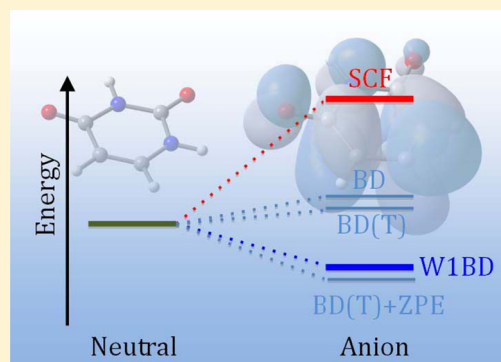


Benchmarking the Electron Affinity of Uracil

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ABSTRACT: The Weizmann Bruecker doubles composite method W1BD has been applied in a benchmark study of electron attachment to the nucleobase uracil. The largest computations involved the BD method with a basis set of 760 contracted Gaussian functions, namely augh-cc-pVQZ+2df. The predictions demonstrate that the adiabatic electron affinity (AEA) of uracil is definitely positive. The most reliable value for the AEA of uracil should be 0.024 ± 0.013 eV. Other high level methods such as CASPT2 and G4 theory also predict the AEA of uracil with reasonable accuracy. Both the Hartree–Fock and MP2 approaches severely underestimate the AEA. The latter two methods are not recommended for the study of electron attachment to the DNA/RNA bases. On the other hand, some commonly used Density functional theory approaches, especially, M06-2X, are promising candidates for the study of electron–DNA/RNA interactions.



1. INTRODUCTION

Low energy secondary electrons produced by the interaction of high-energy particles with cellular constituents^{1–3} can lead to mutagenic, recombinogenic, and other lethal DNA lesions.^{4–7} Experimental studies suggest that electrons with low-kinetic energies play an important role in inducing damage to DNA.^{8–18} The detailed mechanisms of processes involving electrons interacting with DNA are critical in understanding this DNA damage. One of most probable initial events due to the interaction of a biomolecule with secondary electrons is the formation of radical anions.¹⁹ Electron attached DNA bases are considered to be precursors in a cascade of events leading to DNA damage.^{20–22}

Electron affinity (EA) is an important physical quantity often used in theoretical and experimental descriptions of electron attachment to a molecule. Experimentally, the adiabatic electron affinity (AEA) may be determined by the onset of structure in the anion photoelectron spectra, whereas the vertical detachment energy (VDE) corresponds to the peak maximum of the anion photoelectron spectra.²³ Theoretically, the AEA corresponds to the energy difference between the equilibrium geometry of the electron-attached radical anion of a molecule and the optimized structure of the neutral molecule. In contrast, the VDE is the energy difference between the optimized structure of the radical anion and the neutral molecule with its structure “frozen” in the radical anion form. Therefore, in this sense, the detection of the AEA of a molecule is equivalent to a measurement of viability of the corresponding radical anion.

The electron affinities of DNA/RNA and its subunits have been investigated experimentally by several different techniques such as cyclic voltammetry,²⁴ Rydberg electron transfer (RET) spectroscopy,^{25–29} photodetachment-photoelectron spectroscopy (PD-PES),^{30–44} and low-energy photoelectron transmission (LEPET) spectroscopy.^{45,46} Such experimental investigations provide valuable information concerning the electron capture abilities of biomolecules. However, direct experimental determination of the electron affinities of the nucleic acid bases is challenging. Two factors might be the sources of this difficulty: the relatively high energies of the lowest unoccupied molecular orbitals of the nucleobases and the large dipole moments of the nucleobases. Thus, instead of forming valence anions, an electron might be easily trapped by the dipole moment of the biomolecule to form a dipole-bound radical anion. Among the five nucleic acid bases, uracil is the one investigated most extensively in experiments, with the goal of the characterization of its canonical anionic states. The capability to capture an excess electron in uracil has been studied by RET^{25,27–29} and by PD-PES.^{22,30–32,35} These experimental determinations of the AEA of uracil may provide benchmarks for justifying and screening various theoretical approaches.

Complementing the recent experimental studies, theoretical investigations at various levels of theory have provided detailed physical pictures, such as the distribution of the excess electron in the radical anions.⁴⁷ Unfortunately, theoretical AEA values of uracil are controversial. Although the Hartree–Fock (HF) method and perturbation theory predict negative AEA values,^{48,49} density functional theories (DFTs) tend to find a positive AEA for the formation of the covalent radical anion of uracil.^{50–53} Even at high levels of theory, the predictions of the AEA of uracil are a subject of controversy. Coupled cluster methods including single, double, and perturbative triple

Received: November 1, 2013
Published: January 8, 2014

excitations (CCSD(T)) with large basis sets have suggested negative AEA values for uracil.^{54,55} However, analogous studies using the Brueckner doubles method with triples contribution (BD(T)) and multiconfigurational perturbation theory (CASPT2) predict positive AEAs for the valence anion of uracil.^{47,56} Therefore, theoretical benchmark studies of the AEA of uracil are of great importance in justifying the proper theoretical approaches for further investigations of electron–DNA/RNA systems. This report provides the AEA values of uracil derived at the highest levels of theory (G4⁵⁷ and W1⁵⁸) yet considered. These methods appear significantly more reliable than the complete basis set model CBS-QB3.⁵⁹

2. METHODS

The most popular ab initio-based schemes that claim “chemical accuracy” are the Gaussian-2 (G2),⁶⁰ Gaussian-3 (G3),⁶¹ and Gaussian-4 (G4)⁵⁷ composite methods of Curtiss, Raghavachari, Pople, and co-workers. Other methods such as CBS-Q and CBS/APNO^{59,62} appear able to approach 0.5 kcal/mol accuracy (restricted to the first-row compounds). The Weizmann-1 (W1) and Weizmann-2 (W2) methods of Martin are less widely used but are more reliable theories that seem to allow accuracies of 0.3 kcal/mol (W1) and 0.23 kcal/mol (W2).⁵⁸ Note that the uncertainty of the AEA of uracil predicted with various high-level theories (−0.05 to +0.001 eV for CCSD(T), 0.01 eV for BD(T), and 0.10 eV for CASPT2)⁴⁷ is about 0.15 eV or 3.5 kcal/mol. Thus, the W1 theory is a reasonable approach to benchmark the AEA of uracil. Because the W1 theory with the Brueckner doubles approach (W1BD) is more reliable for high spin systems,⁶³ the W1BD scheme is adopted in the present study. In the Brueckner doubles method, the molecular orbitals are not Hartree–Fock orbitals but optimized within a coupled cluster framework.

On the basis of the W1 protocol, both uracil and the corresponding radical anion were optimized at the B3LYP/cc-pVTZ+d level of theory. Zero-point energies obtained from B3LYP/cc-pVTZ+d harmonic frequencies were scaled by 0.985. BD/augh-cc-pVDZ+df, BD/augh-cc-pVTZ+2df, and BD/augh-cc-pVQZ+2df single point energies were computed for extrapolating the BD correlation component of TAE by applying $A + B/l^\beta$ ($\beta = 3.22$, $l = 3, 4$). The BD(T)/augh-cc-pVDZ+2df and BD(T)/augh-cc-pVTZ+2df single-point energy calculations were performed to obtain the (T) valence correlation component by applying $A + B/l^\beta$ ($\beta = 3.22$, $l = 2, 3$). The SCF component of the total atomization energies is extrapolated using $A + B/C^l$ ($l = 2, 3, 4$). The core correlation contributions are obtained at the BD(T)/MTsmall (see ref 58) level of theory. The scalar relativistic and spin–orbital coupling effects are computed with the BD(T, Full)/MTsmall method using the Douglas–Kroll–Hess model.⁶⁴

In the course of the present W1 study, the most demanding computation used the Brueckner doubles method with basis set augh-cc-pVQZ+2df. The latter basis set includes 760 contracted Gaussian basis functions.

3. RESULTS AND DISCUSSIONS

The geometrical parameters of the optimized structures of the neutral and radical anion of uracil are depicted in Figure 1. The large structural variations of the radical anion suggest that the excess electron is covalently bound to uracil. This is further confirmed by the analysis of the singly occupied molecular orbital of the radical anion of uracil.

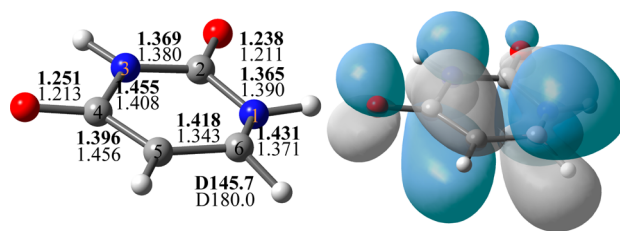


Figure 1. Geometrical parameters of the optimized structures of neutral and anionic uracil (left). Bond lengths in Å. Dihedral angle in degrees. D represents the N1C5C6H6 dihedral angle. Normal (lower) print refers to neutral uracil, whereas bold (upper) print is for the radical anion of uracil. On the right is depicted the singly occupied molecular orbital (SOMO) of radical anion of uracil. Color legend: red for oxygen; blue for nitrogen; gray for carbon; white for hydrogen.

Table 1 summarizes the predicted components of the W1BD for uracil, along with other high level theoretical predictions and the “best” experimental results.

Earlier ROHF studies with basis sets aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pVSZ produced negative AEA values for uracil (−0.86 eV to −0.91 eV).^{54,65} On the other hand, the spin-unrestricted open-shell Hartree–Fock (UHF) model with various basis sets somewhat improves the viability of the radical anion of uracil. The UHF predicted AEA of U varies from −0.67 eV (aug-cc-pVDZ) to −0.72 eV (aug-cc-pVSZ).⁶⁵ The extrapolated SCF value for the AEA of uracil is found to be −0.826 eV in the present study, between the ROHF and UHF predictions with the largest basis set aug-cc-pVSZ. The BD method improves the viability of the radical anion of uracil significantly. The BD correlation component is extrapolated to 0.681 eV. This part of the correlation is the most important in the realization of the radical anion of uracil. The corresponding (T) valence correlation is extrapolated to be 0.054 eV, less than one-tenth of the BD correlation component in magnitude. Without zero-point vibrational energy (ZPE) corrections and the scalar relativistic and spin–orbital coupling effects, the extrapolated BD(T) prediction for the AEA of uracil is −0.091 eV.

Previous theoretical studies revealed that at the CCSD(T)/aug-cc-pVDZ level of theory, the AEA of the covalent anion of uracil was predicted to be −0.05 eV (−0.15 eV without zero-point energy corrections).⁵⁵ With the aug-cc-pVTZ basis set, the CCSD(T) method increases the EA by 0.043 eV (−0.12 eV without zero-point-energy (ZPE) corrections).⁶⁵ For comparison, the AEA value predicted at the BD(T)/augh-cc-pVDZ+df level is −0.153 eV and that with augh-cc-pVTZ+2df is −0.119 eV. With a modified version of CCSD(T), spin-adaption included (SA) CCSD(T), Urban and co-workers reported an AEA of −0.11 eV using the aug-cc-pVQZ basis without ZPE corrections.⁵⁴ Their AEA value is about 0.02 eV (0.46 kcal/mol) less than the extrapolated BD(T) prediction.

Another important factor in stabilizing the radical anion of uracil is the ZPE correction. The ZPE contribution to the AEA of uracil is 0.125 eV. On the other hand, the scalar relativistic and spin–orbital coupling effects contributions are −0.010 eV. Finally, the W1BD prediction of the AEA of uracil has risen to 0.024 eV. Considering that the estimated error of 0.013 eV for the W1 theory, the true value of AEA of uracil may be between 0.011 and 0.037 eV.

Using the Pople model chemistry method, Gaussian-4 theory (G4),⁵⁷ the AEA of uracil is predicted to be 0.11 eV.⁴⁷ A similar

Table 1. Adiabatic Electron Affinities (AEA) of Uracil at Different Levels of Theory (in eV)

contribution to W1		comparison
extrapolated SCF	−0.826	ROHF, −0.86 −0.91; ^{65,54} UHF, −0.67; ⁶⁵ −0.72 ⁶⁵
extrapolated BD	0.681	
extrapolated (T)	0.054	
total extrapolated BD(T)	−0.091	CCSD(T), −0.15 ⁵⁵ −0.11; ⁵⁴ MP2, −0.51 ⁶² — −0.10 ⁶⁵
scalar relativistic effects	−0.010	
ZPE correction	0.125	
total W1BD	0.024	G4: 0.11 ⁴⁷ BD(T), 0.01; ⁴⁷ CASPT2, 0.10 ⁵⁶ M06-2X, 0.11; ⁴⁷ B3LYP, 0.18–0.24 ⁴⁷
experiment		
	PD-PES	0.15 ± 0.12; ²² 0.16 ³²
	RET	0.06 ± 0.03 ²⁷

AEA of uracil is also predicted at the CASPT2 level of theory (0.10 eV).⁵⁶ Thus, the AEA of uracil is definitely positive.

It is clear that HF methods and the MP2 method (see Table 1) severely underestimate the valence AEA of uracil. Therefore, these two methods may be questionable tools for the study of the electron–DNA interactions. Prior to ZPE corrections, negative AEAs of uracil are predicted by the CCSD(T) and BD(T) methods when the basis sets are sufficiently large (at least aug-cc-pVTZ). On the other hand, some commonly used approaches of density functional theory (DFT) predict positive AEAs for uracil. It is important to mention that the more recently developed Minnesota density functional M06-2X⁶⁶ along with the Pople triple- ζ basis set (6-311++G(d,p)) is able to predict an AEA of 0.11 eV for uracil,⁴⁷ very close to that of G4 theory.

The dipole-bound radical anion of uracil is not of primary interest in the present study, because it has been well characterized both by experimental and theoretical studies.^{22,55} However, it is important that with the planar-structure constraints on the radical anion, one can locate the radical anion of uracil in the dipole-bound form in our W1BD study. The AEA for formation of the dipole-bound radical anion of uracil is predicted to be 0.039 eV by the W1BD approach, close to the photodetachment-photoelectron spectroscopic determination (0.05 eV)²² and the previous CCSD(T) study (0.07 eV).⁵⁵

4. CONCLUSIONS

Using the high level composite W1BD approach of Martin, we conclude that the adiabatic electron affinity (AEA) of uracil is definitely positive. Our most reliable value of the AEA of uracil is 0.024 ± 0.013 eV for the formation of covalent radical anion, slightly lower than that of the dipole-bound uracil radical anion (0.039 eV). Other high level methods such as CASPT2 and G4 theory are shown to predict the AEA of uracil with reasonable accuracy. Both HF and MP2 approaches are not recommended for the study of the electron attachment to the DNA/RNA bases, due to these methods severely underestimating the AEA. On the other hand, several commonly used DFT approaches such as B3LYP and M06-2X are acceptable candidates for the study of electron–DNA/RNA interactions.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the U.S. National Science Foundation, Grant CHE-1054286.

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