Ab initio determination of the electron affinities of DNA and RNA nucleobases

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High-level quantum-chemical *ab initio* coupled-cluster and multiconfigurational perturbation methods have been used to compute the vertical and adiabatic electron affinities of the five canonical DNA and RNA nucleobases: uracil, thymine, cytosine, adenine, and guanine. The present results aim for the accurate determination of the intrinsic electron acceptor properties of the isolated nucleic acid bases as described by their electron affinities, establishing an overall set of theoretical reference values at a level not reported before and helping to rule out less reliable theoretical and experimental data and to calibrate theoretical strategies. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Ionization potentials (IPs) and electron affinities (EAs) are intrinsic properties of the DNA and RNA nucleic acid bases (NABs) whose determination enables a deep understanding of all phenomena related to the electron donor and acceptor abilities of the NABs, such as those involving charge transfer and transport along the DNA strand,[1] radiation damage and repair of the genetic material,[2–4] DNA-protein interaction,[5,6] DNA phototherapy,[7] and DNA-based molecular technologies.[8] Despite the crucial information that the IPs and EAs of isolated nucleobases can provide to elucidate different biochemical mechanisms, there is a too dispersed set of experimental values available in the literature, mainly in the case of the EAs, whereas the theoretical determination has been so far carried out, except in a few cases, at modest computational levels.[9–39] Recently, we applied high-level quantum-chemical *ab initio* coupled-cluster and multiconfigurational perturbation methods (CASPT2) to compute the vertical IPs (VIPs) and adiabatic IPs (AIPs) of the canonical RNA and DNA bases, uracil (U), thymine (T), cytosine (C), adenine (A), and guanine (G), establishing theoretical reference values for this property at a level of calculation not reported before.[40] In that study we found really good agreement (<0.03 eV) between the highest-level methods employed, which were coupled-cluster theory up to triplet excitations, CCSD(T)/aug-cc-pVDZ, and multiconfigurational perturbation theory at the CASPT2/ANO-L 431/21 level, providing IPs in accordance with experiment. As expected, pyrimidines and purines were found to have the highest and lowest VIPs and AIPs, respectively. Canonical NABs were found to have computed CASPT2//CASSCF VIPs [U (9.42 eV), T (9.07 eV), C (8.73 eV), A (8.37 eV), and G (8.09 eV)] and AIPs [U (9.12 eV), T (8.84 eV), C (8.56 eV), A (8.11eV), and G (7.65 eV)].[40]

Compared to IPs, the determination of the EAs of NABs is more difficult both experimentally and theoretically and the uncertainties range up to several eV, including also changes in the sign of the energies. The first reason is related to the possibility of formation of two types of negatively charged systems: dipole-bound (DB) and valence-bound (VB) or covalent anions. The VB anions are characterized by an extra electron occupying a valence antibonding molecular orbital (MO), leading to an electronic state that may considerably alter the molecular structure of the neutral precursor. On the other hand, the attachment of an excess electron to a polar molecule with a dipole moment equal or higher than a critical value, established as 2.5 D,[41–43] as is the case of NABs,[44] can produce additional DB (or multipole-bound) anions, in which the electrons are weakly bound to the polar molecules primarily by electrostatic charge-dipole interactions and consequently the molecular structure is hardly modified. Since the electrons are placed far from the system, although somewhat localized, very diffuse basis functions are required to describe DB anions using MO theory, even more diffuse than those required to compute Rydberg states. In this type of anions the binding energy between the molecule and the distant electron is small (and positive). In systems such as the nucleobases, in which both VB and DB anions may be located within a small range of energies, the determination of accurate EAs is uncertain, especially because the type of anion formed may vary with the different experimental conditions. Apart from that, new difficulties interfere with the experimental determination of EAs of nucleobases, such as the presence of different tautomers of the nucleobases, which are close in energy in the gas phase. In particular, the canonical (keto) form of guanine, which is the biologically relevant tautomer, has a very low concentration in the vapor and there is no direct experimental value reported for the corresponding EA.[13,25] From the theoretical standpoint, the problems are related to the fact that the energy of the NAB anions is in principle higher than that of the neutral systems, implying temporary anion states that are unstable with respect to electron detachment. These temporary

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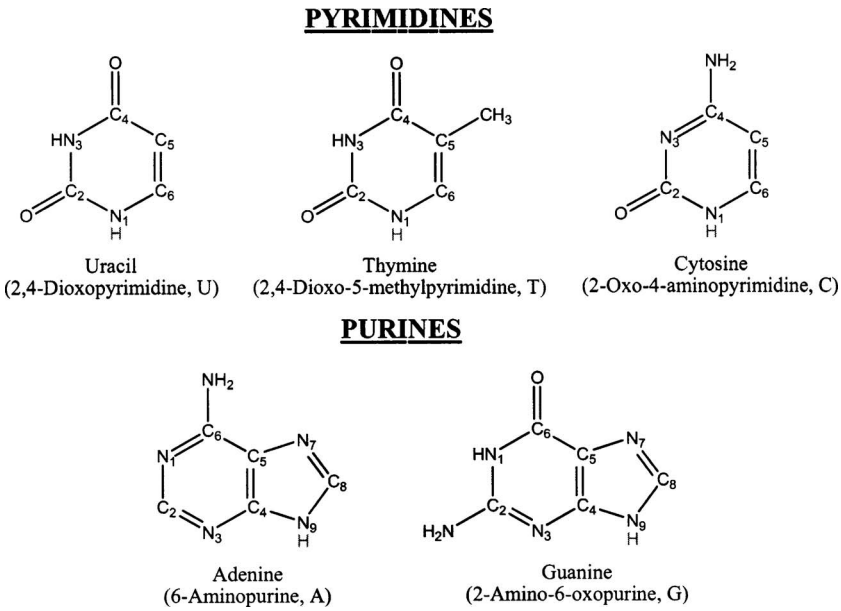

FIG. 1. DNA and RNA nucleobase structures and labeling with their conventional name and, within parentheses, the IUPAC name and the abbreviation.

anion states, named resonances, lie in the continuum of the neutral species plus the free electron and are difficult to treat with conventional quantum-chemical techniques. The description of EAs requires, in general, highly accurate quantum-chemical methods and one-electron basis sets with diffuse functions, allowing a maximum spatial and angular flexibility.[45–47]

Taking into account the current situation, we present in this paper the second report on the accurate theoretical determination of the intrinsic electron donor and acceptor properties of the DNA and RNA nucleobases (see Fig. 1), focused now in the VB EAs (hereafter EAs), trying to establish benchmark reference values for the analysis of these properties, allowing the selection of the best available experimental data, and also enabling the analysis of the adequacy of different computational strategies employed nowadays in the theoretical study of these and similar systems.

The EA of a neutral molecule is the energy required to detach an electron from a singly charged negative ion, or equivalently, the energy released when an electron is attached to the neutral system. Thus, the EA of a neutral molecule can be defined as the energy difference between the ground state of the neutral system and that of the anion. A positive EA implies that the anion is more stable than the neutral. As in the case of the IP,[40] three theoretical magnitudes (see Fig. 2) are used for describing this transition: the vertical electronic energy difference [VEA_e or vertical EA (VEA)] between the ground states of the neutral system and the anion at the equilibrium geometry of the neutral molecule, the adiabatic energy gap (AEA_e) between the minima of the neutral and anion molecule ground states, and the corrected adiabatic property [AEA_0 or adiabatic EA (AEA)] with the addition of the zero-point vibrational energy correction. Thus, positive VEAs indicate that the molecule acts as a trap for an excess electron, with an attachment energetically favored, and therefore the anion can be created spontaneously. In this case, positive AEAs follow, and the system becomes stable, that is, it does not undergo autodetachment and can take part in chemical reactions. On the other hand, negative values for VEAs and AEAs represent temporary states of the anion named transient negative ion states or resonances, existing in short periods of time and becoming prone to photodetachment.[48]

Since the EAs of NABs can help understand many phenomena related to DNA and RNA, their determination has been the objective of many experimental and theoretical groups during the past decades. Some of the results obtained by different techniques and methodologies were reviewed by Svozil *et al.*[36] Analysis of the experimental literature on

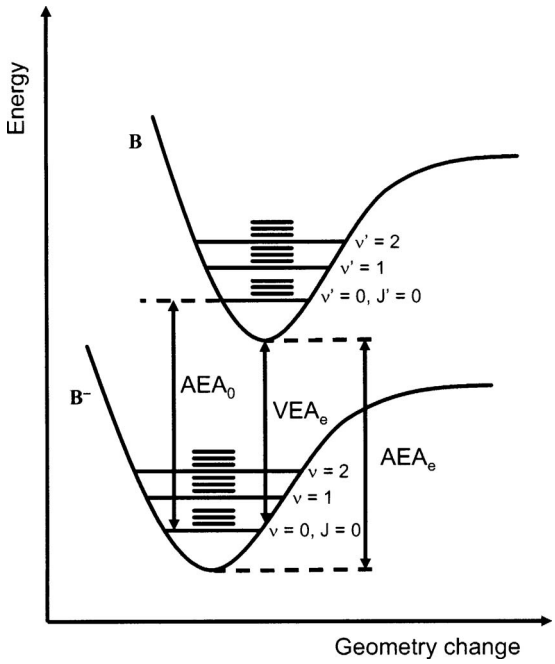

FIG. 2. EA diagram. Definitions of the theoretical magnitudes related to EA are graphically shown through the electronic, vibrational, and rotational potential energy levels. Those magnitudes are VEA_e (vertical electronic EA, from the neutral ground-state minimum), AEA_e (adiabatic electronic EA, from minimum to minimum), and AEA_0 (AEA including the zero-point vibrational corrections of the minima).

nucleobase EAs shows an extremely confuse situation in which completely different values are reported by using distinct experimental procedures, ranging from clearly negative values (−0.56 eV) up to largely positive energies (1.51 eV), and including EAs close to 0 eV. In general, the determination of EAs represents a technical challenge, especially when they have negative values, and in many cases it is based on indirect measurements. Negative EAs can be experimentally measured by electron transmission spectroscopy (ETS).[49] The technique is able to detect negative ion resonance states, which are energetically unstable with respect to electron autodetachment. It is unclear when the experiment is measuring VEA or AEA attachments, or if the indirectly obtained data truly represent the molecular EAs.[25] In general, however, ETS is the only direct experimental technique that is expected to provide actual VB anions in the region of the resonance states.[46] In particular, for gas-phase NABs (except G, which cannot be isolated), ETS measurements report EA values clearly in the negative region (from −0.22 to −0.54 eV).[13] Less reliable are some of the EA values extrapolated from aqueous media or obtained from reversible reduction potentials, such the estimations from Chen *et al.*[9] or Wiley *et al.*,[10] leading to highly positive values (0.56–1.51 eV). More realistic data (0.12–0.13 eV) have been indirectly determined by Schiedt *et al.*[14] for pyrimidine NABs. Hendricks *et al.*[15] and Desfrançois *et al.*,[16] by means of photoelectron and Rydberg electron transfer (RET) spectroscopies, respectively, analyzed how well-defined gas-phase DB anions, with small and positive EAs, transformed to conventional VB (covalent) anions with large and positive EAs in solvated phases. In particular, Hendricks *et al.*[15] observed how just the attachment of one single water molecule or a xenon atom to the uracil anion stabilized what seemed to be the VB anions of the corresponding $U^-(H_2O)$ or $U^-(Xe)$ complexes, both displaying slightly positive EA values. Desfrançois *et al.*[16] reported the presence of VB U anions with small positive EAs, but only after evaporation of previously formed argon cluster atoms. Similar conclusions were obtained by Periquet *et al.*[25] by studying solvated NABs with RET techniques and extrapolating to isolated phases, yielding estimated AEA values roughly zero for uracil and thymine. In conclusion, and except probably for the ETS experiments, producing clearly negative values, there are no direct measurements for the VB EAs of the nucleobases in the gas phase and, in any case, only uracil and thymine can be considered candidates to have small positive AEA values.

This statement implies a challenge to theoreticians who have been applying different approaches to estimate the EAs of NABs, from density functional theory[17–20,23,24,27–29,32–35,37–39] to modest-level *ab initio* methods, such as the simple qualitative Hartree–Fock[11–13,31] (HF) description in which Koopman's theorem (KT) was used, and second- and fourth-order perturbation treatments (MP2 and MP4).[12,22–24,26] Whereas almost all theoretical computations of VEAs are negative, the computed AEA values include both negative and positive results. High-level *ab initio* calculations have been reported by Gutowski and co-workers[50–54] on the AEAs of three of the nucleobases (U, T, and G) and of several of their tautomers and for cytosine tautomers.[26] These results will be discussed here together with our reported values for VEAs and AEAs.

According to this panorama, it is necessary to carry out accurate calculations able to provide conclusive results of these magnitudes for all NABs in order to establish the sequence of their VEAs and AEAs and, quantitatively, the differences between them. Thus, we report in this paper computations on the lowest VEAs and AEAs of the NABs performed with different *ab initio* methods [Möller–Plesset second-order singly (MP2) and multiconfigurational (CASPT2) perturbation theories[55] and coupled-cluster singles and doubles (CCSD) or singles, doubles, and triples [CCSD(T)] approaches] and employing different types of one-electron basis sets. As in the case of IPs,[40] the obtained results will allow to discard odd experimental values, to set up accurate data for all the nucleobases, and to check the accuracy on the EA values yielded by different computational strategies, such as by using atomic natural orbital (ANO)-type basis sets within the CASPT2//complete active space self-consistent field (CASSCF) approach, which provide well-localized solutions (resonances) to temporary anion states,[46,56,57] and the inclusion of the IPEA correction to the CASPT2 methodology. The CASPT2//CASSCF approach is widely employed in the computation of excited states[48,58–67] and its calibration with the CCSD(T) method would be very useful to know the precision of both strategies when applied to the determination of the EAs of nucleobases *in vacuo*, to which the present paper is focused. This will allow to extend with accuracy the studies to nucleosides and nucleotides,[68,69] isolated and embedded in a double helix surrounded by a biological environment, and to the analysis of charge transfer and transport processes through the DNA molecule.[70,71]

II. COMPUTATIONAL DETAILS

In order to compute accurate theoretical results for the VEA and AEA of NABs, different levels of theory were taken into account, employing the MP2, CCSD, and CCSD(T), and the CASSCF and CASPT2 methods as implemented in the GAUSSIAN-03 (Ref. 72) and MOLCAS-6.0 (Refs. 73–75) packages, respectively, in conjunction with the 6-31G(*d*), cc-pVDZ, aug-cc-pVDZ, ANO-L C,N,O [4*s*3*p*1*d*]/H [2*s*1*p*] (hereafter ANO-L 431/21), and ANO-L C,N,O [4*s*3*p*2*d*1*f*]/H [3*s*2*p*1*d*] (hereafter ANO-L 4321/321) basis sets. Methods and basis sets were selected to obtain the most accurate values from preliminary calculations on atomic systems, in which the required levels of highly flexible enough basis sets and strongly correlated methods to obtain predictive EAs was determined. Geometry optimizations of both neutral and anionic NABs were carried out at the MP2/6-31G(*d*), MP2/aug-cc-pVDZ, CASSCF/cc-pVDZ, CASSCF/ANO-L 431/21, and CCSD/aug-cc-pVDZ levels of theory. No symmetry restrictions (C_1 symmetry) were imposed, whereas all minima were characterized by computing second derivatives at the same level, except in the case of CCSD/aug-cc-pVDZ where the geometries were tested comparing with the optimized parameters at the other levels of theory. At the respective equilibrium structures, additional

TABLE I. Structural differences of the nucleobase anion and neutral systems optimized at the MP2/aug-cc-pVDZ, CCSD/aug-cc-pVDZ, and CASSCF/ANO-L 431/21 levels of theory. The values listed concern the largest difference for the corresponding geometrical parameter and system. Bond lengths are in angstroms and bond and dihedral angles in degrees.

		MP2/aug-cc-pVDZ–CCSD/aug-cc-pVDZ		CASSCF/ANO-L 431/21–CCSD/aug-cc-pVDZ	
		Neutral	Anion	Neutral	Anion
Uracil	Bond length (Å)	0.010 C_4—C_5	0.008 N_3—C_4	0.025 C═O	0.030 C═O
	Bond angle (deg)	0.6	0.7	0.9	1.1
	Dihedral angle (deg)	0.2	3.0 puckering	0.2	5.3
Thymine	Bond length (Å)	0.011 C_4—C_5	0.01 N_3—C_4	0.026 C═O	0.029 C═O
	Bond angle (deg)	0.5	0.9	0.8	1.2
	Dihedral angle (deg)	0.2	3.7 puckering	0.2	3.7
Cytosine	Bond length (Å)	0.011 C_4—C_5	0.019 N_3—C_4	0.035 N_3—C_4	0.027 C═O
	Bond angle (deg)	0.6	1.9	1.7	1.3
	Dihedral angle (deg)	1.1 NH_2	9.5 puckering	6.6 NH_2	5.4 puckering
Adenine	Bond length (Å)	0.018 N_7—C_8	···	0.036 N_1—C_6	···
	Bond angle (deg)	0.5	···	1	···
	Dihedral angle (deg)	0.3	···	7.9	···
Guanine	Bond length (Å)	0.018 N_7—C_8	0.016 C_8—N_9	0.031 C_2—N_3	0.031 N_3—C_4
	Bond angle (deg)	0.6	1.2	1.1	1.4
	Dihedral angle (deg)	1.4 NH_2	6.9 puckering	3.3 NH_2	4.7 puckering

CASPT2 and CCSD(T) calculations were performed to account for the most accurate energy values. Zero-point energy (ZPE) corrections were included at different levels using the harmonic approach.[48] The active space for the CASSCF calculations in geometry optimizations comprises the full π-valence system, except the MO localized mainly on the nitrogen atom of the NH_2 group in the case of the cytosine, adenine, and guanine NABs, whose occupation number is very close to 2. This MO is further included in conjunction with the lone pair electrons and orbitals of the heteroatoms in the final CASSCF and CASPT2 calculations of VEAs and AEAs except when the large ANO-L-type basis set, ANO-L 4321/321, was employed. As in the computation of the NABs IPs,[40] the CASPT2 calculations were performed both with the standard zeroth-order Hamiltonian[55] and including the recent IPEA correction with a selected value of 0.25 a.u., as recommended.[76] Cartesian coordinates of the optimized geometries discussed below can be obtained from the authors upon request.

III. RESULTS AND DISCUSSION

A. Geometries of the neutral and anionic nucleobases

MP2/aug-cc-pVDZ and CASSCF/ANO-L 431/21 optimized geometries are compared in Table I with those at the CCSD/aug-cc-pVDZ level for the neutral and anionic NABs. In particular, the largest differences in bond lengths, bond angles, and dihedral angles are displayed. In general the discrepancies between the three methodologies are smaller than 0.03 Å and 2° and 10° for the bond length and bond and dihedral angles, respectively. The anionic systems are more sensitive to the level of theory employed. The differences in bond lengths between the MP2 and CCSD geometries are found in the C═C or C═N double bonds, whereas the largest deviation in bond and dihedral angles are related to the ring-puckering distortion (deviation from planarity of the ring) in the case of the anions and to the NH_2 group in cytosine and guanine neutral molecules. Regarding the comparison between CCSD and CASSCF geometries, differences in bond lengths are also related to the double bonds and increase slightly up to a value of 0.036 Å, which takes place in the N_1—C_6 double bond of adenine; for the neutral nucleobases the largest deviations appear in cytosine, adenine, and guanine, corresponding to the amino group, while in the case of the anions, it is again mainly the ring-puckering that causes the largest difference, although smaller than those related to the comparison of MP2 versus CCSD. The valence anion of adenine at the CCSD/aug-cc-pVDZ level did not converge toward a minimum on the potential energy surface, and therefore it is not included. The only converged solution corresponds to the unpaired electron occupying a diffuse orbital with a geometry, as expected, only slightly distorted with respect to the neutral optimized structure, contrary to the MP2/aug-cc-pVDZ and CASSCF/ANO-L 431/21 results. However, as stated above, the MP2 and CCSD geometries in the other cases are very similar and minor changes are expected in the results of the AEA of nucleobases when using the MP2 geometries instead of CCSD optimized structures. CASSCF, although it does not include dynamic correlation, also provides good overall geometries. We selected this method for the analysis of the geometry changes undergone by NABs when an electron is attached to the neutral systems and geometry relaxation takes place.

Figure 3 displays the largest differences obtained at the CASSCF/ANO-L 431/21 level of theory between the struc-

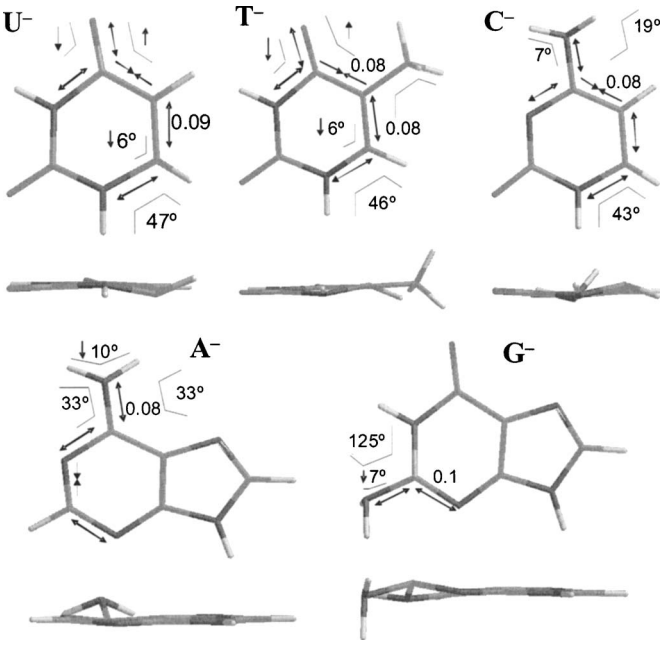

FIG. 3. Front and side views of the optimized geometries of the nucleobase anion systems at the CASSCF/ANO-L 431/21 level of theory and their major structural changes, that is, bond length (in Å) and bond and dihedral angle (in degrees) differences, with respect to the geometry of the neutral DNA and RNA NABs optimized at the same level.

tural parameters of the neutral and anionic systems of the DNA and RNA bases. Concerning the pyrimidine systems (C, T, and U), the most important changes in the bond lengths are a decrease in the C_4C_5 bond of the anions with respect to the neutral bases and an increase in the C_5C_6 and C_6N_1 distances. This feature is consistent with the bonding and antibonding characters at these bonds, respectively, of the single-occupied natural orbitals (SONOs) shown in Fig. 4. The enlargement in the C_5C_6 bond is common in the reactivity of pyrimidine molecules.[77] It also occurs in the cation of the bases[40] and in the singlet and triplet states of two π-stacked pyrimidines, precursors of the cyclobutane dimers formed by the cyclation between the C_5 and C_6 atoms of both adjacent nucleobases, a common DNA and RNA lesion.[78,79] Another important aspect in the comparison of the anionic and neutral pyrimidine structures is the puckering of the ring, observed in the lateral perspective of Fig. 3 and reflected by a value of 45° for the difference in the HC_6N_1H dihedral angle. This angle is related to the site where pyrimidines are bound to the sugar and could be the origin of the dissociation undergone by these nucleobases after the addition of one electron.[80] Unlike for the cation of NABs,[40] the methyl group is twisted in the anion of thymine with respect to the neutral base and the deviation from planarity in the amino group of the neutral cytosine remains in the anion (the cation has an almost planar structure of the amino group). In the case of purine NABs, the attachment of an electron to a neutral adenine induces the amino group to leave the molecular plane (33° for the dihedral angles related to the amino group). One important difference between adenine and the other NABs is the nearly absence of ring puckering in the former. This feature is noticeable when comparing the side views in Fig. 3 and is most probably caused by the fact that

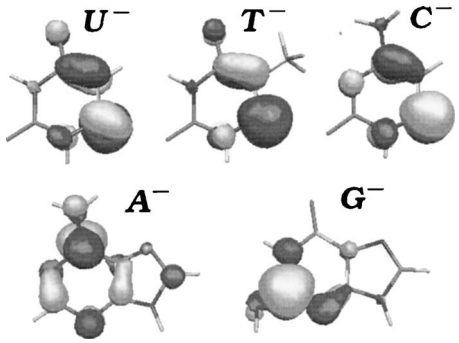

FIG. 4. SONOs of nucleobase anions obtained at the CASSCF/ANO-L 431/21 level of theory.

adenine is the only molecule without a keto group in the six member ring. However, the most significant change in the geometric parameters occurs in guanine concerning the amino group of this nucleobase. As can be observed in Fig. 3, a difference of 125° for the N_1C_2NH dihedral angle exists between the neutral and anionic forms of guanine. The geometry optimization of guanine anion leads to a structure in which the amino group is twisted with respect to the neutral form and one of the NH bonds becomes almost perpendicular to the purine ring. This feature seems to be a characteristic of the guanine anion and will have important consequences on its molecular properties.

B. Vertical electron affinities of the nucleobases

Table II compiles the few available experimental data for the VEA of NABs together with earlier and present theoretical results. The range of experimental values corresponds to ETS measurements,[13] employing a cluster solvation method combined with RET spectroscopy,[25] and estimations from the enthalpy of formation.[30] As mentioned previously, no experimental data are available for the natural guanine keto tautomer, which is not the most stable in the gas phase. Apart from that, both experiment and theory provide negative VEAs at all levels, although the trend on the series of NABs is not very clear from the viewpoint of the experimental measurements. If we only take into account the direct techniques, the sequence concerning to the ETS measurements is established as U>T>C>A. Discarding the somewhat erratic DFT/B3LYP values, this sequence is maintained in all the theoretical methods, whereas guanine VEA has the most negative value of all NABs. When comparing the theoretical *ab initio* methods, in particular, our reference benchmark CCSD(T) and CASPT2(IPEA) results, with the experimental ETS values, the latter seem to be overestimated by near 0.3–0.4 eV. Such deviation might be attributed to the difficulty in the assignment of the vibrational states of the anion in an ETS spectrum. As pointed out by Periquet *et al.*,[25] in those cases the band maxima are expected to be intermediate between the adiabatic and vertical values. According to this statement, the VEA of nucleobases must be more negative than the data interpreted in the ETS experiments and therefore nearer to our computed CCSD(T) and CASPT2(IPEA) results. In any case, the overall conclusion is that the creation of a VB anion of NABs in the gas phase by direct electron

TABLE II. Low-lying vertical VB AEs (eV) of DNA and RNA nucleobases obtained by different experimental and theoretical methods.

Method	Uracil	Thymine	Cytosine	Adenine	Guanine
Experimental range[a]	−0.30 to −0.22	−0.53 to −0.29	−0.55 to −0.32	−0.56 to −0.45	···
Expt. (ETS)[b]	−0.22	−0.29	−0.32	−0.54	···
Scaled Koopman/D95V[c]	−0.11	−0.32	−0.40	−0.74	−1.23
B3LYP range[d]	−1.09 to −0.11	−1.05 to −0.28	−1.42 to −0.31	−1.57 to −0.34	−2.07 to −0.08
MP2/6-31G(*d*)[e]	−1.77	−1.85	−1.97	−2.54	−2.82
PMP2//MP2/6-31G(*d*)[e]	−1.63	−1.69	−1.76	−2.07	−2.48
MP2/aug-cc-pVDZ[e]	−0.69	−0.73	−0.91	−1.42	−1.57
PMP2//MP2/aug-cc-pVDZ[e]	−0.56	−0.58	−0.73	−0.99	−1.30
CCSD//CCSD/aug-cc-pVDZ[e]	−0.63	−0.65	−0.77	···	···
CCSD(T)//CCSD/aug-cc-pVDZ[e]	−0.64	−0.65	−0.79	···	···
CASPT2//CASSCF/cc-pVDZ[e]	−1.42	−1.44	−1.49	−1.65	−2.14
CASPT2//CASSCF/ANO-L 431/21[e]	−0.68	−0.69	−0.76	−1.06	−1.30
CASPT2/ANO-L 4321/321//CASSCF/ANO-L 431/21[e]	−0.49	−0.45	−0.59	−0.74	−0.94
CASPT2(IPEA)/ANO-L 4321/321//CASSCF/ANO-L 431/21[e]	−0.61	−0.60	−0.69	−0.91	−1.14

[a]References 13, 25, and 30.
[b]Reference 13.
[c]Reference 12.
[d]References 20, 23, 28, 34, 38, and 39.
[e]Present work.

attachment of one electron to the neutral bases is not a favorable process, especially in the case of purines, since all VEA values are negative.

Regarding the analysis of the theoretical methodologies employed for the computation of the VEA of NABs, the simplest qualitative approach, that is, via KT, predicts poor values. Whereas in the case of IPs this approximation yields somewhat reasonable data, the outcome is much worse for the determination of EAs. Table II compiles the results by Sevilla *et al.*,[12] who employed modification of the KT procedure with some scale factors to lead to values more or less similar to the experimental ones. The set of B3LYP results is extremely scattered, reaching a range of near 2.0 eV for guanine. In most cases the dispersion and, in particular, the low-lying values can be surely be attributed to the calculation of a spurious diffuse solution instead of a VB resonance. Such results are obtained as a consequence of the basis set cage effect and, in general, they correspond to solutions in the continuum that, upon increasing the diffusivity of the basis set and therefore the corresponding MO, lead to the neutral molecule plus a free electron.[45–49] Apart from that, the B3LYP EA results are strongly dependent on the employed basis set.[81,82] Other DFT functionals have been employed, such as in the DFT–generalized gradient approximation calculations reported by Preuss *et al.*,[35] which yield positive VEAs, far from the rest of theoretical and experimental results compiled in Table II and, therefore, they can be clearly ruled out. Regarding our MP2 findings, they enable the evaluation of two effects: inclusion of diffuse functions in the basis set and spin contamination. When the diffuse aug-cc-pVDZ basis set is used instead of 6-31G(*d*), the MP2 VEA values become an average of 1.13 eV closer to our benchmark data, CCSD(T) and CASPT2(IPEA). On the other hand, similarly to the case of IPs,[40] the unrestricted MP2 wave functions of the nucleobase anion have a noticeable spin contamination. The use of corrected projection techniques (PMP2) was, however, not as crucial here as in the case of IPs, in which the energies improved in some cases by 1 eV.[40] The PMP2 method increases the VEA values near 0.2 and 0.4 eV for pyrimidines and purines, respectively, and approaches the results to the reference values, in particular, to near 0.1 and 0.15 eV for pyrimidine and purine NABs, respectively.

In the present work, CCSD and CCSD(T) calculations were performed for pyrimidine NABs at the neutral ground-state geometries optimized at the CCSD/aug-cc-pVDZ level of theory. Similar to the accurate determination of NABs IPs,[40] the triples correction is of minor importance since it modifies the values of VEAs by no more than 0.02 eV. The CASSCF wave functions have single-reference character and the T_1 diagnostic gives values not larger than 0.02. Therefore, the CCSD(T) method can be considered to be accurate and the computed value can be used as reference as the best that quantum-chemical theories (excluding the effects of the continuum) can presently provide. It must be emphasized here that the main factor to achieve accurate results for the VEA of NABs by using *ab initio* methods is the employment of atomic orbital one-electron basis sets flexible enough to describe both the spatial distributions of electrons and their correlation effects and including functions decaying slowly with the radial distance. Taking into account that it is not favorable to attach an electron to NABs, the employment of this type of basis sets is not free of problems for the determination of the VEA of nucleobases. This is especially the case of adenine and guanine, whose affinity for electron attachment is smaller than that of pyrimidines. It is important to emphasize at this point that there is an inherent difficulty in the calculation of molecular anions when they lie in regions of the energy spectrum simultaneously containing diffuse (multipole-bound or simply spurious solutions due to the basis set cage effect[45,48,49]) and VB anions. This is particularly true for single-reference procedures such as DFT, MP2, or CCSD/CCSD(T) because they can only compute one single solution of the Hamiltonian. For instance, at the corresponding geometry of the neutral species, adenine and guanine, in which the VB anion state lies much higher than

TABLE III. Theoretical lowest-lying adiabatic VB AEs (eV) of DNA and RNA nucleobases.

Method	Uracil	Thymine	Cytosine	Adenine	Guanine
Scaled Koopman/D95V[a]	0.4	0.3	0.2	−0.3	−0.7
B3LYP/6-31G(*d*)[b]	−0.52	−0.49	−0.69	−1.18	−1.51
B3LYP/6-311++G(2*d*,*p*)[b]	0.20	0.22	−0.05	−0.30	−0.01
B3LYP/6-31++G(Ryd)[c]	—	0.34	0.20	0.08	0.25
MP2/6-31G(*d*)[d,e]	−1.16	−1.20	−1.31	−1.98	−1.63
PMP2//MP2/6-31G(*d*)[d,e]	−1.06	−1.09	−1.17	−1.81	−1.55
MP2/aug-cc-pVDZ[d,f]	−0.21	−0.26	−0.40	−1.06	−0.71
PMP2//MP2/aug-cc-pVDZ[d,f]	−0.09	−0.14	−0.25	−0.88	−0.63
CCSD/aug-cc-pVDZ[d,f]	−0.07	−0.12	−0.18	−0.90[i]	−0.50
CCSD(T)//CCSD/aug-cc-pVDZ[d,f]	−0.05	−0.09	−0.17	−0.84[i]	−0.44
CASPT2//CASSCF/cc-pVDZ[d,g]	−0.69	−0.74	−0.77	−1.02	−1.00
CASPT2//CASSCF/ANO-L 431/21[d,h]	−0.03	0.06	−0.03	−0.54	−0.31
CASPT2/ANO-L 4321/321//CASSCF/ANO-L 431/21[d,h]	0.10	0.19	0.08	−0.39	−0.20
CASPT2(IPEA)/ANO-L 4321/321//CASSCF/ANO-L 431/21[h]	−0.01	0.05	−0.04	−0.57	−0.35
CASPT2(IPEA)/ANO-L 4321/321//CCSD/aug-cc-pVDZ[d,f]	0.03	0.02	−0.10	−0.72[i]	−0.44

[a]Reference 12.
[b]Reference 28.
[c]Reference 33.
[d]Present work.
[e]ZPE: MP2/6-31G(*d*).
[f]ZPE: MP2/aug-cc-pVDZ.
[g]ZPE: CASSCF/cc-pVDZ.
[h]ZPE: CASSCF/ANO-L 431/21.
[i]Geometry optimized at the MP2/aug-cc-pVDZ level. See text.

other diffuse states, the CCSD and CCSD(T) computations led to a diffuse and low-energy spurious solution in which a delocalized electron was located far from the molecule in a diffuse orbital. This type of problems is difficult to detect in the calculations, and it cannot be discarded that some results in the literature reported such type of solutions. The VB solution was found for guanine at the coupled-cluster levels close to the MP2 geometry of its anion, which could be then optimized at the CCSD level. Particularly relevant for getting the VB anion solution was the selection of the initial orbitals to obtain the HF reference. The use of a semiempirical intermediate neglect of differential overlap guess has been proven here to be more convenient than the Harris functional.[72,83] The corresponding CCSD optimization of anionic adenine led, however, to the DB anion solution, displaying a geometry very similar to the neutral ground state, as could be expected due to the minor effect of the distant electron.

These challenges are especially suited for the CASPT2//CASSCF strategy when computing accurate values for the EAs of NABs since it can overcome those problems by computing several states of the system. We employed the CASPT2//CASSCF methodology with three distinct basis sets, that is, cc-pVDZ, ANO-L 431/21, and ANO-L 4321/321. As explained above, the ANO-type basis sets are intrinsically more flexible and diffuse than other classes of one-electron basis functions; therefore they are especially adequate for the treatment of anions. In fact, using the ANO-L 431/21 basis set instead of cc-pVDZ at the CASPT2//CASSCF level leads to an improvement in the results ranging from 0.59 eV in adenine to 0.84 eV in guanine. Increasing the diffuse character of the ANO-type basis set produces an average overestimation of the results of 0.2 eV for the pyrimidines with respect to the CCSD(T) results. This effect is eliminated when the IPEA correction of the CASPT2 Hamiltonian is considered. As in the case of IPs,[40] the application of the CASPT2/IPEA approach leads to a general increase of almost 0.2 eV in the absolute VEA values and it has to be taken into account for an accurate determination of this magnitude. This new definition of the CASPT2 zeroth-order Hamiltonian, including the recommended shift value of 0.25 a.u. corrects the slight overestimation in the correlation energy on open shells that was already detected in the original standard CASPT2 approach.[55,76] The final CASPT2(IPEA=0.25)//CASSCF/ANO-L 4321/321 results for pyrimidines are in almost perfect correspondence with the CCSD(T) results with differences smaller than 0.1 eV, confirming the accuracy of the CASPT2 results obtained for the purines and the suitability of the computational strategy to deal with this type of sys-

TABLE IV. Zero-point vibrational energy corrections (eV) of DNA and RNA neutral and anion nucleobases calculated at different levels of theory within the harmonic approach.

	ZPE (neutral/anion/difference)				
Method	Uracil	Thymine	Cytosine	Adenine	Guanine
MP2/6-31G(*d*)	2.39/2.30/0.09	3.17/3.08/0.09	2.71/2.64/0.07	3.07/3.08/−0.01	3.20/3.18/0.02
MP2/aug-cc-pVDZ	2.36/2.26/0.10	3.12/3.01/0.11	2.67/2.59/0.08	3.04/3.07/−0.03	3.17/3.14/0.03
CASSCF/cc-pVDZ	2.51/2.42/0.09	3.32/3.28/0.04	2.86/2.83/0.03	3.24/3.12/0.12	3.40/3.29/0.11
CASSCF/ANO-L 431/21	2.56/2.48/0.08	3.36/3.20/0.16	2.84/2.74/0.10	3.34/3.24/0.10	3.38/3.27/0.11

tems. The VEAs for adenine and guanine are computed to be more negative than those for pyrimidines, the difference between uracil and guanine being about 0.5 eV. The sequence for the VEAs of NABs obtained with our reference CCSD(T) and CASPT2(IPEA) levels of theory is established as U $\approx$T>C>A>G, ranging from −0.61 eV (U) to −1.14 eV (G) at the CASPT2(IPEA)//CASSCF/ANO-L 4321/321 level of calculation.

C. Adiabatic electron affinities of the nucleobases

Table III compiles different theoretical results for the lowest-energy AEA (AEA_0) of DNA and RNA NABs. No experimental datum is included because it is improbable that the magnitude has been measured in the gas phase, except for uracil, in which the existence of a stable VB anion with a slightly positive EA ($0.03 < EA < 0.09$ eV) has been reported.[16] The first general observation we make is that the values increase (toward more positive EAs) with respect to the vertical magnitude, VEA, in accordance to the geometry relaxation of the molecules, which follows the attachment of an electron to the neutral systems (about 0.6 eV in pyrimidines, 0.3 eV in adenine, and, the largest difference, 0.8 eV in guanine) if we compare with the reference CCSD(T) and CASPT2(IPEA) levels of theory. As mentioned above and displayed in Fig. 3, the geometry relaxation taking place in guanine consists mainly of a large twist of the amino group, becoming almost perpendicular to the purine ring. Reorganization of the structure is reflected by the large difference between the computed VEA and AEA of guanine that causes a change in the trends of nucleobase EAs. Guanine, therefore, although less favorable than all other NABs to vertical electron attachment, has a less negative AEA than adenine.

The results of the present work reported in Table III include the ZPE vibrational correction at the mentioned levels of theory, yielding therefore AEA_0 values (see Fig. 2). Table IV compiles the ZPEs for the neutral and anionic species of NABs at the different levels of theory employed in our calculations. Except for adenine, in which the sign of the correction can even change between the different levels, the discrepancies in the other NABs are within the 0.1 eV expected accuracy. Regarding the DFT/B3LYP data taken from literature and listed in Table III, it can be noted that they display the same large dependence of the results as the *ab initio* methods when going from a compact valence 6-31G(*d*) to a diffuse 6-31G++(2*d*,*p*), although the results for AEA are clearly biased toward too positive values. Increasing the diffusivity of the basis set to 6-31++G(Ryd) deteriorates the results even more, yielding also a wrong trend for the AEAs of purines. The strong dependency and poor convergence to stable values on the number and type of diffuse functions shown by the standard DFT methods,[84] together with their well-known deficiencies to deal with negative centers,[85] make the calibration of these approaches extremely difficult. Careful DFT studies on different NAB tautomers, derivatives, or solvated species have been performed, leading in most cases to stabilized anionic species.[17–19,23,27,29,32,38,39] Regarding the *ab initio* results and starting by the MP2 data, similarly to the analysis of VEAs, the use of the aug-cc-pVDZ basis set improves the results on AEAs by near 1.0 eV with respect to a compact basis set such as 6-31G(*d*). Also, the projected PMP2 technique is necessary in order to eliminate spin contamination. The PMP2/aug-cc-pVDZ values are close to the reference CCSD(T) results, showing differences near 0.05 eV in uracil, thymine, and adenine, 0.08 eV in cytosine, and 0.19 eV in guanine. These values are in agreement with the *ab initio* MP2 and MP4 data obtained by Smith *et al.*[22] and Dolgounitcheva *et al.*[26] employing Pople-type basis sets enlarged with diffuse functions. As regards the CCSD and CCSD(T) values, they represent a further increase in the AEAs toward positive values, which places anionic uracil and thymine very close to the neutral molecule (0.0 eV), anionic cytosine near 0.2 eV above the respective neutral system, and adenine and guanine still displaying clearly pronounced negative EAs. Inclusion of the triply excited terms in CCSD does not modify the results by more than 0.06 eV. Our benchmark CCSD(T) AEA_0 results will be therefore U (−0.05 eV), T (−0.09 eV), C (−0.17 eV), A (−0.84 eV), and G (−0.44 eV). As explained in the previous section for adenine, we employed a MP2 instead of a CCSD geometry because of the difficulties in obtaining a converged solution for the lowest VB anion state of adenine. We proved the minor influence of using the MP2 geometry by computing AEA_0 of the other NABs at the CCSD and CCSD(T) levels. All the results differ by less than 0.01 eV.

If compared with other *ab initio* results in the literature, our CCSD and CCSD(T) negative AEA values agree with the results obtained by Gutowski and co-workers[50–53] at the same level of theory for U, T, and G. Energy extrapolation schemes aimed to reach method and basis set limits were also employed to predict positive AEA value for uracil, 0.04 V,[86] and thymine, 0.18 eV,[87] although an optimistic estimate of the accuracy of the extrapolation procedures rises to 0.30 eV,[88,89] questioning the nature of the results, in particular, for thymine, predicted at all the previous levels similar or less positive than uracil.

The CASPT2//CASSCF strategy is also considered here for the determination of the AEAs in order to calibrate its suitability for dealing with the anionic NAB systems. As in the case of VEAs, there is a significant improvement when employing the ANO-L 431/21 instead of the cc-pVDZ due to the inherent flexibility of the general contraction scheme in the former, which includes also a balanced participation of quite diffuse functions. Increasing the size of the basis set to ANO-L 4321/321 decreases the energy of the anion by near 0.10–0.15 eV with respect to the neutral molecule, leading to possibly too positive AEA values. The opposite effect is obtained when applying the IPEA CASPT2 Hamiltonian. As it occurred for IPs, and it can be expected from a correction that avoids overshooting correlation effects in open shell situations, the anionic CASPT2(IPEA) solution is destabilized with respect to the neutral molecule, yielding less positive AEAs. We consider this solution, CASPT2(IPEA)/ANO-L 4321/321//CASSCF/ANO-L 431/21, our reference result at the multiconfigurational level of calculation. The differences with respect to the other reference values, CCSD(T)//CCSD/aug-cc-pVDZ, are U (0.04 eV), T

(0.14 eV), C (0.13 eV), A (0.27 eV), and G (0.09 eV), in all cases leading to less negative EAs. In order to check the influence of employing CASSCF geometries for the CASPT2 results, we employed instead the CCSD/aug-cc-pVDZ optimized geometries (except for adenine, in which a MP2 geometry was used). The changes were minor, and except for the slight 0.04 eV increase of AEA in uracil, in all other cases the modification in geometry led toward more negative results. For adenine, in particular, its value decreases to −0.72 eV, much closer to the CCSD(T) datum.

Taken together, the deviations between the highest-level *ab initio* results, such as those previously reported by Bachorz *et al.*[86] and Svozil *et al.*[87] and the present ones, range in a few tenths of an eV. Getting higher accuracy is difficult, considering that, in particular, for uracil and thymine, the lowest EAs or VB (covalent) anion states are almost isoenergetic with the DB anions, first predicted theoretically with positive values in uracil by Oyler and Adamowicz in 1993.[90] The main conclusion obtained from the theoretical results is that the gas-phase AEAs for uracil and thymine are very close to zero, and they can be even slightly positive, whereas cytosine has a small negative AEA. The sequence of AEAs for isolated NABs can be established as 0 eV ~ U ~ T > C > G > A. Purines are much less favorable than pyrimidines to retain the electron attached to the neutral nucleobase, and after geometry relaxation, adenine becomes the poorest electron acceptor of all NABs, in contrast to what occurred for the VEAs, in which guanine had the more negative value. The observed trends can be understood by analyzing the EAs of some related systems. Attaching an electron to the NAB molecules is more favorable than for their arene counterparts. For instance, benzene has a highly negative EA, −1.12 eV.[91] Adding a C═N bond favors the affinity of the system for an extra electron as in azabenzenes, in which the EA increases with the number of N ring atoms: −0.62 eV for pyridine, −0.01 eV for pyrazine, or 0.02 eV for tetrazine.[92,93] As a matter of fact, azabenzenes are very similar to pyrimidine NABs: up to pyrazine, which is a diazine-like NAB, no isolated VB anion has been described with positive EAs, and it also requires the attachment of a water molecule or a noble gas atom.[15,16] Adding keto groups to the benzene ring has even more dramatic consequences regarding the EA, which is measured to be highly positive: 1.62 eV for *o*-benzoquinone[94] and 1.86 eV for *p*-benzoquinone.[95] The structure of the single-occupied MO in the NAB anion (see Fig. 4), basically a π^* antibonding C═C and C═N ring orbitals in pyrimidines and purines, respectively, indicates that the addition of charge takes place basically at the six-membered ring. The three pyrimidine NABs add the electron essentially to the C═C ring antibonding orbital, something much more favorable for U and T, with two electron withdrawing keto groups, than for C, with one keto group and one C═N ring bond. These effects lead U and T to have almost positive EAs. In the purinelike fused rings the negative charge is withdrawn from the intermediate C═C bond toward the N ring atoms. In particular, and as it has been observed in systems such as 7-azaindole,[64,96–98] the six-membered ring increases its net negative charge. It is then understandable that, with respect to the pyrimidine species, purine NABs decrease their IPs and increase their EAs, since both are related to the six-membered ring (see Fig. 4). Adenine, despite lacking keto groups, displays, at the neutral geometry, a larger affinity than guanine due to its two C═N ring bonds, a situation that guanine restores by twisting its amino group at the equilibrium geometry of the anion.

IV. SUMMARY AND CONCLUSIONS

Quantum-chemical *ab initio* coupled-cluster and multiconfigurational perturbation methods have been used to compute and establish benchmark reference values for the VEAs and AEAs of the isolated five canonical DNA and RNA nucleobases: uracil, thymine, cytosine, adenine, and guanine. The present analysis leads to the selection of the CCSD(T) and CASPT2(IPEA) as the most accurate *ab initio* methodologies to determine the VEAs and AEAs of the NABs, as it was previously established for the corresponding IPs, whereas the CASPT2//CASSCF approach is established as the only strategy able to treat the valence state of the purine NAB anion at the geometry of the neutral molecule. Analysis of the corresponding T_1 parameter, the single-reference character of the wave function, and the absence of spin contamination point out to the accuracy of the CCSD(T) approach in the present case. The reference CCSD(T)//CCSD/aug-cc-pVDZ and CASPT2(IPEA)/ANO-L 4321//CASSCF/ANO-L 431/21 results differ by less than 0.10 and 0.14 eV in the calculation of VEAs and AEAs, respectively. The IPEA definition of the zeroth-order Hamiltonian in the CASPT2 method improves the results up to 0.2 eV and it is proved necessary to obtain accurate values.

Regarding the values and trends for EAs, accurately computed VEAs of NABs yield CASPT2(IPEA) values of −0.61 eV for U, −0.60 eV for T, −0.69 eV for T, −0.91 eV, for A, and −1.14 eV for G, guanine being less favorable to accept an electron at the neutral molecule geometry. These results are somewhat smaller than the reported ETS band maxima, considered to produce intermediate values between vertical and band origins. After geometry optimization of the lowest state of the anion, the AEAs of the isolated nucleobases, in particular, those of the pyrimidine species, become closer to the energy of the neutral molecule. Geometrical changes are characterized mainly by distortions from planarity of the ring in pyrimidines and large twist of the amino group in guanine. The best computed values yield AEAs of nearly zero for U (−0.05 to 0.03 eV) and T (−0.09 to 0.05) and slightly negative for C (−0.17 to −0.04). As regards purine NABs, their AEAs are obtained to be largely negative, confirming that they do not have electron attractor character in the gas phase. In purines the least favorable electron attachment is related to A (−0.84 to −0.57 eV), whereas G yields less negative AEAs (−0.44 to −0.35 eV).

According to the present results it is unlikely that the reported experimental positive EA values actually correspond to VB anion states. Uracil and thymine could be an exception because both DB and VB anions are expected to share, unlike the other NABs, the same energy region. Therefore, estimated gas-phase or theoretical EAs for NABs with highly positive values can be safely ruled out.

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