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N-K Spectra of Adenine Amino Tautomers

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Abstract.
Adenine tautomeric process is not a small perturbation but a significant change of the inner shell configuration. For canonical adenine, ade n9, the inner-shell configuration in the ground electronic states (X^1A') is given by $1a'(N_{(9)})2a'(N_{(10)})3a'(N_{(7)})4a'(N_{(3)})5a'(N_{(1)})$ $6a'(C_{(6)})7a'(C_{(8)})8a'(C_{(4)})9a'(C_{(2)})10a'(C_{(5)})$. Although the five N1s orbitals in the core shell of all adenine amino tautomers are always given as $1a'2a'3a'4a'5a'$. The profound tautomer dependent inner-shell electronic reconfiguration has been largely masked by small net differences in their total electronic energies and subtle differences in their valence shell electronic structures. The present quantum mechanical spectral study demonstrates that inner-shell chemical shift of N1s orbitals of adenine amino tautomers is atomic site and tautomer specific: the orbital binding energy shifts of the amino N1s sites (-N-) are smaller than those of the imino N1s sites (-N=) in the same tautomer. The nitrogen $N^{@}$1s site (an amino site) which connects the mobile hydrogen exhibits the smallest energy shift within a tautomer and therefore, is an indicator of the specific tautomer. The preferential adenine (ade n9) protonation sites are the imino sites in the order of $5a'(N_{(1)})$, $4a'(N_{(3)})$ and $3a'(N_{(7)})$ which agrees with previous observations.

1. Introduction

Tautomers of DNA bases are vital for the understanding of chemical reactivity [1, 2] but experimental detection/identification of tautomers has been a challenge even in the gas phase [3, 4]. Molecules of biological relevance often are thermally labile and hardly be brought into the gas phase by sample heating, and for most of DNA bases the spectra of different tautomers superimpose and make the spectra congested [5, 6]. As a result, the study of DNA base tautomers has been largely based on computational methods [7, 8, 9, 10, 11, 12, 13]. Most of structural studies with respect to tautomerism of DNA bases, however, has concerned on the valence space [6, 7, 9, 11, 12, 14, 15], which hardly provides a thorough understanding of the role of possible proton transfer reactions without the recognition of inner-shell re-configuration process. For example, valence shell information has yet to interpret the reason why the preferential protonation sites [16, 14, 6] of ade n9 is in the order of $N_{(1)}$, $N_{(3)}$ and $N_{(7)}$ ($N_{(10)}$, $N_{(9)}$) andor why proton affinity of these sites is in such the order. Unfortunately, many DNA base tautomeric studies have treated proton transfer as small perturbations, and frozen core (FC) treatment [6] are popular in these studies, which miss the most important information on tautomerism.

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2. Method and Computational Details

Adenine amino tautomers are slightly non-planar [17, 18, 19]. In the present study, adenine tautomers are treated as if they were planar molecules by imposing the C_s point group symmetry (σ-plane). This idealization to planarity not only simplifies the electronic calculations because the a' and a'' states are treated in separated and independent Hamiltonian matrices, but also provides insight into the chemical bonding by separating in-plane σ bonds from out-of-plane π bonds, as well as for other applications such as valence space studies [8, 19].

The planar geometries of the four planar amino tautomers of adenine are optimized respectively using the hybrid density functional theory (DFT) B3LYP/TZVP model. The TZVP basis set is a reasonably large triple zeta with valence polarized (TZVP) basis set [20], which has been proved reliable in our previous investigations of valence electronic properties of adenine amino tautomers [8], amino acids [21] and core shell of bicyclic-hydrocarbons [22] and DNA bases such as purine and adenine [23]. Based on the B3LYP/TZVP geometries of the tautomers, core ionization orbital energies of each tautomer are produced from single point calculations emplying the LB94/TZ2P model. All electronic calculations are performed using the GAUSSIAN03 [24] and Amsterdam Density Functional (ADF) [25] packages of computational chemistry programs.

3. Results and discussion

The inner-most five core orbitals, $1a'$, $2a'$, $3a'$, $4a'$ and $5a'$, of the tautomers are always the contributions from the N1s orbitals. Our simulated x-ray photoemission spectroscopy (XPS) of the canonical adenine (ade n9) using the LB94/T2ZP model has been proved accurate when compare to recent XPS experiments [23, 26]. As a result, this experimentally validated model is applied to study its amino tautomers theoretically in the present study.

The orbital energies change with respect to specific atom sites in the tautomers. The assignment of the inner-shell XPS of adenine tautomers will be completely different from each other. For example, the $N_{(9)}$ site, which locates in very different regions where a few electron volts are observed in the tautomers, is even larger than the total electronic energy differences among the tautomers. Figure 1 gives the simulated N-K spectra for the tautomers, based on the present LB94/TZ2P model. A theoretical resolution of 0.13 eV (FWHM) in the gaussian shape function is employed. The best experimentally available resolution used for adenine in gas phase [26] is 0.57 eV. The high theoretical resolution in the simulation is to resolve individual core states so that each spectral peak of adenine can be assigned to an individual N-K site of the molecule. The inner-shell spectra in Figure 1 indicates that the tautomers have significantly different inner-shell electronic structures, although they can be related in a certain manner. Although shifted by energy, the $N^{@}$-K site of a tautomer is always the highest energy peak in the spectra. When the $N^{@}$-K sites locate in the hexagon ring of the tautomer, such as ade n9 and ade n7, the chemical environment in energy term seems more similar as the three imino N-K peaks are closely positioned. When the $N^{@}$-K sites locate in the pentagon ring of the tautomer, such as ade n1 and ade n3, the N-K sites in the hexagon ring, $N_{(7)}$ and $N_{(9)}$, exhibit similar energy environment. In summary, the adenine tautomers are apparently different in their inner-shell N-K spectra.

4. Conclusions

The mobile proton causes significant reconfiguration in the inner-shell electronic structures in the adenine tautomeric processes. All N1s orbitals in the adenine tautomers exhibit energy shift in their binding energy spectra with respect to their corresponding free atoms. The electronic structural variations among adenine amino tautomers are **not** perturbations, but exhibit profoundly different tautomer dependent changes in inner-shell configurations. Therefore, studies based on valence shell alone and/or using the frozen core (FC) approximation unlikely produce reliable tautomer structural information of DNA bases and cannot interpret the order of

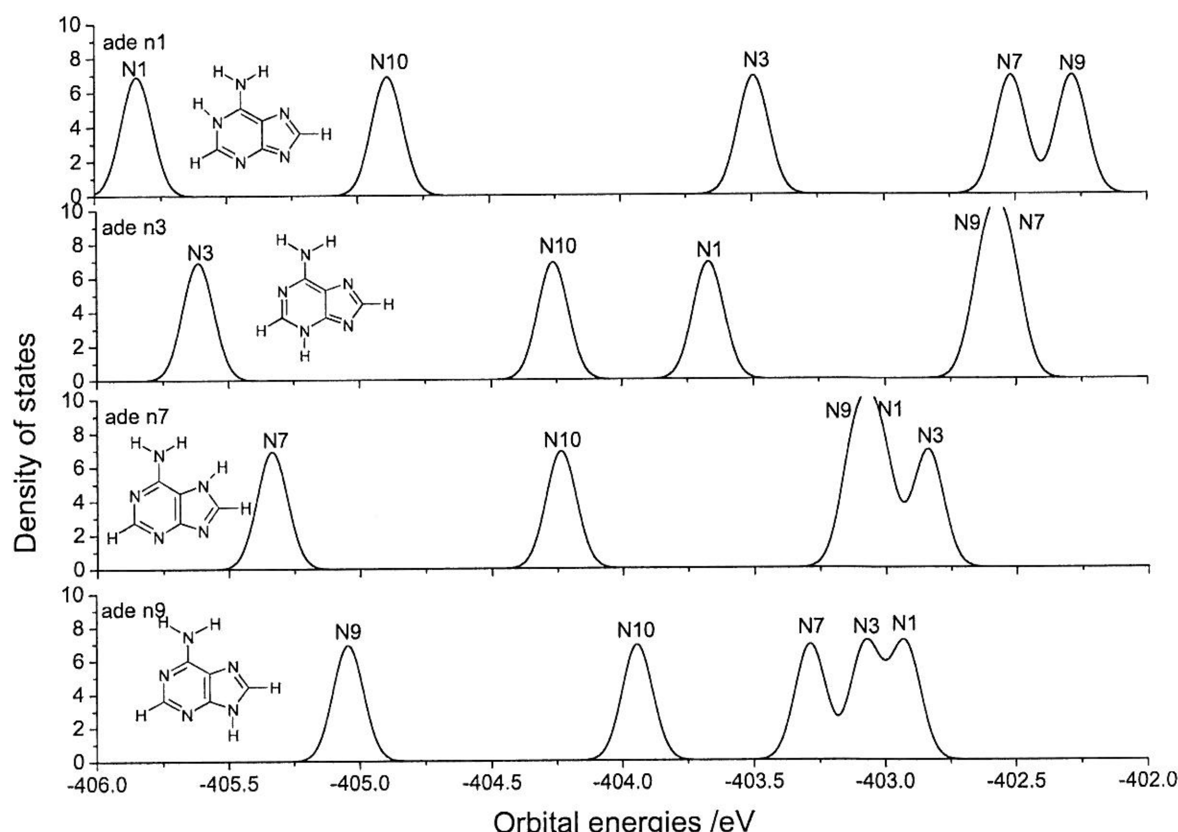

Figure 1: Density of states spectra of the N-K sites of adenine amino tautomers.

protonation sites in DNA bases. Core orbitals contain a dominant amount of energy in a molecule and cannot be ignored. Inner shell spectroscopy, when coupled with powerful synchrotron radiation sources and appropriate computational tools, is able to achieve the ultimated goal of identifying detailed electronic structures of DNA tautomers, their stabilities and properties, which will impose significant influences on biochemistry.

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