

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/221800638>

Electron Affinities of Uracil: Microsolvation Effects and Polarizable Continuum Model

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2012

Impact Factor: 2.69 · DOI: 10.1021/jp211994k · Source: PubMed

CITATIONS

10

READS

27

4 AUTHORS:



Miroslav Melichercik

Univerzita Mateja Bela v Banskej Bystrici

4 PUBLICATIONS 20 CITATIONS

[SEE PROFILE](#)



Lukas Felix Pasteka

Massey University

8 PUBLICATIONS 33 CITATIONS

[SEE PROFILE](#)



Pavel Neogrády

Comenius University in Bratislava

50 PUBLICATIONS 2,655 CITATIONS

[SEE PROFILE](#)



Miroslav Urban

Comenius University in Bratislava

119 PUBLICATIONS 3,334 CITATIONS

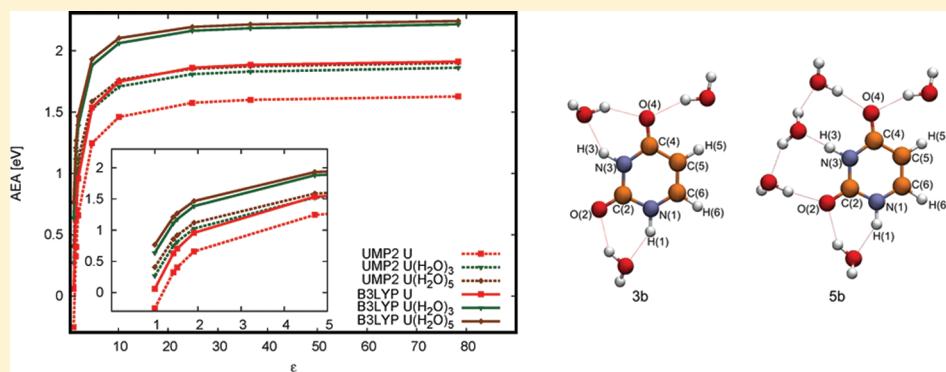
[SEE PROFILE](#)

Electron Affinities of Uracil: Microsolvation Effects and Polarizable Continuum Model

Miroslav Melicherčík,[†] Lukáš F. Paštka,[†] Pavel Neogrády,[†] and Miroslav Urban^{*,†,‡}

[†]Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, SK-842 15 Bratislava, Slovakia

[‡]Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Institute of Materials Science, Bottova 25, SK-917 24 Trnava, Slovakia



ABSTRACT: We present adiabatic electron affinities (AEAs) and the vertical detachment energies (VDEs) of the uracil molecule interacting with one to five water molecules. Credibility of MP2 and DFT/B3LYP calculations is supported by comparison with available benchmark CCSD(T) data. AEAs and VDEs obtained by MP2 and DFT/B3LYP methods copy trends of benchmark CCSD(T) results for the free uracil and uracil–water complexes in the gas phase being by 0.20–0.28 eV higher than CCSD(T) values depending on the particular structure of the complex. AEAs and VDEs from MP2 are underestimated by 0.09–0.15 eV. For the free uracil and uracil–(H₂O)_n ($n = 1, 2, 3, 5$) complexes, we also consider the polarizable continuum model (PCM) and discuss the importance of the microsolvation when combined with PCM. AEAs and VDEs of uracil and uracil–water complexes enhance rapidly with increasing relative dielectric constant (ϵ) of the solvent. Highest AEAs and VDEs of the U(H₂O)₅ complexes from B3LYP with $\epsilon = 78.4$ are 2.03 and 2.81 eV, respectively, utilizing the correction from CCSD(T). Specific structural features of the microsolvated uracil–(H₂O)_n complexes and their anions are preserved also upon considering PCM in calculations of AEAs and VDEs.

1. INTRODUCTION

Interactions of nucleic acid bases (NABs) with their environment have significant impact on their chemical properties. Clearly, this holds also for the low-energy electron binding processes that participate in the mechanism of the radiation damage to living tissues that can cause strand breaks in the DNA duplex.^{1–5}

Convincing theoretical evidence^{6–9} and experimental indication^{10,11} shows that the valence adiabatic electron affinity of the free uracil either is zero or only slightly positive, partly due to the vibrational effect. Other free NABs attract an electron even less. Solvent effects, particularly with water as a solvent, lead to significant enhancement of electron affinities. In their pioneering work Kim and Schaefer¹² investigated microsolvation effects on the stability of the neutral uracil molecule and its anion considering several structures of complexes with 1–5 water molecules at the DFT B3LYP level of theory. Their results demonstrate a gradual enhancement of AEA and VDE with the number of hydrating water molecules for uracil.

Precisely the same trend follows from photoelectron spectroscopy studies performed by Schiedt et al.¹⁰ and more recently by Eustis et al.¹¹ Similar calculations accompanied by the electron structure analysis for the H-bonding patterns were published by Bao et al.¹³ for U(H₂O)_n complexes and their anions ($n = 1, 2, 3$). Li and Ai¹⁴ studied catalysis effects of water molecules on intramolecular proton transfer of the three uracil isomers and their neutral, positive, and negative charged multihydrates using the DFT method. Calculations of uracil and its anion solvated by one to three water molecules were published recently in the present journal by our group.^{7,15} We have reconfirmed that water molecules stabilize the anion more efficiently than the neutral molecule leading to the enhancement of AEA by about 250 up to 570 meV, depending on the geometry of the complex. Thanks to the reduction of the optimized virtual orbital space (OVOS), we were able to treat the neutral and

Received: December 13, 2011

Published: February 2, 2012

anion uracil complexes with up to three water molecules by a highly sophisticated CCSD(T) method with a reasonably large aug-cc-pVTZ basis set. So, obtained AEAs and VDEs may serve as a benchmark for other methods. For example, we showed that B3LYP DFT overestimates electron affinities by about 300 meV, but trends with microsolvation are represented quite reasonably. Important theoretical work on the effect of microhydration on other NABs, nucleosides, nucleotides, and oligonucleotides was published by Schaefer and his group,^{16–18} supported by photoelectron spectroscopic studies by Li, Wang, and Bowen.¹⁹

In addition to the microhydration, several authors considered bulk solvent effects using the polarizable continuum and/or the QM/MM model. Specific interactions between NAB and the bulk solvent effects are accounted for combining the microsolvation of NABs by several water molecules and applying the PCM to the resulting NAB–water complexes.²⁰ Brancato, Rega, and Barone^{21,22} used QM/MM model to study microsolvation effects on uracil and the uracil anion radical in the liquid phase stressing the specific problem of characterizing the tautomers of the uracil anion radical in aqueous solution. Saettel and Wiest²³ studied effects of solvation on the vertical and adiabatic electron affinities of uracil and uracil dimers as well as on the mechanism of the cycloreversion of the uracil dimer radical anion using DFT with the B3LYP functional. They considered a model systems with up to 3 explicit solvent molecules and the implicit PCM solvation. Solvation interactions in the product complexes responsible for the overall reaction thermochemistry could not be satisfactorily described by the PCM cavity solvation alone.

A combined microsolvation–continuum model was employed in several other studies of NABs, e.g., in calculations of ionization potentials by Leszczynski et al.^{24–26} and excitation energies of uracil and 5-fluorouracil in water and acetonitrile²⁷ and in studies on relative stabilities of canonical and other tautomers of cytosine, guanine, and adenine in the gas phase, microhydrated environment, and in aqueous solution.^{28–31} Kumar et al.³² in their work on microhydration of the guanine–cytosine base pair concluded that the PCM model yields nearly the same value for the AEA regardless of the level of hydration. This suggests that the PCM model adequately accounts for the hydration stabilization in this system. DFT B3LYP and MP2 calculations²⁶ of uracil and thymine show that placing the microhydrated structures in a PCM cavity was seen to make a little difference in ionization energy threshold (IET) when compared to the IET of ordinary (free) uracil or thymine in a PCM cavity.

Most of the above cited theoretical papers on electron affinities and other properties of NAB complexes and their interactions with the solvent were treated by DFT methods, which unfortunately are not particularly reliable for calculations of AEAs and VDEs.^{6,7} The control of accuracy of DFT in some applications is questionable, in contrast to Coupled Cluster or some other wave function methods that allow hierarchical improvements in constructing the wave function and the resulting energy. Further on, the reliability of CCSD(T) results can be supported by careful inspection of the single and double excitations amplitudes and by the T₁ diagnostics,^{33–35} which can help in revealing possible quasidegeneracy problems when using a single determinant reference approach. Therefore, we decided to utilize the availability of highly accurate CCSD(T) electron affinities for free uracil and the uracil molecule solvated by up to three water molecules as an instrument for tuning

DFT B3LYP AEAs and VDEs and the second order perturbation MP2 calculations. We know from ours and others calculations^{6,7} that the most frequently used B3LYP functional overestimates the valence electron binding energy to uracil by as much as 300 meV, while MP2 underestimates both AEA and VDE by about 100–150 meV in comparison with benchmark CCSD(T) results. Alternative functionals can possibly provide more accurate electron affinities (for example, a promising alternative for EAs of uracil seems to be a BH&HLYP functional),^{20,36} but problems with controlling the accuracy remain.

In the present article, we wish to systematically investigate the bulk effects using PCM combined with the microsolvation of uracil including one to five water molecules focusing on trends of electron affinities affected by microsolvation as obtained from MP2, B3LYP, and (for singly, doubly, and triply hydrated complexes) CCSD(T) calculations. Clearly, the study of the damage to DNA caused by low energy electrons needs much larger models, including solvated hydrogen bonded³² and stacked NAB pairs,³⁷ and considering the sugar and phosphate groups^{2,5,17–19,38} to mention at least the most obvious steps. Also, NABs and solvation effects should be considered for different tautomeric forms of NABs that play an important role as well, see e.g., refs 22, 28–30, 39, and 40. A variety of structures including large molecular complexes that represent a real situation better than the simplified model of a canonical structure of uracil interacting with just a few water molecules are not amenable to accurate CCSD(T) treatment. Also, PCM is routinely available when combined with DFT and MP2 methods.^{41–46} Newly developed PCM with CCSD gradient optimization was recently published by Cammi,⁴⁷ but for larger microsolvated complexes of uracil, the method is computationally too demanding. We believe, however, that even if less sophisticated methods cannot provide accurate electron affinities of NABs (difficult to calculate accurately by any method), careful comparison with benchmark CCSD(T) data can give some insight on the reliability of less accurate but less demanding methods.

2. METHODS

The adiabatic electron affinity (AEA) and the vertical detachment energy (VDE) were calculated from energies of the neutral and anion energies using the following common definitions:

$$\text{AEA} = E(\text{optimized geometry of neutral uracil}) - E(\text{optimized geometry of the anion})$$

$$\text{VDE} = E(\text{neutral uracil at optimized geometry of the anion}) - E(\text{optimized geometry of the anion}).$$

Optimized geometries of the free neutral molecule and its anion were taken from ref 6. They represent tautomeric structures and were obtained at the second order perturbation (MP2) level of theory using the aug-cc-pVTZ basis set.⁴⁸ Reference electron affinities and detachment energies of uracil and its anion were calculated⁷ with a series of basis sets up to aug-cc-pVQZ using the ROHF (restricted open shell Hartree–Fock) spin adapted CCSD(T) approach⁴⁹ as implemented in the MOLCAS 7 program.⁵⁰ In alleviating high computer demands (particularly for anion radicals), we profited from using the OVOS technique developed and verified in our laboratory.^{34,51,52} Principal subjects of this article are microhydrated complexes of uracil U(H₂O)_n (*n* = 1, 2, 3, 5) and their anions. Initial geometries of these species were taken from ref

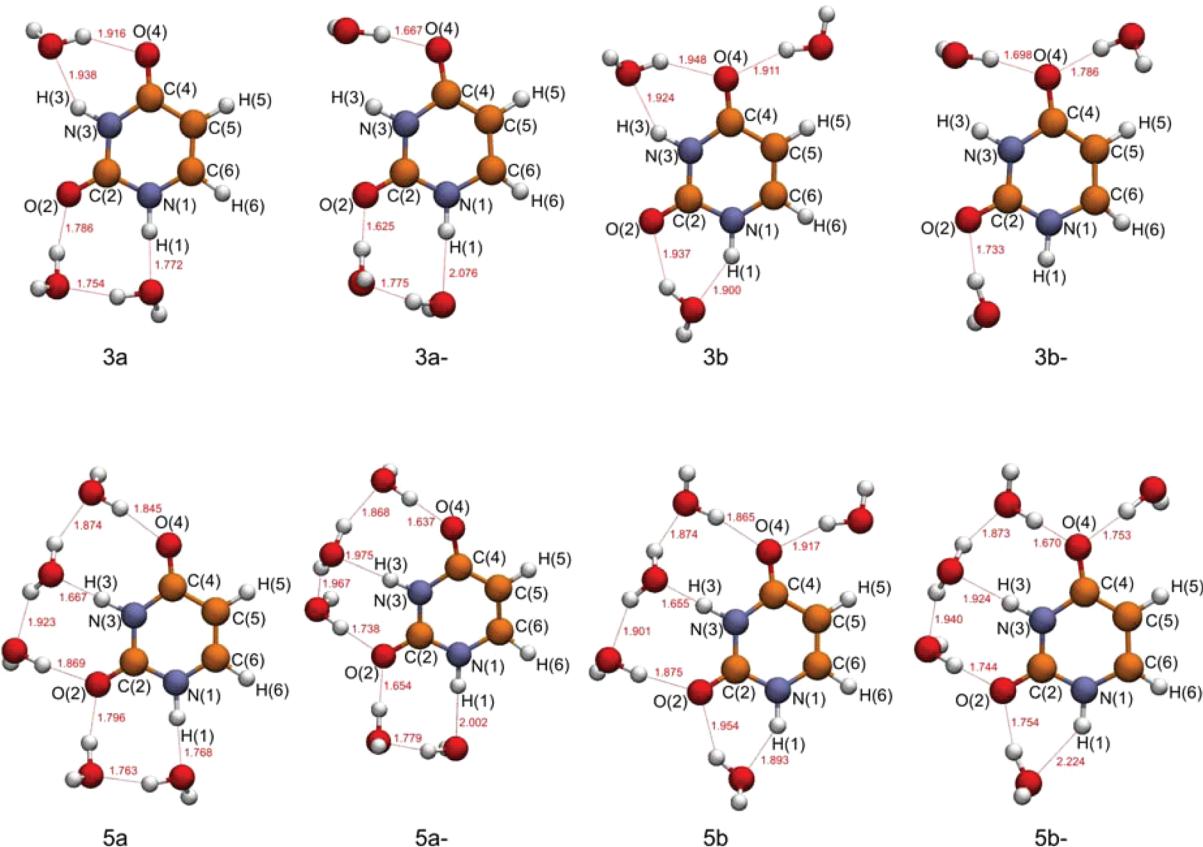


Figure 1. Optimized geometries of the microhydrated $\text{U}(\text{H}_2\text{O})_3$ and $\text{U}(\text{H}_2\text{O})_5$ complexes 3a, 3b, 5a, 5b and corresponding anions 3a^- , 3b^- , 5a^- , and 5b^- . Threshold for labeling H-bonds by dotted lines is the O–H bond distance of 2.3 Å.

12 as a starting point for further reoptimization. Analogous complexes were also treated in ref 53 and in a series of other papers with one to seven hydrating water molecules.^{13,14,20,21,23,26,54} We have considered two basic frameworks for each microhydrated complex. They represent the most stable neutral uracil–water complexes (denoted as a) and the most stable anion uracil–water complexes (denoted as b), according to Kim and Schaefer,¹² who considered four water binding sites, which can be occupied by one or two water molecules. These structures were reoptimized at the MP2 level with the aug-cc-pVQZ basis set using the Gaussian09 software package.⁵⁵ Anionic structures were reoptimized by the unrestricted UMP2 method with the same basis set used. Uracil mono-, di-, and trihydrate neutral and anionic complexes are the same as in our previous benchmark CCSD(T) calculations¹⁵ with the aug-cc-pVTZ basis set in which we used the OVOS technique, like for the unsolvated uracil. The optimized structures of the uracil trihydrate complexes (3a and 3b structures preferring neutrals; 3a⁻ and 3b⁻ structures preferring anions) are compared with uracil pentahydrate complexes (5a and 5b structures for neutrals; 5a⁻ and 5b⁻ structures for anions) in Figure 1. Typically, water molecules interact with CO and NH amide groups of uracil, leaving the C(5)H(5)=C(6)H(6) site unsolvated. In structures 3a and 3a⁻, a single water molecule is hydrogen bonded to the C(4)O(4) carbonyl group, and two water molecules form a chain structure hydrogen bonded to the C(2)O(2) and N(1)H(1) groups. Pentahydrate 5a and 5a⁻ complexes are analogous. Again, two water molecules form a chain structure hydrogen bonded to the C(2)O(2) and N(1)H(1) groups, one

water molecule creates the hydrogen bond with O(4) and additional two water molecules create another chain structure around the CO–NH–CO part of uracil. The structural framework of b is different. Two water molecules bind to the O(4) oxygen in structures 5b and 5b⁻, and the three-water chain is created around the CO–NH–CO part of uracil. C(2)O(2) and N(1)H(1) groups bind only a single water molecule in all b-type structures. MP2/UMP2 and DFT B3LYP calculations of electron affinities were performed at the same geometries of the free and microsolvated uracil with the aug-cc-pVTZ basis set. For these calculations we used the Gaussian09 program.⁵⁵

Bulk solvation effects in free uracil and its microhydrated structures were studied by employing the polarizable continuum model (PCM) developed by the Italian school^{41,42,46} as implemented in the Gaussian09 program.⁵⁵ AEAs and VDEs were calculated by MP2/UMP2 and DFT B3LYP methods with the aug-cc-pVTZ basis set as a function of relative dielectric constant (ϵ). For the uracil anion radical, we used the unrestricted Hartree–Fock reference (UHF). This is reasonable since Bachorz et al.⁶ have observed for the canonical tautomer of uracil a variation in the final values of AEAs and VDEs of only 20–30 meV depending on the HF reference wave function (UHF or ROHF). Default ϵ values for the following solvents were taken directly from the Gaussian09 manual:⁵⁵ argon (1.43), krypton (1.52), heptane (1.91), chloroform (4.71), dichloroethane (10.13), ethanol (24.85), nitromethane (36.56), and water (78.36).

Table 1. B3LYP, UMP2, and CCSD(T) Adiabatic Electron Affinities AEA [eV] of the Uracil Molecule (U) and U(H₂O)_n Complexes (*n* = 1, 2, 3, 5) with aug-cc-pVTZ Basis Set^a

	B3LYP			UMP2			CCSD(T)
	$\epsilon = 1.0$	$\epsilon = 78.4$	diff	$\epsilon = 1.0$	$\epsilon = 78.4$	diff	$\epsilon = 1.0$
U	0.059	1.912	1.853	-0.254	1.627	1.881	-0.157
U(H ₂ O) ₁ a	0.182	2.002	1.820	-0.158	1.682	1.840	-0.045
U(H ₂ O) ₁ b	0.377	2.033	1.656	0.044	1.720	1.676	0.164
U(H ₂ O) ₂ a	0.156	1.957	1.801	-0.165	1.651	1.816	-0.045
U(H ₂ O) ₂ b	0.576	2.162	1.586	0.230	1.828	1.598	0.374
U(H ₂ O) ₃ a	0.328	2.047	1.719	-0.023	1.710	1.733	0.117
U(H ₂ O) ₃ b	0.637	2.216	1.579	0.270	1.862	1.592	0.423
U(H ₂ O) ₅ a	0.468	2.068	1.600	0.135	1.746	1.611	
U(H ₂ O) ₅ b	0.764	2.242	1.478	0.407	1.901	1.494	

^aCCSD(T) values were taken from ref 15. Diff means a difference between AEA in PCM corresponding to the water solution ($\epsilon = 78.4$) and AEA of the free or microsolvated uracil ($\epsilon = 1.0$). Structures representing the framework of solvating water molecules preferred by neutral systems are denoted by the symbol a; structures representing the framework of solvating water molecules preferred by anions are denoted by symbol b; see Figure 1.

Table 2. B3LYP, UMP2, and CCSD(T) Vertical Detachment Energies VDE [eV] of the Uracil Molecule (U) and U(H₂O)_n Complexes (*n* = 1, 2, 3, 5) with aug-cc-pVTZ Basis Set^a

	B3LYP			UMP2			CCSD(T)
	$\epsilon = 1.0$	$\epsilon = 78.4$	diff	$\epsilon = 1.0$	$\epsilon = 78.4$	diff	$\epsilon = 1.0$
U	0.736	2.549	1.813	0.373	2.229	1.856	0.467
U(H ₂ O) ₁ a	1.078	2.758	1.680	0.698	2.417	1.719	0.802
U(H ₂ O) ₁ b	1.337	2.801	1.464	0.957	2.465	1.508	1.073
U(H ₂ O) ₂ a	1.068	2.755	1.687	0.691	2.417	1.726	0.800
U(H ₂ O) ₂ b	1.620	2.933	1.313	1.237	2.590	1.353	1.376
U(H ₂ O) ₃ a	1.337	2.884	1.547	0.958	2.540	1.582	1.089 ^b
U(H ₂ O) ₃ b	1.748	2.999	1.251	1.362	2.652	1.290	1.508
U(H ₂ O) ₅ a	1.565	2.921	1.356	1.179	2.573	1.394	
U(H ₂ O) ₅ b	1.908	3.053	1.145	1.519	2.709	1.190	

^aCCSD(T) values were taken from ref 15. Diff means a difference between VDE in PCM corresponding to the water solution ($\epsilon = 78.4$) and VDE of the free or microsolvated uracil ($\epsilon = 1.0$). Structures representing the framework of solvating water molecules preferred by neutral systems are denoted by the symbol a; structures representing the framework of solvating water molecules preferred by anions are denoted by symbol b; see Figure 1. ^bNote the misprint (1.189 instead of 1.089 eV) for the CCSD(T) value of VDE for the U(H₂O)_{3a} complex in ref 15.

3. RESULTS AND DISCUSSION

Results for AEAs and VDEs of the free and microsolvated uracil complexes in the gas phase (more precisely in vacuum, with $\epsilon = 1$) and in PCM representing the bulk water ($\epsilon = 78.4$) are collected in Tables 1 and 2. In these tables, we also present the bulk effects within PCM. For AEA with B3LYP, it ranges from 1.85 eV for free uracil to 1.48 eV for the pentuple hydrated uracil. For VDE, it ranges from 1.81 eV for free uracil to 1.15 eV for the pentuple hydrated uracil. Corresponding data with MP2 are similar. Qualitatively similar shifts of AEAs due to continuum water solvent effects (1.682–1.877 eV) were reported by Saettel and Wiest.²³

DFT B3LYP and MP2 results are compared with benchmark CCSD and CCSD(T) aug-cc-pVTZ data for the free uracil and free U(H₂O)_n complexes, *n* = 1–3. Preliminary comparisons of DFT with benchmark CCSD(T) electron affinities mentioned in the Introduction^{6,7} were based on published results with slightly different basis sets and geometries and are just estimates. This time our comparisons are more systematic. We note, first, that B3LYP AEAs are overestimated by 201–227 meV in comparison with CCSD(T), irrespective of the number of hydrating water molecules and the structural framework a or b of U(H₂O)_{n=1,2,3} complexes. VDEs from DFT B3LYP are by 244–276 meV higher than CCSD(T) benchmark results. Analogous MP2 AEAs and VDEs are underestimated by 94–

153 meV. As it is generally accepted, hydration contributes to the enhancement of the electron affinity of uracil.^{10–12,15} Let us remind that AEA of the free uracil is either zero or is slightly positive^{6,7} only when correcting the energies of uracil and its anion by the vibrational contribution,⁶ about 0.10 eV. Considering the most accurate CCSD(T) results,¹⁵ the electronic component of the uracil AEA becomes positive, i.e., the anion species is more stable than the mother molecule, only upon solvating the most stable neutral a structures by three water molecules. For structures b, even a single water molecule suffices for turning AEA from negative to a positive value. In general, uracil–water b structures stabilize the anion with respect to the neutral complexes more efficiently than structures a. Alterations of AEAs and VDEs of uracil with the number and the structure of solvating water molecules are visualized in Figures 2 and 3. Both AEAs and VDEs exhibit an interesting stair-like character when going from the free uracil to microstructures a with one, two, and three solvating water molecules. The enhancement of AEAs due to microsolvation with structures b is monotonous. Note that the same pattern, particularly a stair-like character of electron affinities for structures a, holds for $\epsilon = 1.0$ (lower parts of Figures 2 and 3) and $\epsilon = 78.4$ (upper parts). Therefore, changes of AEAs and VDEs introduced by the microsolvation in the gas phase are preserved also in the bulk. In Figure 2, we also present AEAs of

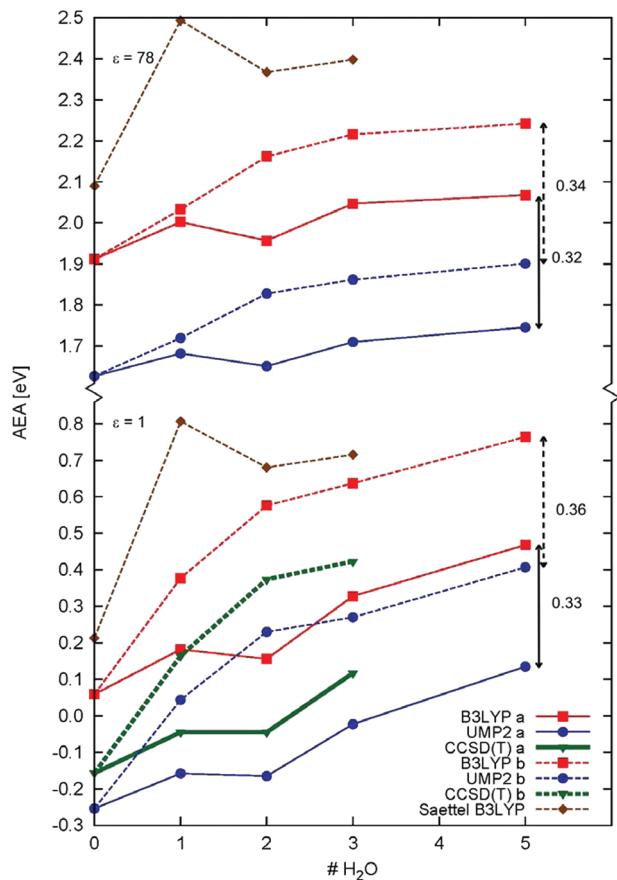


Figure 2. Adiabatic electron affinities (AEA) [eV] of the uracil (U) and U(H₂O)_n ($n = 1, 2, 3, 5$) complexes in the bulk water (PCM with $\epsilon = 78.4$, upper part) and in the gas phase ($\epsilon = 1.0$, lower part). B3LYP and UMP2 results for uracil and microsolvated uracil without and with PCM using aug-cc-pVTZ basis set. Symbols a and b represent geometries as indicated in Figure 1. B3LYP results taken from ref 23 represent alternative structures of the neutral and anionic complexes. CCSD(T) results are from ref 15.

the free uracil and U(H₂O)_{n=1,2,3} complexes published by Saettel and Wiest.²³ Complexes with two and three water molecules are more like our b-type geometries with similar trends of AEA. The U(H₂O)₁ complex appears out of this trend due to a different geometry than that used in the present work and sensitivity of AEAs to a specific geometry particularly for complexes with a small hydration level. Alterations of electron affinities of uracil, as large as 0.3 eV, depending on specific structures of U(H₂O)_n complexes were first observed by Kim and Schaefer.¹² Their AEA for the complex similar to our U(H₂O)_{sb} calculated with B3LYP is slightly larger (0.85 eV) than our value in Table 1 due to differently optimized geometries.

Trends of AEAs and VDEs obtained from CCSD(T) calculations for U(H₂O)_{n=1,2,3} complexes are perfectly copied by DFT and MP2 results, even if the absolute numbers are significantly different. Electron affinities for pentuple hydrated uracil are not available at the CCSD(T) level. Nevertheless, the trend of further enhancement of AEAs and VDEs considering U(H₂O)₅ complexes remains parallel for DFT and MP2. At this level of microhydration, PCM data for $\epsilon = 78.4$ approach the saturation (upper part of Figures 2 and 3 for AEAs and VDEs, respectively), while AEAs and VDEs of the gas phase U(H₂O)_n complexes ($\epsilon = 1.0$) depend on the number of water molecules

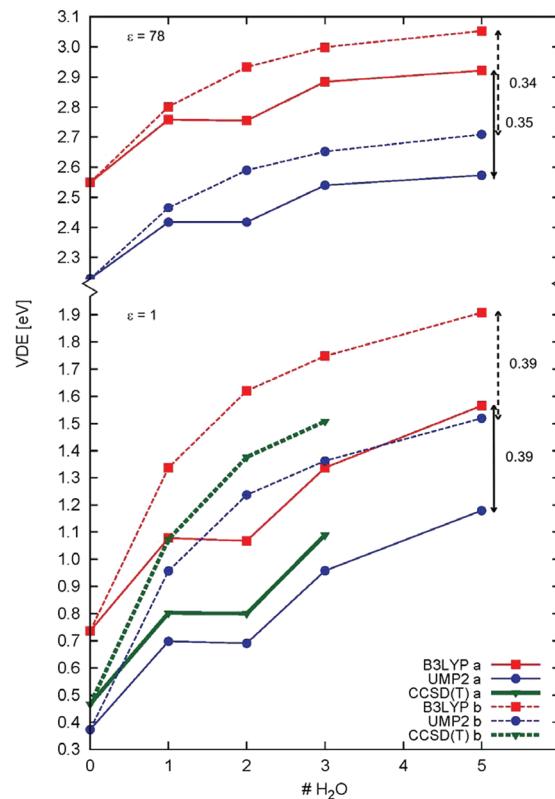


Figure 3. Vertical detachment energies (VDE) [eV] of the uracil (U) and U(H₂O)_n ($n = 1, 2, 3, 5$) complexes in the water solution (PCM with $\epsilon = 78.4$, upper part) and in the gas phase ($\epsilon = 1.0$, lower part). B3LYP and UMP2 results for uracil and microsolvated uracil without and with PCM using aug-cc-pVTZ basis set. Symbols a and b represent geometries as indicated in Figure 1. CCSD(T) results are from ref 15.

and specific microhydration structures much more. Nevertheless, differences between MP2 and B3LYP results for pentahydrated U(H₂O)₅ complexes with structures 5a/5a⁻ (full vertical lines in Figures 2 and 3) and 5b/5b⁻ (broken vertical lines) all lie within a narrow interval of 0.32–0.36 eV (AEAs, Figure 2) and 0.34–0.39 eV (VDEs, Figure 3), respectively, for both $\epsilon = 78.4$ and $\epsilon = 1.0$.

B3LYP data in Table 1 show that AEA of the free uracil ($\epsilon = 1.0$) increases by 409 meV upon the microsolvation by five water molecules with the U(H₂O)_{5a} structure and by 705 meV with the U(H₂O)_{5b} structure. Bulk effect within PCM ($\epsilon = 78.4$) contributes to the large additional enhancement of AEA of the U(H₂O)_{5b} structure leading to the final value of 2.242 eV with the B3LYP functional. The analogous value from MP2 is lower, 1.901 eV. Nevertheless, MP2 data lead essentially to the same picture of changes (not absolute values) of AEAs due to the microsolvation and the bulk solvent effects as data from B3LYP and need not be further commented.

PCM contribution to the enhancement of AEAs corresponding to the effect of the bulk water ($\epsilon = 78.4$) with respect to the species in vacuum ($\epsilon = 1.0$) is largest for the unsolvated uracil, as expected. Data in Table 1 show that the importance of PCM contributions decrease with the extent of the microsolvation, but there are notable differences between a and b structures with the same number of hydrating molecules (ranging in the interval of 122 to 215 meV for U(H₂O)_{na} and U(H₂O)_{nb} structures with $n = 1–3, 5$). It is important to stress that AEA of uracil with no explicit water molecules is 1.912 eV, by 330 meV lower than is AEA (2.242 eV) of the microsolvated

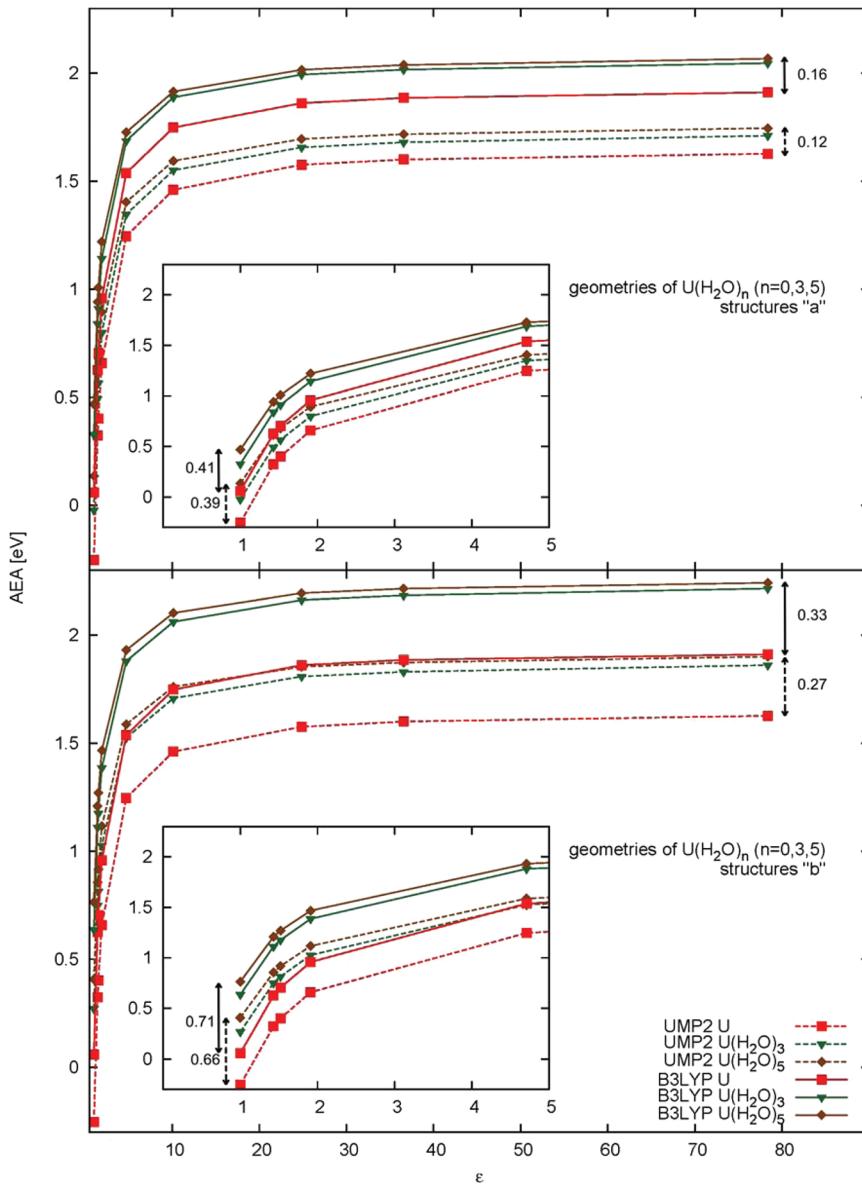


Figure 4. UMP2 and B3LYP adiabatic electron affinities (AEA) [eV] of uracil (U) and $\text{U}(\text{H}_2\text{O})_n$ ($n = 3, 5$) complexes as a function of the relative dielectric constant ϵ of the solvent. The upper part represents results for the structural framework a; the lower part represents results for the structural framework b. Note the effect of the microsolvation with UMP2 (dotted vertical lines) and B3LYP (full vertical lines) for the relative dielectric constant $\epsilon = 1.0$ and 78.4 (with PCM), respectively.

$\text{U}(\text{H}_2\text{O})_{5b}$ complex exposed to PCM with $\epsilon = 78.4$. The analogous value for the $\text{U}(\text{H}_2\text{O})_{5a}$ complex is 2.068 eV.

Qualitatively, the same picture of the microsolvation and the PCM bulk solvation effects is also valid for VDEs (see Table 2 and Figure 3). Note, that with DFT/B3LYP is VDE for the free uracil 0.736 eV, within PCM ($\epsilon = 78.4$) it is as large as 2.549 eV, for the microsolvated $\text{U}(\text{H}_2\text{O})_{5a}$ complex it increases to 2.921 eV, and for the microsolvated $\text{U}(\text{H}_2\text{O})_{5b}$ complex to 3.053 eV. Within PCM, the effect of microsolvation of uracil is larger for VDE than for AEA. On the contrary, the effect of the particular structure of the complex, $\text{U}(\text{H}_2\text{O})_{5a}$ or $\text{U}(\text{H}_2\text{O})_{5b}$ is larger for AEA (compare data in Tables 1 and 2, respectively).

Some literature data on solvation effects in various other properties of the NABs led to the conclusion that the microsolvation affects final values obtained by PCM very little.^{23,26,32} Our data show that microsolvation is not only quite significant but also that a variety of structures,^{12,13,21} preferring

either the neutral complexes (structures a in our treatment) or the anion complexes (our structures b) affect final AEAs and VDEs.

We present the dependence of AEAs and VDEs on selected values of the dielectric constant ϵ in Figures 4 and 5, respectively, for the free uracil and for $\text{U}(\text{H}_2\text{O})_{n=3,5}$ complexes. Curves for microhydrated structures a are shown in the upper and structures b in the lower parts of Figures 4 and 5. Insets in both figures show detailed insight into curves for low values of ϵ . Enhancement of the electron affinity with increasing ϵ is considerable. Already for $\epsilon = 10$, both AEAs and VDEs are close to the value for $\epsilon = 78.4$ corresponding to the bulk water. The trend is, again, essentially the same with MP2 (broken lines) and DFT B3LYP (full lines).

Figures 4 and 5 are useful for a transparent comparison of alterations of AEAs and VDEs upon applying PCM to the free (unsolvated) uracil and microsolvated $\text{U}(\text{H}_2\text{O})_{n=3,5}$ complexes.

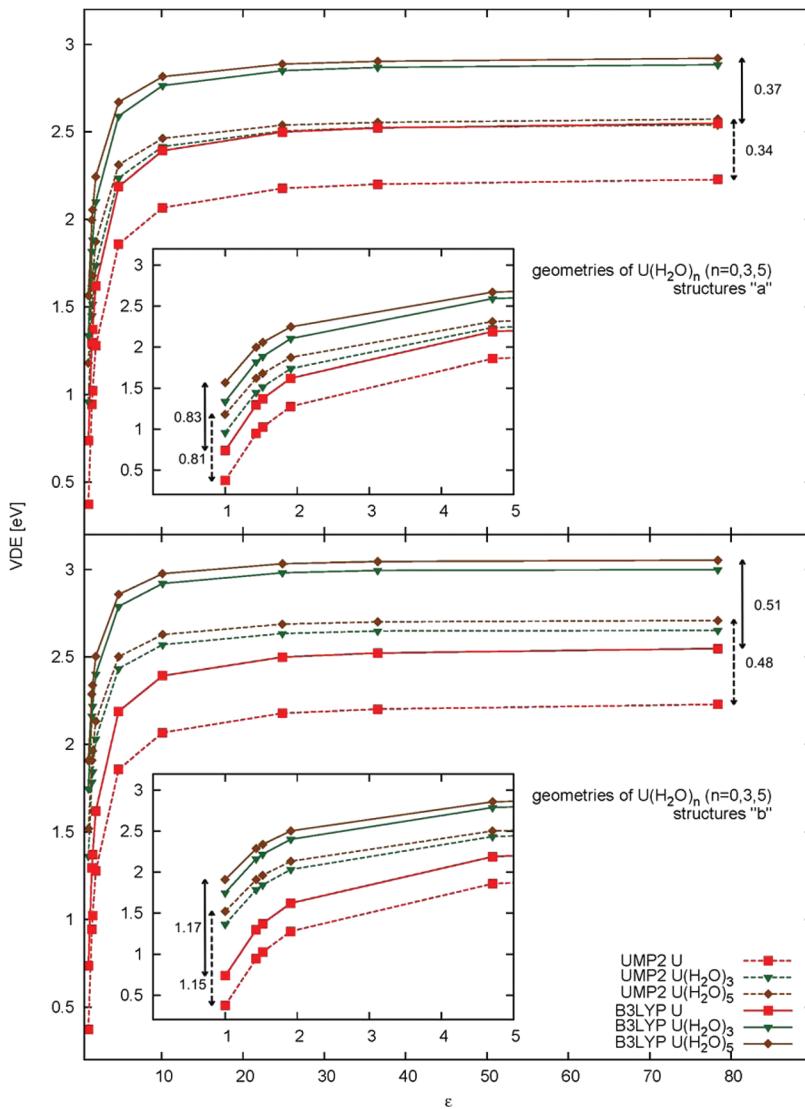


Figure 5. UMP2 and B3LYP vertical detachment energies (VDE) [eV] of uracil (U) and U(H₂O)_n ($n = 3, 5$) complexes as a function of the relative dielectric constant ϵ of the solvent. The upper part represents results for the structural framework a; the lower part represents results for the structural framework b. Note the effect of the microsolvation with UMP2 (dotted vertical lines) and B3LYP (full vertical lines) for the relative dielectric constant $\epsilon = 1.0$ and 78.4 (with PCM), respectively.

First, we note that the curves for complexes with three and five water molecules, respectively, differ very little. Actually, all essential effects due by taking the microsolvation become evident already with structures with three solvating water molecules.

Upon microsolvation by five water molecules, AEA of the unsolvated uracil in vacuum ($\epsilon = 1$) is enhanced by 0.39–0.41 eV for the structure a and even more, by 0.66–0.71 eV, for structure b. With B3LYP and structures optimized by Saettel and Wiest,²³ microsolvation by three water molecules results in the enhancement of AEA by 0.5 eV, similar to our finding. Upon increasing ϵ up to 78.4, the importance of microsolvation was reduced to 0.12–0.16 eV for structure 5a and to 0.27–0.33 eV for structure 5b. However, with increasing ϵ , AEAs approach different values for structures a and b, respectively. At $\epsilon = 78.4$, AEAs of microsolvated U(H₂O)_{5a} and U(H₂O)_{5b} differ by 0.17 eV using B3LYP values. The effect of microhydration is even larger for VDEs than for AEAs. At $\epsilon = 78.4$, VDEs of the free uracil and the U(H₂O)₅ complexes differ by 0.34–0.37 eV

(structures a) and 0.48–0.50 eV (structures b) with MP2 and B3LYP methods.

Vibrational effects were not considered in this work. In general, they contribute to an additional increase of the electron capturing ability of the free uracil and also of uracil hydrated by up to five water molecules by about 0.10–0.13 eV.^{6,12,13}

4. CONCLUSIONS

Although DFT with the B3LYP functional overestimates absolute values of electron affinities of uracil (AEAs and VDEs) in comparison with available CCSD(T) data by up to 0.20–0.28 eV, all trends due to microsolvation copy benchmark CCSD(T) results irrespective of the number and structural framework of water molecules in uracil–water complexes. MP2 values are underestimated with respect to available CCSD(T) data by 0.09–0.15 eV. We believe that CCSD(T) can be used as a correcting instrument of DFT and MP2 for obtaining more accurate affinities of systems not presently amenable to the more accurate CCSD(T) method.

B3LYP AEAs and VDEs of the free uracil ($\epsilon = 1.0$) increase by 0.41–0.71 eV, and by 0.83–1.17 eV, respectively, due to microsolvation in $U(H_2O)_5$ complexes, depending on the particular structure of the complex. Higher AEAs are calculated for the structural pattern, b, representing structures preferring the uracil anion radical. For a rough estimate of AEA of the microsolvated uracil–water complex in the most stable anion structure 5b, several corrections to B3LYP values can be implemented. First, the difference between B3LYP and CCSD(T) benchmark AEA taken from the analogous $U(H_2O)_{3b}$ complex leads to the lowering of AEA in Table 1 (0.76 eV), by 0.21 eV. Enlargement of the basis set to aug-cc-pVQZ for the unsolvated uracil leads to a very small increase of AEA, by 0.01 eV.⁷ Considering that AEA of free uracil is close to zero,^{6,7} even small basis set effects matter, but for solvated uracil, they are completely unimportant. Vibrational effects are larger, 0.10–0.13 eV,^{6,12,13} leading to final value of AEA of the $U(H_2O)_{5b}$ complex from B3LYP, 0.66 eV. This value is significantly lower than the experimental estimate of Eustis et al.¹¹ based on the photoelectron intensity threshold E_T of pentahydrated uracil, 1.26 eV. Aside from problems in attempting to extract experimental AEA from vibrationally unresolved photoelectron spectra, a part of the difference between our and spectroscopic AEA can be attributed also to specific effects related to a variety of structures of uracil–water complexes in the theoretical treatment. Nevertheless, our structures b represent the uracil–water complexes having the largest AEA for a selected number of hydrating molecules. Other theoretical AEAs^{12,13,23} are also much lower than experimental data for 3–5 hydrating water molecules. We are unable to see how computational data can be reconciled with experiment. We note that in relation to the DNA damage by low energy electrons, reasonably accurate electron affinity of uracil microsolvated just by a few water molecules is important since original experiments from the Sanche group¹ concern dry DNA having only the structural water molecules; see also detailed discussion by Simons.² Concerning VDEs, B3LYP results should be corrected by 0.24 eV considering a difference between B3LYP and CCSD(T) for smaller uracil–water complexes. Using this correction, we arrive at VDEs for $U(H_2O)_{5a}$ and $U(H_2O)_{5b}$ complexes, respectively, 1.32 and 1.67 eV, which bracket experimental value¹¹ for pentahydrated complexes, 1.49 eV.

AEAs and VDEs of both the free uracil and uracil–water complexes are growing rapidly with increasing ϵ in the polarizable continuum model. Bulk effects are almost saturated for $\epsilon = 10$. Upon including the bulk water effect on the free uracil employing PCM ($\epsilon = 78.4$), AEA increases from 0.06 to 1.91 eV using B3LYP (similar enhancement of AEA is also obtained with MP2). With PCM applied to the $U(H_2O)_{5b}$ complex, AEA increased from 0.76 to 2.24 eV. Corresponding values for the $U(H_2O)_{5a}$ complex are 0.47 and 2.07 eV, respectively. VDEs from B3LYP approach the values of 2.92–3.05 eV with increasing ϵ depending on the specific structure of $U(H_2O)_5$ complexes.

AEAs and VDEs exhibit a stair-like shape when going from free uracil to $U(H_2O)_{1-5}$ complexes with structures a, while the shape for complexes with structures b is monotonous. Uracil microsolvated with discrete water molecules in $U(H_2O)_n$ complexes treated by PCM with $\epsilon = 78.4$ exhibit the same specific structural features as do complexes in the gas phase ($\epsilon = 1$). Therefore, specific interactions (essentially hydrogen

bonds involving uracil and water molecules) are preserved within PCM.

There is a widespread and controversial debate about the importance of microsolvation within the PCM treatment of biomolecules. Kumar et al.³² report a small effect of microhydration on AEAs of the guanine–cytosine base pair. Saettel and Wiest²³ obtained a significant difference of 0.3 eV between AEAs of free uracil and the triply hydrated uracil for $\epsilon = 78.4$. Close et al.²⁶ observed that the ionization energy threshold of the uracil complex hydrated by three water molecules and free uracil placed in a PCM cavity differ by no more than 0.07 eV. They conclude that accurate calculations of IETs of uracil and thymine can be obtained simply by considering long-range solvation effects. We should note, however, that adding 1–3 discrete water molecules around the uracil molecule results in a decrease of IET gradually by no more than 0.33 eV, i.e., much less than are changes of AEAs and VDEs (up to 0.6 and 1.0 eV, respectively) reported in the present article. It appears that the microsolvation effect is much lower for the neutral uracil and its cation than for anionic species reflecting larger sensitivity of anions to specific hydrogen bond formation. This view is supported by the hydrogen bonding analysis and quantum mechanical/molecular mechanical study of Brancato et al.²¹ on microsolvation of uracil and its anion combined with the bulk solvent effects considered via PCM. The spatial function of water distribution is broader around the radical, as seen in the hydrogen bonding analysis. Therefore, as expected, water molecules interact more tightly with the uracil anion radical. We believe that this explains a marked difference of 0.30 eV between AEA of microsolvated uracil and free uracil, both placed in a PCM cavity representing bulk water. For VDEs, the difference is even larger, 0.50 eV. AEAs and VDEs are also affected by structural effects of neutral and anion uracil–water complexes.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: urban@fns.uniba.sk.

■ ACKNOWLEDGMENTS

This research was supported by the Slovak Grant Agency, grant VEGA-1/0520/10, and grant of the Slovak Research and Development Agency APVV (contract no. LPP-0155-09). Support from the Centers of Excellence program of the Slovak Academy of Sciences (COMCHEM; contract no. II/I/2007) is also gratefully acknowledged.

■ REFERENCES

- (1) Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M. A.; Sanche, L. *Science* **2000**, 287, 1658.
- (2) Simons, J. How Very Low-Energy (0.1–2 eV) Electrons Cause DNA Strand Breaks. In *Advances in Quantum Chemistry*; Elsevier: San Diego, CA, 2007; Vol. 52, p 171.
- (3) Gu, J. D.; Wang, J.; Leszczynski, J. *Nucleic Acids Res.* **2010**, 38, S280.
- (4) Cai, Z. L.; Li, X. F.; Sevilla, M. D. *J. Phys. Chem. B* **2002**, 106, 2755.
- (5) Gu, J. D.; Wang, J.; Leszczynski, J. *ChemPhysChem* **2010**, 11, 175.
- (6) Bachorz, R. A.; Klopper, W.; Gutowski, M. *J. Chem. Phys.* **2007**, 126, 085101.
- (7) Dedíková, P.; Demovič, L.; Pitoňák, M.; Neogrády, P.; Urban, M. *Chem. Phys. Lett.* **2009**, 481, 107.
- (8) Li, X. F.; Cai, Z. L.; Sevilla, M. D. *J. Phys. Chem. A* **2002**, 106, 1596.

- (9) Wesolowski, S. S.; Leininger, M. L.; Pentchev, P. N.; Schaefer, H. F. *J. Am. Chem. Soc.* **2001**, *123*, 4023.
- (10) Schiedt, J.; Weinkauf, R.; Neumark, D. M.; Schlag, E. W. *Chem. Phys.* **1998**, *239*, 511.
- (11) Eustis, S.; Wang, D.; Lyapustina, S.; Bowen, K. H. *J. Chem. Phys.* **2007**, *127*, 224309.
- (12) Kim, S.; Schaefer, H. F. *J. Chem. Phys.* **2006**, *125*, 144305.
- (13) Bao, X. G.; Sun, H.; Wong, N. B.; Gu, J. D. *J. Phys. Chem. B* **2006**, *110*, 5865.
- (14) Li, D. J.; Ai, H. Q. *J. Phys. Chem. B* **2009**, *113*, 11732.
- (15) Dedíková, P.; Neogrády, P.; Urban, M. *J. Phys. Chem. A* **2011**, *115*, 2350.
- (16) Kim, S.; Schaefer, H. F. *J. Chem. Phys.* **2007**, *126*, 064301.
- (17) Kim, S.; Schaefer, H. F. *III. J. Chem. Phys.* **2010**, *133*, 144305.
- (18) Gu, J. D.; Xie, Y. M.; Schaefer, H. F. *Chem. Phys. Lett.* **2009**, *473*, 213.
- (19) Li, X.; Wang, H.; Bowen, K. H. *J. Chem. Phys.* **2010**, *133*, 144304.
- (20) Motegi, H.; Takayanagi, T. *J. Mol. Struct.* **2009**, *907*, 85.
- (21) Brancato, G.; Rega, N.; Barone, V. *Chem. Phys. Lett.* **2010**, *500*, 104.
- (22) Brancato, G.; Rega, N.; Barone, V. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10736.
- (23) Saettel, N. J.; Wiest, O. *Tetrahedron* **2006**, *62*, 6490.
- (24) Shukla, M. K.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 7775.
- (25) Shukla, M. K.; Leszczynski, J. *Int. J. Quantum Chem.* **2010**, *110*, 3027.
- (26) Close, D. M.; Crespo-Hernandez, C. E.; Gorb, L.; Leszczynski, J. *J. Phys. Chem. A* **2005**, *109*, 9279.
- (27) Improta, R.; Barone, V. *J. Mol. Struct.* **2009**, *914*, 87.
- (28) Trygubenko, S. A.; Bogdan, T. V.; Rueda, M.; Orozco, M.; Luque, F. J.; Šponer, J.; Slavíček, P.; Hobza, P. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4192.
- (29) Hanuš, M.; Ryjáček, F.; Kabeláč, M.; Kubar, T.; Bogdan, T. V.; Trygubenko, S. A.; Hobza, P. *J. Am. Chem. Soc.* **2003**, *125*, 7678.
- (30) Hanuš, M.; Kabeláč, M.; Rejnek, J.; Ryjáček, F.; Hobza, P. *J. Phys. Chem. B* **2004**, *108*, 2087.
- (31) Mazzuca, D.; Marino, T.; Russo, N.; Toscano, M. *J. Mol. Struct.* **2007**, *811*, 161.
- (32) Kumar, A.; Sevilla, M. D.; Suhai, S. *J. Phys. Chem. B* **2008**, *112*, 5189.
- (33) Urban, M.; Neogrády, P.; Hubač, I. Spin Adaptation in the Open Shell Coupled Cluster Theory with a Single Determinant Restricted Hartree–Fock Reference. In *Recent Advances in Coupled Cluster Methods*; Bartlett, R. J., Ed.; World Scientific: Hackensack, NJ, 1997; p 275.
- (34) Neogrády, P.; Pitoňák, M.; Granatier, J.; Urban, M. Coupled Cluster Calculations: OVOS As an Alternative Avenue Towards Treating Still Larger Molecules. In *Recent Progress in Coupled Cluster Methods*; Čársky, P., Ed.; Springer Science+Business Media B.V.: New York, 2010; p 419.
- (35) Watts, J. D.; Urban, M.; Bartlett, R. J. *Theor. Chim. Acta* **1995**, *90*, 341.
- (36) Takayanagi, T.; Asakura, T.; Motegi, H. *J. Phys. Chem. A* **2009**, *113*, 4795.
- (37) Voityuk, A. A. *Phys. Chem. Chem. Phys.* **2009**, *11*, 10608.
- (38) Li, X. F.; Sevilla, M. D.; Sanche, L. *J. Am. Chem. Soc.* **2003**, *125*, 13668.
- (39) Kabeláč, M.; Hobza, P. *Phys. Chem. Chem. Phys.* **2007**, *9*, 903.
- (40) Haranczyk, M.; Gutowski, M.; Warshel, A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4442.
- (41) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.
- (42) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *J. Chem. Phys. Lett.* **1996**, *255*, 327.
- (43) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.
- (44) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032.
- (45) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.
- (46) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.
- (47) Cammi, R. *J. Chem. Phys.* **2009**, *131*, 164104.
- (48) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (49) Neogrády, P.; Urban, M. *Int. J. Quantum Chem.* **1995**, *55*, 187.
- (50) Aquilante, F.; De Vico, L.; Ferre, N.; Ghigo, G.; Malmqvist, P. A.; Neogrády, P.; Pedersen, T. B.; Pitoňák, M.; Reiher, M.; Roos, B. O.; Serrano-Andres, L.; Urban, M.; Veryazov, V.; Lindh, R. *J. Comput. Chem.* **2010**, *31*, 224.
- (51) Šulka, M.; Pitoňák, M.; Neogrády, P.; Urban, M. *Int. J. Quantum Chem.* **2008**, *108*, 2159.
- (52) Neogrády, P.; Pitoňák, M.; Urban, M. *Mol. Phys.* **2005**, *103*, 2141.
- (53) Bachrach, S. M.; Dzierlenga, M. W. *J. Phys. Chem. A* **2011**, *115*, 5674.
- (54) Wang, F. F.; Zhao, D. X.; Yang, Z. Z. *Chem. Phys.* **2009**, *360*, 141.
- (55) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.