au, thymine-Au, and cytosine-Au anions. The bond distances are in angstrom and the bond angles are in degrees.

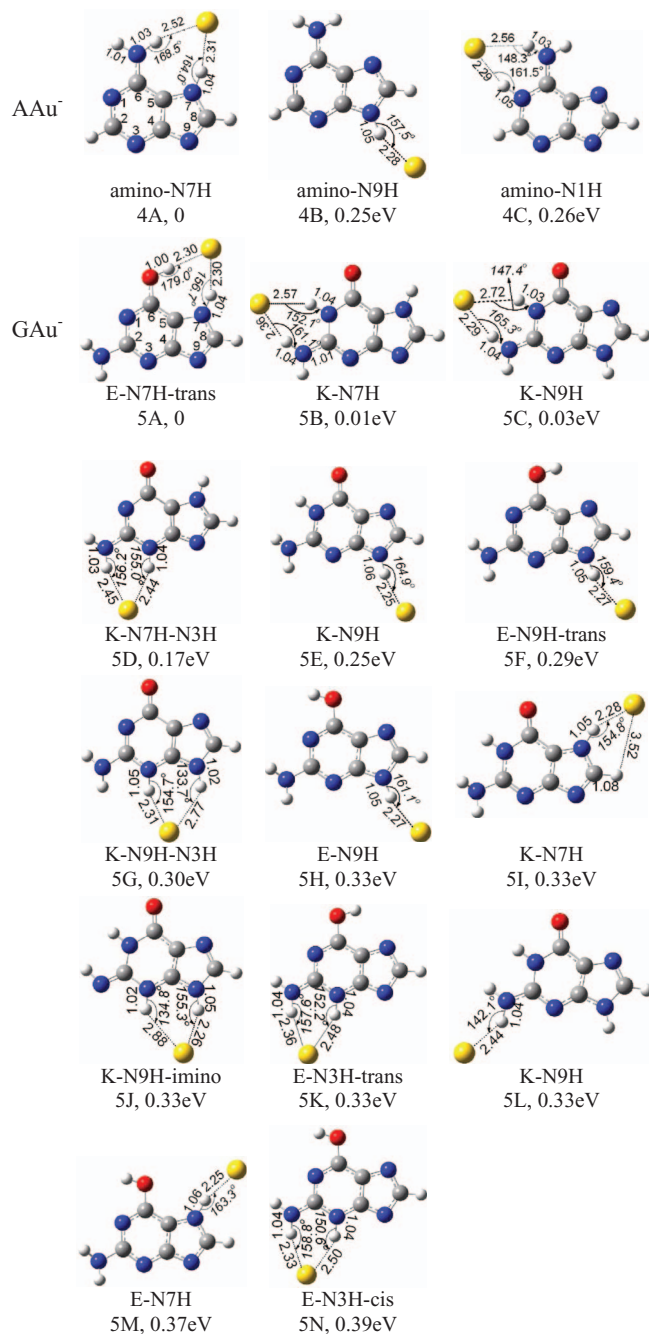


FIG. 3. Structures and relative energies of the low-lying isomers of adenine-Au and guanine-Au anions. The bond distances are in angstrom and the bond angles are in degrees.

shown in Figure 3. The calculated relative energies, VDEs, ADEs, some geometrically important distances, and the other key features of these isomers are summarized in Table II.

### A. UAu<sup>-</sup>, TAU<sup>-</sup>, and CAu<sup>-</sup>

As can be seen in Figure 2, the low-lying isomers of UAu<sup>-</sup> all have planar structures with C<sub>s</sub> symmetry. In isomer 1A, the gold anion interacts with the N1-H and C6-H bonds of the 2,4-diketo tautomer of uracil. The VDE and ADE of isomer 1A are calculated to be 3.41 and 3.28 eV, respectively, in good agreement with the experimental values (3.37

and 3.27 eV). The  $\angle$ N1-H... Au angle in 1A is about 149.1°. The N1-H bond elongates by 0.04 Å relative to that of uracil monomer. Isomers 1B and 1C are less stable than isomer 1A by 0.33 and 0.45 eV, respectively. In isomer 1B, the gold anion interacts with the O7-H and N3-H bonds of the 2-hydroxy-4-oxo tautomer of uracil. In isomer 1C, the gold anion interacts with the O8-H and N3-H bonds of the 2-oxo-4-hydroxy tautomer of uracil. The theoretical VDEs and ADEs of isomers 1B (3.85 and 3.70 eV) and 1C (3.90 and 3.78 eV) are much higher than the experimental measurements. Thus, isomer 1A is the most probable isomer detected in our experiments. Isomers 1B and 1C may contribute to the low-intensity shoulder at  $\sim$ 3.8 eV in the photoelectron spectrum of UAu<sup>-</sup>. The structure of isomer 1A from our calculations is consistent with theoretical calculations conducted by Valdespino-Saenz and Martinez<sup>33</sup> although their calculated VDE (3.8 eV) is higher than our experimental and theoretical values.

The low-lying isomers of TAU<sup>-</sup> also have C<sub>s</sub> symmetry. The isomers of TAU<sup>-</sup> can be considered as derived from the isomers of UAu<sup>-</sup> by attaching a CH<sub>3</sub> group to the C5 atom of uracil. Isomers 2A, 2B, and 2C correspond to the 2,4-diketo, 2-hydroxy-4-oxo, and 2-oxo-4-hydroxy tautomers of thymine, respectively. The VDE and ADE of isomer 2A are calculated to be 3.36 and 3.24 eV, respectively, in excellent agreement with the experimental values (3.40 and 3.29 eV). Similar to isomer 1A, the  $\angle$ N1-H... Au angle of isomer 2A is about 147.0°. The N1-H bond elongates by 0.04 Å compared to that of thymine monomer. Isomers 2B and 2C are less stable than isomer 1A by 0.32 and 0.49 eV, respectively. The theoretical VDEs of isomer 2B and 2C are calculated to be 3.80 and 3.88 eV, respectively. These values are very close to the low-intensity shoulder behind the first main peak in the photoelectron spectrum of TAU<sup>-</sup>. We suggest that isomer 2A corresponds to the major peaks observed in the spectrum of TAU<sup>-</sup>, while isomers 2B and 2C contribute to the low-intensity shoulder at  $\sim$ 3.80 eV. The structure of isomer 2A is in good agreement with the calculations of Kryachko.<sup>37</sup> The theoretical VDE and ADE from our calculations are slightly higher than those calculated by Kryachko (3.258 and 3.030 eV), but they can still be considered as reasonable agreement at this level of theory.

Figure 2 shows eight low-lying isomers of CAu<sup>-</sup>. They are very close in energy, with the energy differences within 0.17 eV. In these isomers, the gold anion mainly interacts with the (N8-H, C5-H), (N8-H, N3-H), or (N1-H, C6-H) bonds of amino-oxo-N1H, amino-oxo-N3H, imino-oxo, or amino-hydroxy tautomer. For example, isomer 3A has the gold anion interacting with the N8-H and C5-H bonds of the amino-oxo-N1H tautomer. It is analogous to the most stable structure of CAu<sup>-</sup> calculated by Kryachko.<sup>37</sup> Isomer 3B has the gold anion interacting with the N8-H and N3-H bonds of the amino-oxo-N3H tautomer. For all the isomers (3A, 3B, 3D, and 3G) with the Au atom interacting with the N8-H bond, the  $\angle$ N8-H... Au angles are near or larger than 170°. For the isomers (3C, 3F, and 3H) with the gold anion interacting with the N1-H bond, the  $\angle$ N1-H... Au angles are near or larger than 140°. The theoretical VDE of isomer 3A is calculated to be 3.22 eV, in excellent agreement with the experimental measurement (3.23 eV). We suggest that it is the most probable isomer in

TABLE II. Relative energies, VDEs and ADEs of the low-lying isomers of nucleobase-Au anions as well as some key features with the N-H...Au hydrogen bond obtained by DFT calculations. The bond distances are in angstrom and the bond angles are in degrees.

Isomer	$\Delta E$ (eV)	Symmetry	state	$\Delta R(\text{N-H})^a$	$R(\text{H}\cdots\text{Au})^a$	$\angle\text{N-H}\cdots\text{Au}^a$	BE (eV)	Natural charge	ADE (eV)		VDE (eV)		
									Au	Theo.	Expt.	Theo.	Expt.
UAu <sup>-</sup>	1A	0.00	C <sub>s</sub>	<sup>1</sup> A'	0.04	2.33	149.1	0.98	-0.86	3.28	3.27	3.41	3.37
	1B	0.33	C <sub>s</sub>	<sup>1</sup> A'	0.02	2.55	145.6	1.46	-0.76	3.70		3.85	
	1C	0.45	C <sub>s</sub>	<sup>1</sup> A'	0.02	2.66	141.2	1.54	-0.75	3.78		3.90	
TAu <sup>-</sup>	2A	0.00	C <sub>s</sub>	<sup>1</sup> A'	0.04	2.37	147.0	0.91	-0.87	3.24	3.29	3.36	3.40
	2B	0.32	C <sub>s</sub>	<sup>1</sup> A'	0.02	2.54	146.0	1.40	-0.77	3.67		3.80	
	2C	0.49	C <sub>s</sub>	<sup>1</sup> A'	0.02	2.68	141.1	1.50	-0.75	3.77		3.88	
CAu <sup>-</sup>	3A	0.00	C <sub>s</sub>	<sup>1</sup> A'	0.03	2.38	172.3	0.83	-0.89	3.14	3.06	3.22	3.23
	3B	0.01	C <sub>1</sub>	<sup>1</sup> A	0.04	2.26	168.6	1.12	-0.84	3.40		3.47	
	3C	0.07	C <sub>s</sub>	<sup>1</sup> A'	0.03	2.39	146.2	0.86	-0.88	3.17		3.29	
	3D	0.09	C <sub>1</sub>	<sup>1</sup> A	0.04	2.25	173.5	1.04	-0.85	3.35		3.43	
	3E	0.14	C <sub>1</sub>	<sup>1</sup> A	0.03	2.35	178.1	0.72	-0.89	3.04		3.10	
	3F	0.14	C <sub>1</sub>	<sup>1</sup> A	0.03	2.54	139.3	0.69	-0.90	3.00		3.13	
	3G	0.14	C <sub>s</sub>	<sup>1</sup> A'	0.03	2.34	179.5	0.75	-0.88	3.06		3.14	
AAu <sup>-</sup>	3H	0.17	C <sub>s</sub>	<sup>1</sup> A'	0.04	2.34	149.7	0.84	-0.87	3.15		3.27	
	4A	0.00	C <sub>s</sub>	<sup>1</sup> A'	0.03	2.52	168.5	1.32	-0.82	3.63		3.74	
	4B	0.25	C <sub>1</sub>	<sup>1</sup> A	0.04	2.28	157.5	0.70	-0.86	3.07	3.15	3.20	3.28
GAu <sup>-</sup>	4C	0.26	C <sub>s</sub>	<sup>1</sup> A'	0.04	2.29	161.5	1.51	-0.81	3.84		3.93	
	5A	0.00	C <sub>1</sub>	<sup>1</sup> A	0.03	2.30	156.7	1.45	-0.77	3.73		3.87	
	5B	0.01	C <sub>1</sub>	<sup>1</sup> A	0.03	2.36	161.1	0.94	-0.84	3.30	3.20	3.38	3.43
	5C	0.03	C <sub>1</sub>	<sup>1</sup> A	0.03	2.29	165.3	0.95	-0.84	3.31		3.37	
	5D	0.17	C <sub>1</sub>	<sup>1</sup> A	0.03	2.44	155.0	1.07	-0.84	3.44		3.54	
	5E	0.25	C <sub>1</sub>	<sup>1</sup> A	0.05	2.25	164.9	0.72	-0.85	3.11		3.22	
	5F	0.29	C <sub>1</sub>	<sup>1</sup> A	0.04	2.27	159.4	0.74	-0.86	3.13		3.25	
	5G	0.30	C <sub>1</sub>	<sup>1</sup> A	0.04	2.31	154.7	1.50	-0.83	3.87		4.07	
	5H	0.33	C <sub>1</sub>	<sup>1</sup> A	0.04	2.27	161.1	0.68	-0.86	3.07		3.18	
	5I	0.33	C <sub>1</sub>	<sup>1</sup> A	0.04	2.28	154.8	0.63	-0.87	3.01		3.14	
	5J	0.33	C <sub>s</sub>	<sup>1</sup> A'	0.04	2.26	155.3	1.25	-0.83	3.63		3.77	
	5K	0.33	C <sub>1</sub>	<sup>1</sup> A	0.03	2.36	157.6	1.22	-0.82	3.58		3.65	
	5L	0.33	C <sub>1</sub>	<sup>1</sup> A	0.03	2.44	142.1	0.65	-0.91	3.05		3.13	
	5M	0.37	C <sub>1</sub>	<sup>1</sup> A	0.05	2.25	163.3	0.75	-0.85	3.14		3.25	
5N	0.39	C <sub>1</sub>	<sup>1</sup> A	0.03	2.33	158.8	1.23	-0.82	3.58		3.65		

<sup>a</sup>For the isomers with two sets of N-H...Au groups, the parameters of the stronger ones are shown here.

the experiments. The calculated VDEs of these isomers from 3B to 3H are 3.47, 3.29, 3.43, 3.10, 3.13, 3.14, and 3.27 eV, respectively, also in reasonable agreement with the experimental measurement. So we suggest that existence of isomers 3B-3H in the experiments is also possible. As can be seen in Figure 1, the spectral features of CAu<sup>-</sup> are broad, which is consistent with the existence of many isomers for CAu<sup>-</sup>.

## B. AAu<sup>-</sup> and GAu<sup>-</sup>

As seen in Figure 3, the lowest energy isomer of AAu<sup>-</sup> (4A) has planar structure with C<sub>s</sub> symmetry. We note that isomer 4A has the gold anion interacting with the N10-H and N7-H bonds of the amino-N7H tautomer. The VDE of isomer 4A is calculated to be 3.74 eV. Isomers 4B and 4C are nearly degenerate in energy. They are higher than isomer 4A by 0.25 and 0.26 eV, respectively. Isomer 4B has the gold anion interacting with the N9-H bond of the amino-N9H tautomer. Isomer 4C has the gold anion interacting with the N1-H and N10-H bonds of the amino-N1H tautomer. The calculated VDE of isomer 4B is  $\sim$ 3.20 eV, in good agreement with the VDE (3.28 eV) of the first strong peak in the spec-

trum of AAu<sup>-</sup> (Figure 1). The calculated VDE of isomer 4C is  $\sim$ 3.93 eV, very close to that of 4A, but much higher than the VDE of the first photoelectron spectral peak. Both isomers 4A and 4C have two sets of N-H...Au groups. Therefore, the interaction between the gold anion with adenine in isomer 4A and 4C is stronger than that in isomer 4B, which is also in accordance with their higher VDEs. Isomers 4A and 4C probably contribute to the low-intensity broad feature observed between 3.5 and 4.0 eV in the spectrum of AAu<sup>-</sup> (Figure 1). The structure and VDE of isomer 4B from our calculations are consistent with those of the stable isomer computed by Kryachko.<sup>37</sup> Besides, Valdespino-Saenz and Martinez found that the VDEs of different isomers of AAu<sup>-</sup> are in the range of 3.2–3.8 eV.<sup>38</sup> Although our theoretical calculations found isomer 4A be the most stable isomer, the comparison of theoretical VDEs with the experimental value suggests that isomer 4B is the major isomer in the experiments. That perhaps is because the amino-N9H tautomer is the canonical (major) tautomer of neat adenine.

Figure 3 shows 14 low-lying isomers of GAu<sup>-</sup>. They all have a gold anion interacting with one or two N-H bonds of different tautomers of guanine. Isomers 5A, 5B, and 5C of

$\text{GAu}^-$  are nearly degenerate in energy. Isomer 5A can be considered as a gold anion interacting with the N7-H and O6-H bonds of the E-N7H-trans tautomer of guanine. The theoretical VDE (3.87 eV) and ADE (3.73 eV) of isomer 5A are much higher than the experimental values (3.43 eV and 3.20 eV) estimated from the first strong peak in the spectrum of guanine (Figure 1). Isomer 5B has the gold anion interacting with the N1-H and N2-H bonds of the K-N7H tautomer of guanine. It is the same as the most stable structure of  $\text{GAu}^-$  computed by Kryachko.<sup>37</sup> The theoretical VDEs of isomer 5B from our calculations and Kryachko are 3.38 and 3.30 eV, respectively, also in good agreement. Isomer 5C has the gold anion interacting with the N1-H and N2-H bonds of the K-N9H tautomer. The calculated VDEs (3.38 and 3.37 eV) of 5B and 5C are very close to the experimental value (3.43 eV) estimated from the first strong peak. Isomers 5B and 5C probably are the major ones that contribute to the experimental signals. However, we cannot exclude the existence of the other isomers since they are all very close in energy. Isomers 5A, 5D, 5G, 5J, 5K, and 5N may contribute to the photoelectron signals detected in the range of 3.5–4.0 eV in the spectrum since their theoretical VDEs fall into that region. Isomers 5E, 5F, 5H, 5I, 5L, and 5M may contribute to the long slope from 3.1 to 3.3 eV in the spectrum since their theoretical VDEs are close. As can be seen in Figure 1, the spectral features of  $\text{GAu}^-$  are much broader than those of the other nucleobase-Au complexes. This is consistent with the co-existence of many isomers for  $\text{GAu}^-$ .

Based on the above comparison between theoretical calculations and experimental measurements, we would like to suggest that the major isomers of  $\text{UAu}^-$ ,  $\text{TAu}^-$ ,  $\text{CAu}^-$ ,  $\text{AAu}^-$ , and  $\text{GAu}^-$  detected in the experiments probably are isomers 1A, 2A, 3A, 4B, and (5B, 5C). In these major isomers, the Au anion mainly interacts with the canonical tautomers of the nucleobase. As can be seen from the calculated results in Figure 2, Figure 3, and Table II, there are some similarities in the geometrical parameters of the low-lying isomers of nucleobase- $\text{Au}^-$ . For example, in these isomers, the gold anion always interacts with the nucleobase through one or two N-H bonds. The N-H...Au interaction exists in all nucleobase- $\text{Au}^-$  complexes. In some cases, the C-H...Au interaction also exists, but it is fairly weak because the H...Au distance for C-H...Au is near or larger than 3 Å, which is larger than the sum of the van der Waals radii of H ( $r_{\text{H}} = 1.20$  Å) (Refs. 77 and 78) and Au ( $r_{\text{Au}} = 1.66$  Å).<sup>57</sup> On the other hand, the H...Au distances for N-H...Au in the most probable isomers are in the range of 2.28–2.38 Å, smaller than the sum of the van der Waals radii of H and Au. Thus, the interactions between  $\text{Au}^-$  and nucleobase are predominantly N-H...Au interactions. The natural bond orbital analysis of nucleobase-Au anions indicates that the excess electron of nucleobase-Au anion localizes mainly on the gold atom. Meanwhile, the negative charge transfers slightly from the  $\text{Au}^-$  to the  $\sigma^*$  orbital of the N-H bond. The N-H...Au unit has a nearly linear arrangement. The N-H...Au hydrogen bonds have the properties of three-center four-electron bonds interaction and electron is donated from a filled metal orbital to the hydrogen. These are all in accordance with the four prerequisites of hydrogen bonds:<sup>28,29,54,56,79</sup> (a) there is

evidence of bond formation; (b)  $\text{Au}^-$  is bonded to nucleobase through N-H...Au which involves the hydrogen; (c) the N-H bond is elongated compared with the isolated nucleobase molecule; (d) the H...Au distance is smaller than the sum of van der Waals radii of H and Au. In addition, N-H...Au hydrogen bonds in these complexes also satisfy the definition of hydrogen bonds proposed by International Union of Pure and Applied Chemistry (IUPAC) recently.<sup>80</sup> Therefore, the combination of the experimental results and theoretical calculations suggests that the Au anion interacts with the nucleobases mainly via N-H...Au hydrogen bonds.

It is interesting to compare the N-H...Au hydrogen bonds with the typical conventional hydrogen bonds. Considering the bond angles, the  $\angle\text{N-H}\cdots\text{O}$  angles in the N-H...O hydrogen bonds can vary between  $127^\circ$  and  $177^\circ$  depending on their strength,<sup>81</sup> while the  $\angle\text{N-H}\cdots\text{Au}$  angles in the nucleobase- $\text{Au}^-$  complexes are in the range of  $133.7^\circ$ – $179.5^\circ$ . According to the classification by Jeffrey,<sup>82</sup> hydrogen bonds with binding energies smaller than 0.17 eV can be characterized as weak hydrogen bonds, such as the C-H...O hydrogen bond (0.03 eV) in  $\text{CH}_4\cdots\text{OH}_2$ ,<sup>83</sup> those between 0.17 and 0.65 eV can be characterized as medium hydrogen bonds, such as the O-H...O hydrogen bond in  $\text{HOH}\cdots\text{OH}_2$  (0.21 eV);<sup>84</sup> those higher than 0.65 eV can be characterized as strong hydrogen bonds, such as the F-H...F hydrogen bond (1.69 eV) in  $[\text{F-H}\cdots\text{F}]^-$ .<sup>85</sup> As shown in Table II, the calculated binding energies between the nucleobases and Au anion are in the range of 0.63–1.54 eV. Since the interactions of Au anion and the nucleobases involve a N-H...Au group plus a X-H...Au (X = C, O) group or two sets of N-H...Au groups, the strengths of N-H...Au hydrogen bond in the nucleobase- $\text{Au}^-$  complexes probably are near or higher than half of binding energies between the nucleobase and Au anions. Thus, the N-H...Au hydrogen bonds in the nucleobase- $\text{Au}^-$  complexes may be characterized as medium or strong hydrogen bonds. It is also worth pointing out that N-H...Au hydrogen bond is quite distinct from the agostic bonds (C-H...M), where M is a transition metal.<sup>86–88</sup> A typical agostic bond involves 3-center-2-electron interaction. The metal center (M) is electron deficient and accepts electrons from a C-H  $\sigma$  bond. While N-H...Au hydrogen bond is characterized by its 3-center-4-electron interaction and electron is donated from a filled metal orbital to the hydrogen.

## V. CONCLUSIONS

We measured the photoelectron spectra of nucleobase- $\text{Au}^-$  complexes and investigated their structures with density functional calculations. The experimental results show that the VDEs of nucleobase- $\text{Au}^-$  complexes shift toward higher binding energy by 0.92–1.12 eV compared to that of isolated gold anion. The structures of nucleobase-Au anions are determined by comparing the theoretical VDEs with the experimental measurements. The existence of N-H...Au hydrogen bonds in the nucleobase- $\text{Au}^-$  complexes is confirmed. The gold anion interacts with the nucleobases mainly via the N-H...Au hydrogen bonds. The N-H...Au bonds in the nucleobase- $\text{Au}^-$  complexes can be characterized as medium or strong hydrogen bonds.

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