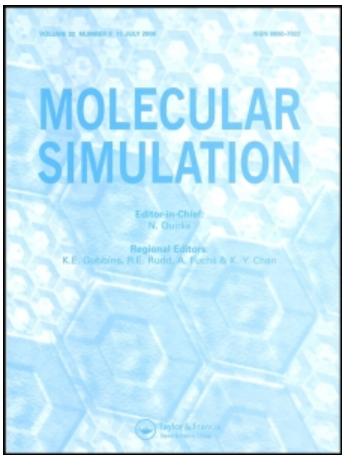

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Density functional studies on the electron affinities of DNA and RNA bases

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Influence of basis sets on electron affinities (EAs) of DNA and RNA bases has been investigated using density functional method (B3LYP functional) with different basis sets (6-31G, TZVP and 6-311 + + G**). Effect of some PBE functionals namely, PBEOP, PBELYP and PBEVWN, on EA values of the nucleobases was studied using basis set which predicted the most reliable values with B3LYP functional. Observation of the trends in the values of EA and dipole moment of the molecules enable us to identify the features of a basis set that shows the presence of dipole-bound state of some of the nucleobases. The vertical electron affinities with B3LYP and PBEOP functionals are close to the experimental values. The adiabatic electron affinities of uracil and thymine were found to be positive for basis set with diffuse functions using B3LYP functional. Adenine does not have a stable covalently bound anion at all levels of basis sets and functionals. The sign of adiabatic electron affinity value of cytosine is inconsistent with that of experimental value but in agreement with previous theoretical results. For guanine the adiabatic electron affinity value with 6-311 + + G** basis set was found to be very high as comparison with other two basis sets confirming the formation of mixed covalent-dipole character.

Keywords: electron affinities; DNA; RNA; DFT calculations

1. Introduction

The knowledge of genetic information requires the study of electronic properties of nucleic acid bases. They provide trapping sites for electrons and form radical anion upon radiation then participate in chemical processes such as protonation and deprotonation that can lead to the permanent alteration of the DNA bases and to genetic damage. Adiabatic electron affinities (AEAs) are the thermodynamic parameters that govern the ease of reduction of each nucleobases. In this context, the determination of electron affinities of DNA and RNA bases have significance in the study of radiation damage as well as excess electron transfer through DNA. Various experimental [1–9] and theoretical [10–23] studies were devoted to this subject in order to investigate the properties of nucleobases. The vertical electron affinities (VEAs) of DNA and RNA bases have been reported experimentally by Aflatooni et al. [5] using electron transmission spectroscopy (ETS) technique where they found vertical attachment energies (VAEs) for all nucleobases are >0 or in the other sense their vertical electron affinities are negative. In the very early 1990s experimental measurement of the AEAs of nucleobases was first estimated and found substantial values with the relative order: Cytosine (C) $<$ Thymine (T) $<$ Uracil (U) $<$ Adenine (A) $\lll$ Guanine (G) [1]. They estimated gas phase adiabatic electron affinities of nucleobases from measurement of reversible reduction potentials of the bases in solution by 'calibration' using acridine and anthracene molecules for which gas phase AEAs are known. The observed electron affinities from their experiment in eV are C(+0.56), T(+0.79), U(+0.80), A(+0.95) and G(+1.51).

In contrast, many computational studies on nucleic acid base anions found negative valence adiabatic electron affinities for some of the nucleobases. For example PMP2 calculations with the 6-311 + G(2df,p) basis set yields negative AEAs values for all DNA bases in the range 0.12–0.73 eV [19]

In the early 1990s, noting the large dipole moments of nucleic acid bases ($\sim$5D), Adamowicz and co-workers [15] conducted calculations which found stable anions of uracil in which their electrons were bound via dipole interactions often referred as 'dipole-bound anion'. In covalent anions the extra electron enters the LUMO of the molecule whereas in dipole-bound anion the excess electron is bound by the dipole fields of the neutral molecule without influencing the structure of the molecule. Following these theoretical predictions two complementary experiments on gas phase nucleic acids base anions were conducted by Desfrancois et al. [2] and Bowen and co-workers [3] with the help of Rydberg electron transfer spectroscopic studies and photoelectron spectroscopy, respectively. Both experiments found stable dipole-bound anions, confirming the theoretical predictions of Oyler and Adamowicz [15]. After verifying the existence of dipole-bound anion, Desfrancois et al. estimated simultaneous existence of both valence and dipole-bound states of uracil anion by using Rydberg

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electron transfer spectroscopy to gas-phase isolated uracil molecules and mixed uracil-argon clusters [4]. In their studies, by observing valence U anions following evaporation of argon atoms, they came to the conclusion that the valence electron affinity must be larger than the binding energies of neutral uracil–argon clusters, typically between 0.030 and 0.060 eV and simultaneously being smaller than dipole-bound EA of 0.093 meV.

By noting the fact that nucleobases in the gas-phase can form dipole-bound anion and on the other hand in the condensed phase nucleobase anions are conventional (covalent) anions, Hendricks et al. [6] performed a series of negative ion photoelectron spectroscopic experiments in gas-phase and solvated uracil cluster anions to assess the point at which the uracil anion converts from dipole-bound to covalently bound state. They observed a sharp peak in the photoelectron spectrum of uracil anion and explained this behavior by suggesting that the uracil anion essentially has the same structure as the neutral, which is typical for dipole bound anion. They have also found the vertical detachment energy (VDE) of uracil anion to be 0.093 ± 0.007 eV which is in good agreement with the adiabatic dipole bound EA estimated by Oyler and Adamowicz [15]. The conversion of dipole-bound state to the covalent anion state was observed by the inclusion of a single water molecule indicating a broad photoelectron spectrum of $U^-(H_2O)$. They saw a dramatic effect of having both dipole-bound and covalent like features of the complex by the replacement of water molecule by Xe as solvating agent. Similar to the studies of Hendricks and co-workers, Schiedt et al. [7] studied the photoelectron spectra of uracil, thymine and cytosine in free and microsolvated form. The reported extrapolated electron affinities from this microsolvation experiments are 0.12, 0.13 and 0.15 eV for T, C and U, respectively.

Density functional theory (DFT) was first used in the determination of AEA for uracil by Desfrancois et al. [4] and found a small but positive value of 0.07 eV. Recently, several studies of nucleobases AEAs have included various DFT computations [19,20,22,23]. Wesolowski et al. [20] used double-ξ plus polarisation plus diffuse (DZP++) basis set with five different density functionals in order to bracket the true AEAs of nucleobases. They have concluded that U and T covalent anions are bound by *ca*. 0.05–0.25 eV whereas adenine does not have a stable covalently bound anion in the gas phase.

Although various experimental and theoretical works has been carried out on the nucleobases, true values of AEAs of the bases is still in a matter of controversy and the precise determination of their electron affinities remains challenging. Therefore, further studies are necessary to determine the true AEAs values of the nucleobases and to investigate the exact nature of their anions. In the present work, the tautomers of nucleic acid bases shown in Figure 1 are chosen on the basis of their stability and biological importance and electron affinities of these bases are determined using hybrid potential B3LYP with different basis sets in order to establish the influence of orbital basis sets in the study of the electronic properties of these biomolecules. Although electron affinity determination of DNA and RNA bases using several density functionals have been reported, to the best of our knowledge, none used PBE

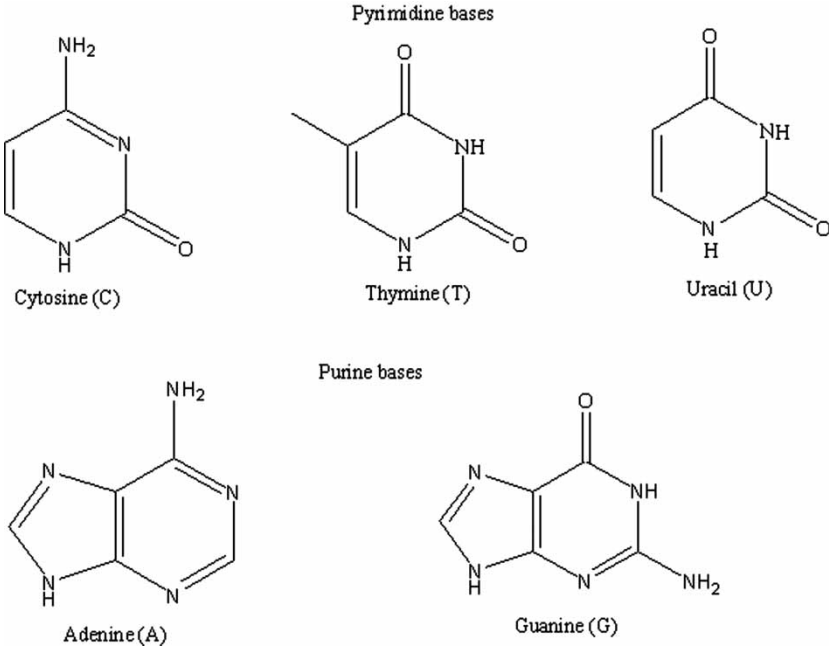


Figure 1. Major tautomeric structures of DNA and RNA bases.

exchange with different correlation functionals to evaluate the electron affinity of nucleobases. The EAs of the selected systems are calculated using the better predicted basis set in combination of GGA exchange-correlation functionals PBEOP and PBELYP. In addition to the GGA functionals, we tested the GGE approach using PBEVWN functional to study how far these methods are able to predict true electron affinities.

2. Computational details

The nucleobases were optimised using DFT theory with hybrid generalised gradient approximation (GGA) exchange-correlation density functional B3LYP in connection with 631-G, TZVP and 6-311 + + G** basis sets. B3LYP is Becke's three parameter exchange functional (B3) [24] in combination with Lee, Yang and Parr (LYP) [25] correlation functional. In this work, the energies were converged to 1×10^{-7} hartrees. Geometries were optimised independently for each molecular species and for each functional using analytic gradient technique. Residual Cartesian gradients were less than 1×10^{-4} hartree/Bohr.

GGA exchange-correlation density functionals PBEOP, PBELYP and GGE exchange-correlation functional PBEVWN were used in connection with better predicted basis set 6-311 + + G** to notice their influence in determining the electron affinities of the nucleobases. These are Perdew–Burke–Ernzerhof exchange [26] plus one-parameter progressive (OP) [27] correlation (PBEOP), Lee, Yang and Parr (LYP) correlation (PBELYP) and Vosko, Wilk and Nusair (VWN5) correlation [28]. GGE (generalised gradient exchange) approach was proposed by Hertwig and Koch [29] in which functionals are the combination of GGA exchange functionals and local correlation functionals. All computations were carried out with the GAMESS [30] programme package.

The electron affinity is the energy of the neutral molecule minus that of the anion radical

$$EA = E_{neutral} - E_{anion}.$$

The adiabatic electron affinity is the difference in total energies between the optimised structures of neutral and anionic systems. The calculation of vertical electron affinity employs the optimised geometry of neutral forms to compute the energy of the corresponding anions.

3. Results and discussions

The adiabatic electron affinities without zero point energy correction, obtained at B3LYP level with 6-31G to 6-311 + + G** basis sets are given in Table 1. Although zero-point vibrational energy corrections are not included to our AEA values, we note significant nuclear rearrangement of the anions relative to their neutrals. The AEA values for basis sets without diffuse functions (' + ' signs) are negative for all bases indicating unstable anion formation whereas for larger basis set containing diffuse functions give positive EA values for U and T in agreement with some of the previous experimental [2,4,7] and theoretical [10,15] results. This is because anions are better predicted with diffuse functions as the description of the spatial expansion of electron density for anions needs additional diffuse basis functions. The attachment of an electron to the planar neutral molecule leads to the deviation of the system from planarity. The anions of all nucleobases deviate largely from planarity, which is evident from the change in dihedral angles of the anions. The main torsional angles of thymine and uracil anions obtained at the B3LYP/6-311 + + G** level are shown in Figure 2. The same dihedral angles of the corresponding neutral systems are equal to 0° or 180°.

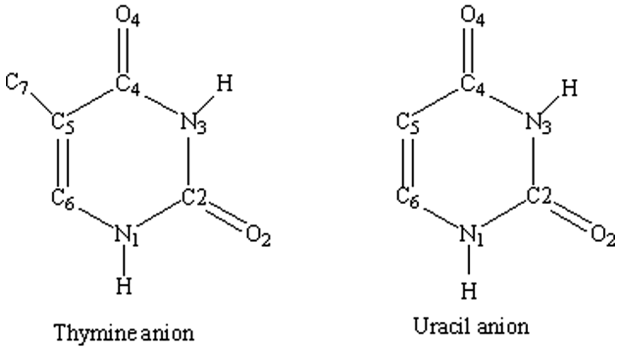
The variation in adiabatic electron affinity with respect to basis set is displayed graphically in Figure 3. We observed similar trends of AEA values for all bases with 6-31G and TZVP basis sets but it differs significantly when diffuse functions are included. The trend obtained by using 6-311 + + G** basis set is shifted to higher EA values from that of the other two basis sets. Almost similar trends are observed for uracil and thymine with slightly different for cytosine with three basis sets. The EA value obtained by basis set with diffuse function is slightly higher than the regular trend predicted with other basis sets for A and much more for G.

The electron affinities of purine bases are very sensitive to diffuse functions. This sensitivity is high for guanine.

Table 1. ZPE uncorrected adiabatic electron affinities (eV) of DNA and RNA bases by different theoretical and experimental methods.

Methods	Uracil	Thymine	Cytosine	Guanine	Adenine
B3LYP/631G	−0.56	−0.61	−0.96	−1.13	−1.25
B3LYP/TZVP	−0.19	−0.21	−0.50	−0.79	−0.89
B3LYP/6-311 + + G**	0.23	0.16	−0.16	−0.14	−0.41
B3LYP/DZP++[a]	0.24	0.20	0.03	−0.01	−0.28
MP2/6-31 + G(d)//6-31G*[b]	−0.51	−0.54	−0.83	−1.79	−1.47
Predicted *ab initio*[b]	0.4	0.3	0.2	−0.7	−0.3
Expt[c]	0.054 ± 0.035	0.068 ± 0.020	–	–	0.012 ± 0.005
Expt[d]	0.150 ± 0.120	0.120 ± 0.120	0.130 ± 0.120	–	–

[a] [20], ZPVE corrected. [b] [10]. [c] [2]. [d] [7], extrapolated values.



Thymine anion	Uracil anion
$N_1C_2N_3C_4 = 0.914$	$N_1C_2N_3C_4 = -2.72$
$C_2N_3C_4O_4 = 176.83$	$C_2N_3C_4O_4 = 177.63$
$O_4C_4C_5C_6 = 176.83$	$O_4C_4C_5C_6 = 176.51$
$C_4C_5C_6N_1 = 11.17$	$C_4C_5C_6N_1 = 10.20$
$C_5C_6N_1C_2 = -15.64$	$C_5C_6N_1C_2 = -21.83$
$C_6N_1C_2N_3 = 9.45$	$C_6N_1C_2N_3 = 12.71$
$O_2C_2N_3C_4 = -179.10$	$O_2C_2N_3C_4 = 178.32$
$N_1C_6C_5C_7 = -172.24$	

Figure 2. Torsional angle values (in degrees) for thymine and uracil at the optimised geometries. The same torsional angles for neutral system are equal to 180° or 0°.

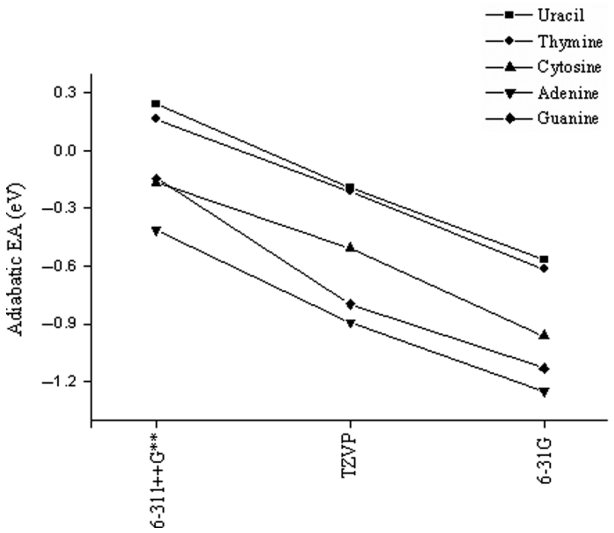


Figure 3. Variation of the DFT-B3LYP calculated adiabatic electron affinities of the DNA/RNA bases at different basis sets. The regular trend lines differ significantly for guanine when diffuse functions are included.

Except for the concordance in sign, its AEA value with 6-311 + + G** basis set is much higher than those obtained by Sevilla et al [10]. This discrepancy could be explained by considering the fact that their MP2 results arise from single-point computations on geometries optimised at the HF level. The dipole moment of G is sufficiently high (6.87 D at B3LYP/6-311 + + G** level) and the higher EA value for G at this level is probably due to the dipole bound contamination. All levels of theory give most negative value for adenine in agreement with earlier DFT calculations [20,22]. The dipole moment of adenine at B3LYP/6-311 + + G** level is found to be 2.46 D which is similar with that of Russo et al. [22]. This amount of dipole moment should not be enough to bind the electrons via dipolar interactions [22,31]. Distortion of the structure of its anion is also not so much influencing. Thus adenine does not have a stable covalently bound anion or dipole bound anion in the gas phase. The reason for getting slightly higher trend for 6-311 + + G** basis set as compared to the other basis set remains unclear. Li et al. [23] reported that the purine anions exhibit a mixed covalent-dipole character when large, diffuse basis sets are employed. Under biological conditions DNA bases are not isolated but rather solvated by water molecules. Since the dipole-bound states are not believed to be relevant to aqueous systems [10], conventional valence electron affinities are the only relevant biological quantity. Thus, the covalent (negative) electron affinities of purine bases are perhaps best estimated using small basis sets that constrain the electron density on the molecular framework [32].

Similar trends are observed for the adiabatic electron affinities of pyrimidine bases with three basis sets. Experimental studies for AEA of U give positive value ranging from 0.030 to 0.093 eV [2,4,7]. Although the experimental determinations of EAs for U and T by Desfrancois et al. [2] and Schiedt et al. [7] yielded positive EAs, their values are significantly different (Table 1). Desfrancois et al. reported the dipole-bound EAs values of the nucleobases whereas Schiedt et al. [7] estimated the valence EAs of the pyrimidine bases by extrapolation of their data for microsolvated anions that may be the reason for disparity between these two experimental results. Our computations yield negative EA for U with 6-31G and TZVP basis sets. This is probably due to the lack of diffuse functions that are mandatory in the description of anions. The AEA value of U obtained with 6-311 + + G** (0.239 eV) is in good agreement with those determined by Schiedt et al. [7] The employed computational level gives positive AEA with significant geometry distortion of the anions with respect to their neutral form. This suggests the entrance of the extra electron in the LUMO of the neutral molecule. The dipole moment of uracil is 4.19 D at B3LYP/6-311 + + G**, and an additional contribution to the stability can arise from the dipole-electron interaction. Our B3LYP/6-311 + + G** value is very similar to the ZPE corrected value at B3LYP/DZP++ level by Wesolowski et al. [20]. Similarly, the sign of adiabatic electron affinity values of thymine for basis sets without diffuse functions is inconsistent with the previously reported experimental [2,7] results. This is again due to the

Table 2. Zero-point uncorrected vertical electron affinities (in eV) of DNA and RNA bases by different theoretical and experimental methods.

Methods	Uracil	Thymine	Cytosine	Adenine	Guanine
B3LYP/631-G	−0.94	−1.02	−1.32	−1.51	−1.86
B3LYP/TZVP	−0.59	−0.64	−0.87	−1.08	−1.58
B3LYP/6-311 + + G**	−0.23	−0.26	−0.25	−0.41	−0.15
MP2/6-31 + G(D)[a]	−0.19	−0.32	−0.40	−0.74	−1.23
B3LYP/D95V + (D)[b]	−0.32	−0.26	−0.63	−0.80	−0.37
Expt[c]	−0.22	−0.29	−0.32	−0.54	–
Expt[d]	−	0	−0.55	−0.45	–

[a] [10], scaled results. [b] [23]. [c] [5]. [d] [8].

lack of diffuse functions, which can describe the spatial expansion of the electron density of the anion. The positive EA value obtained with 6-311 + + G** basis set is in agreement with experimental and most of theoretical [10,19,20,22,23] data previously reported. This suggests a covalent electron attachment that can be confirmed by the rather large rearrangement of the geometry in the anion. But the dipole bound state can also be possible due to dipole moment value that is 4.54D (B3LYP/6-311 + + G**). The AEA value obtained with 6-311 + + G** basis set falls in the range reported by Schiedt et al. [7]. For cytosine we found negative adiabatic electron affinities at all level of calculations that agree with some of the previous theoretical [19,22,23] determination but inconsistent with the experimental information available in the literature [7,9]. The AEAs obtained by Wesolowski et al. [20] oscillate between small positive and negative values for the three most reliable functional combinations and they have concluded that the AEA of cytosine remains ambiguous. Due to the large dipole moment of this molecule (6.77D at B3LYP/6-311 + G** level) the contributions from dipole-bound state must be considered. At this level we found comparatively higher electron affinity value than with the other two basis sets but disagreement in sign with the experimental data prevents a definitive conclusion.

Table 2 lists the calculated vertical electron affinities (VEAs) values. Some previous theoretical and experimental results are also reported for the purpose of comparison. In Figure 4, we display the variation of vertical electron affinities with respect to the basis sets. All values are found to be negative in good agreement with the results of ETS technique by Aflatooni et al. [5]. The trend lines for C and A obtained at B3LYP/6-311 + + G** level slightly differ and for G it substantially differs at the same level of theory from the other two basis sets. This is because G is more sensitive to the diffuse functions and the VEA obtained at this level is probably due to the dipole bound contribution. The vertical EAs obtained with 6-31G basis set are much more negative whereas values obtained by B3LYP functional coupled with TZVP basis set are twice as large as those obtained by experimental measurement. The results obtained by B3LYP/6-311 + + G** method are closer to the experimental counterparts.

The adiabatic electron affinities computed with the better-predicted basis set 6-311 + + G** for two GGA exchange correlation functionals PBEOP and PBELYP are given in Table 3. Neither the PBEOP nor PBELYP calculations indicate positive AEA as found experimentally. Both these methods yield negative EA for U and T with more negative value for U anion than T, which is inconsistent with reported experimental and theoretical data. However, AEA values of cytosine obtained with these two GGA functionals move slightly more close to the previous theoretical [19,22,23] determination than that of hybrid B3LYP functional. But, its sign is inconsistent with the experimental information available in the literature [7,9]. Due to the large dipole moment of this molecule (∼7.0 D) an additional contributions from dipole-bound state must be considered. On the other hand, these two functionals predict comparable AEAs for purines. For adenine the AEA is found to be negative with both PBEOP and PBELYP methods in agreement with earlier DFT

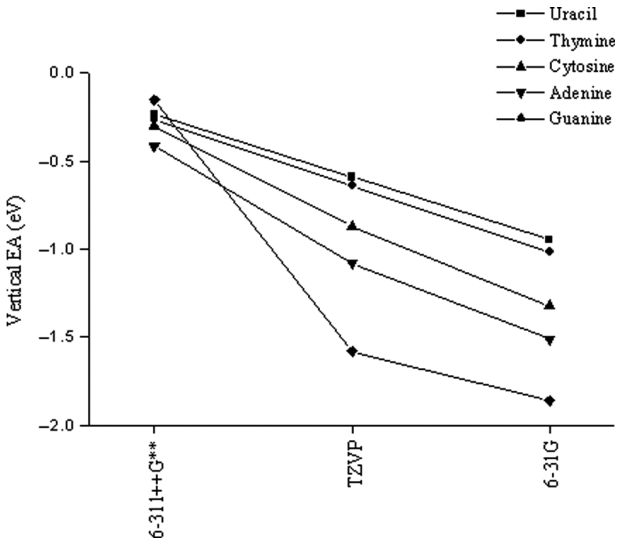


Figure 4. Variation of the DFT-B3LYP calculated vertical electron affinities of the DNA/RNA bases at different basis sets.

Table 3. Electron affinities (in eV, ZPE uncorrected) calculated by PBEOP and PBELYP functionals with 6-311 + + G** basis set.

	Adiabatic EA		Vertical EA	
System	PBEOP	PBELYP	PBEOP	PBELYP
Uracil	−0.320	−0.182	−0.246	−0.146
Thymine	−0.122	−0.003	−0.250	−0.071
Cytosine	−0.150	−0.129	−0.277	−0.099
Adenine	−0.282	−0.273	−0.331	−0.238
Guanine	−0.053	0.054	−0.062	−0.038

calculations [20,22] and experimental [8] gas-phase value. The PBELYP/6-311 + + G** level predicts small positive value of AEA for guanine while small negative value is obtained with PBEOP method. This oscillation is in agreement with the result obtained by Wesolowski et al. [20]. The AEA values calculated for U, T and G using PBEVWN functional and 6-311 + + G** basis set are 0.013, 0.347 and 0.291 eV, respectively. The sign of the adiabatic electron affinities obtained with this functional are in agreement with experiments.

The PBEOP and PBELYP vertical electron affinities for all nucleobases are listed in Table 3. All values are found to be negative in good agreement with the results of ETS technique by Aflatooni et al. [5] The variation in VEAs with respect to the PBEOP and PBELYP functionals along with the ETS data of Aflatooni et al., are displayed graphically in Figure 5. Although PBELYP predicts higher VEAs for all the selected systems, PBEOP values are in agreement with the experimental values. For U, T and C the PBEOP values slightly deviate from the experimental one while for A its value deviates more. The small amount of dipole moment of A (2.42 D) at this level cannot be a reason for this deviation. However, higher value of VEA for G may be due to the additional contribution from dipole bound state with dipole moment 6.88 D.

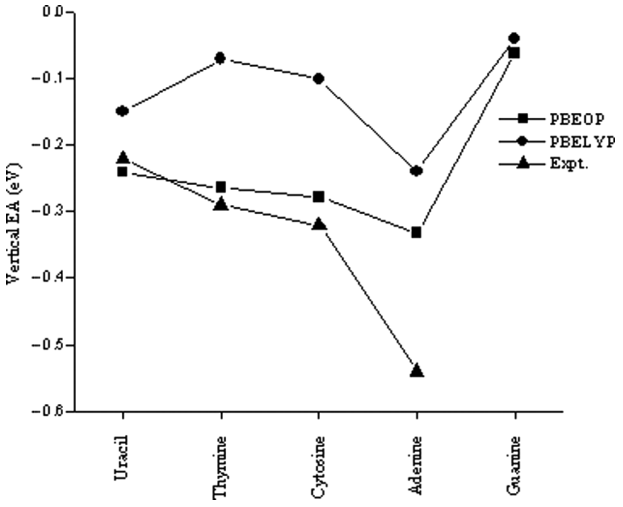


Figure 5. Variation of the vertical electron affinities of the DNA/RNA bases.

4. Conclusions

Computed electron affinities for nucleobases in the gas phase using different basis sets suggest that the VEA of all nucleobases are negative in all cases with B3LYP, PBEOP and PBELYP functionals in agreement with available experimental data. The basis sets without diffuse functions give more negative values of VEA as compared to the experimental values. The VEA values for 6-311 + + G** basis set with B3LYP functional follow the same trend as the other basis sets and close to that of the experimental values. The basis set with diffuse functions confirms the positive value of adiabatic electron affinities of uracil and thymine at B3LYP/6-311 + + G** level in agreement with the experimental and theoretical results. The dipole moment of cytosine is very high at this level and we can assume dipole bound state at this level. For adenine we found an unstable covalently bound anion in the gas phase in agreement with previous theoretical data. Guanine is most sensitive to diffuse functions and its AEA value for 6-311 + + G** basis set is more than that of Sevilla et al. [10]. This is due to the large dipole moment of the molecule for which it can exhibit mixed covalent-dipole character. Thus, the improved techniques that can handle such mixed state systems are useful to provide the more accurate electron affinities values of the nucleobases.

Acknowledgements

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