ELECTRON BINDING TO NUCLEIC ACID BASES. EXPERIMENTAL AND THEORETICAL STUDIES. A REVIEW

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Received April 27, 2004
Accepted June 9, 2004

An in-depth knowledge of an excess electron binding mechanism to DNA and RNA nucleobases is important for our understanding of radiation damage influence on the biological functions of nucleic acids, as well as for the possible use of DNA molecules as wires in molecular electronic circuits. The of anions created by electron attachment to individual nucleic acid bases is discussed in detail. The principles of the experimental and theoretical approaches to the description of these anions are outlined, and the available results concerning valence- and dipole-bound anions of nucleic acid bases are reviewed. A review with 167 references.

Keywords: DNA; RNA; Nucleobases; Anions; Dipole-bound; Valence-bound; Ab initio calculations; Photoelectron spectroscopy; Rydberg electron transfer; Vertical detachment energy; Adiabatic electron affinity; Vertical electron affinity; Uracil; Thymine; Adenine; Guanine; Cytosine.

1. INTRODUCTION

Biochemists perceive double-helical DNA primarily as a target for molecular recognition. To understand in detail the remarkable variety of reactions involving the double helix in the cell, such as repair of DNA damage or coordination of the transcription of different genes, it becomes important to explore and consider also the rich physical chemistry of DNA.

One of the most intriguing and fascinating issues is the charge transfer process in DNA. DNA-mediated charge transfer processes can be categorised either as oxidative hole transfer or as reductive electron transfer. Major efforts have focused on the investigation of oxidative hole transfer[1–4], resulting in detailed insights on the mechanism[5,6]. On the other hand, the details of the electron transfer are still unclear. The biological implications of charge transfer in DNA are considerable. This is because the most important harmful effect of UV radiation on the living cell is the damage to the DNA component of the chromosome[7]. Radiation triggers[8,9] a release of free electrons and, consequently, single-electron oxidation or reduction initiates a cascade of reactions, the outcomes of which are far-reaching[10,11]. Ionising radiation can be absorbed directly by DNA, leading to the ionization of bases[12,13] (the direct effect), or react indirectly with the surrounding water molecules[14,15], creating highly reactive radicals (the indirect effect). Radiation damage to DNA can be classified as (i) structural damage leading to a breakage of phosphodiester bonds and subsequent single-strand or double-strand breaks and, (ii) change in information caused by the chemical modification of individual DNA bases[16–18]. Both types of damage can be lethal, and both may lead to mutagenic changes causing aging and disease[7].

Reactions on DNA through charge transfer chemistry are not restricted to damage only. For example, the repair of thymine dimers over a distance may be triggered either oxidatively[19–21], or reductively[22,23]. Certainly, charge transport chemistry mediated by DNA offers opportunities to carry out a range of reactions from a distant position on the DNA helix.

Another impact of charge transfer through DNA is the possible protection of genes against mutations[24]. Under the conditions of oxidative stress, DNA bases (especially guanine) are oxidised to heterocycles, which cause mutations in the replication step. If this mutation occurs in the encoding area, mutated proteins will be synthesised. But several genes possess G:C-rich sequences outside of the encoding area. These sequences act as sinks for the positive charge, so that the mutation occurs in the non-encoding area of DNA and the gene is protected against mutation.

The sensitivity of DNA charge transport to base stacking[25,26] provides the basis for sensor applications. Examining DNA film containing daunomycin (a redox active antitumor agent) covalently bound to guanine sites, it has been found[27] that the presence of an intervening CA mismatch shuts off the reduction of daunomycin. The electrochemical detection of DNA mismatches using different redox-active intercalators bound non-covalently to DNA-modified surfaces has also been reported[28]. The ability to detect single base mismatches by DNA-mediated charge transfer was exploited for mutational analysis in electrochemistry-based arrays[29]. The assay consisting of methylene blue coupled to $Fe(CN)_6^{3-}$ has increased mismatch discrimination and signal-to-noise ratio using electro-catalysis offering a completely new technology for the rapid detection of single nucleotide polymorphisms.

Apart from the physiological importance, electron transport in DNA is also interesting from the technological point of view[30–32]. The past decade has seen an increase in the need for more powerful computational devices. At present, this demand is accomplished with the miniaturisation of existing silicon-based chips – the top-down approach. An alternative is the bottom-up approach, where molecules are synthesised to possess some inherent functions and then are assembled with other components to build an electronic device[33]. The use of DNA molecules as wires in molecular electronic circuits[34] offers attractive advantages, which are consequences of its molecular recognition and self-assembly properties[32].

In 1962, Eley and Spivey proposed[35] that π–π interactions between stacked base pairs could provide a conduction band pathway for charge separation. Using a full range of physical and biochemical methods, studies have now established that double-helical DNA is a suitable medium for the efficient transport of electrons[36–38]. As a result, the focus of the field has shifted from asking whether DNA can mediate long-range charge transport to questions concerning the mechanism of charge transfer and how DNA structure and sequence affect this reaction.

A key to understanding the mechanism of electron transfer is the determination of the initial ion radical distribution in DNA. The location of the initial charges in DNA will largely affect and govern the creation of nucleotide radicals, which are formed by protonation of radical anions and deprotonation of radical cations. As a result of the relevance of DNA bases to the above mentioned issues, nucleic acid bases anions have been the subject of many experimental and theoretical studies.

The probability of reduction of a particular nucleobase is directly correlated with its properties such as vertical detachment energy (VDE), adiabatic electron affinity (AEA), vertical attachment energy (VAE), or vertical

electron affinity (VEA). Those properties are most easily envisioned from the qualitative diagram of potential energy surfaces for an anion and neutral molecule (Fig. 1), which is discussed in detail below.

The transition between a neutral system and a corresponding anion is accompanied by a change in the position of the nuclei. This introduces two Born–Oppenheimer potential energy surfaces requiring the specification of the geometries of both the neutral system and the anion. If there is no time for geometry rearrangement during the process of reduction, the transition is called vertical. If geometry relaxation takes place, the transition is called adiabatic.

The electron affinity of a neutral molecule is the negative of the binding energy of an electron to the molecule, and is defined by the negative of the energy change in the reaction

$$B + e \rightarrow B^{-}, \tag{1}$$

where B denotes a nucleic acid base and B^- its anion. The vertical electron affinity (VEA) and the vertical attachment energy (VAE) are obtained as

$$VEA = -\left(E^{B}_{B^-} - E^{B}_{B}\right) \tag{2}$$

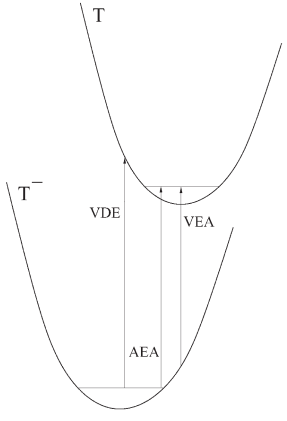

FIG. 1

Definition of the energetic quantities for molecular anions. The horizontal axis corresponds to an intermolecular coordinate. The vertical electron affinity (VEA) is the negative of the vertical attachment energy (VAE). The VDE and the VEA represent the upper and lower bounds to the AEA, respectively. If the VEA is positive, the molecule is able to spontaneously attract the electron. If the AEA is positive, the anion is stable with respect to the electron autodetachment. The VDE is always positive for stable anions

$$\mathrm{VAE} = -\mathrm{VEA} ,$$

where *E* stands for energy, the subscript denotes anion or neutral, while the superscript defines at what geometry the energy is evaluated. If the VEA is positive, the molecule acts as a trap for an excess electron, the attachment of the electron is energetically favoured and the anion can be spontaneously created. Anions of molecules with negative vertical electron affinities corresponding to their negative ion resonances do not exist for any chemically significant period of time.

The adiabatic electron affinity (AEA) is given as

$$\mathrm{AEA} = -\left(E_{\mathrm{B}^-}^{\mathrm{B}^-} - E_{\mathrm{B}}^{\mathrm{B}}\right). \qquad (3)$$

If the AEA is positive, then the anion is stable with respect to the autodetachment of the electron. This means that once the electron is trapped "inside" the molecule, it stays there long enough to play a role in chemical reactions.

The vertical detachment energy (VDE) of an anion is the energy required for the near-instantaneous removal of an electron from an anion

$$\mathrm{B}^- \rightarrow \mathrm{B} + \mathrm{e} \qquad (4)$$

Note that while the electron affinity is defined as the negative of the energy change in Eq. (*1*), the detachment energy is defined as the energy change

$$\mathrm{VDE} = -E_{\mathrm{B}}^{\mathrm{B}^-} - E_{\mathrm{B}^-}^{\mathrm{B}^-} . \qquad (5)$$

If the VDE is positive, the energy of the anion is lower than that of the neutral molecule and the anion is stable with respect to the vertical electron autodetachment. VDE is sometimes referred to as the first vertical ionization potential of the anion.

Vertical quantities give limiting values for most molecules. If the nuclear configuration of the anion does not drastically differ from that of the neutral, the VEA and the VDE provide lower and upper bounds to the AEA (see Fig. 1). An exception to this rule is, for example, the ClF_7 molecule[39], where the addition of an electron significantly changes the geometry and, consequently, the VDE (5.57 eV) is lower than the AEA (8.65 eV). This can be explained by the instability of ClF_7^- with respect to dissociation.

The attachment of an excess electron to a polar molecule can produce two different types of anions[40,41]: a valence-bound (VB) anion which is also called a covalent or conventional anion, or a dipole-bound (DB) anion (Fig. 2).

In VB anions the extra electron occupies a valence molecular orbital and is strongly bound, which leads to considerable alteration of the molecular structure of the neutral precursor. In contrast, DB electrons are weakly bound to polar molecules primarily by electrostatic charge-dipole interactions. Consequently, a dipole-bound attachment affects the intramolecular structural parameters much less than that of a valence-bound electron. An overview of the historical development of DB states as well as detailed reviews are given in[42–44]. The first treatise on this topic appeared in the seminal paper of Fermi and Teller[45]. An interesting overview of their pioneering work can be found in[46]. The critical dipole moment for binding an excess electron depends on the molecule moment of inertia[47–49], but, as a rule of thumb, a value of 2.5 D is often adopted[50,51]. The number of bound states is finite and usually equals to one. The existence of two dipole-bound states in strongly polar molecules has been predicted[52–54] but, so far, not confirmed experimentally.

The excess electron does not have to be bound only by electrostatic interactions resulting from permanent charge distributions; systems for which the excess electron is bound predominantly or entirely by polarisation forces have also been described. Metal surfaces[55,56] and certain inert-gas clusters (e.g. Xe_n, $n \geq 6$, see[57–59]) possess bound states where electron binding is dominated by polarisation. Recently, the existence of so-called

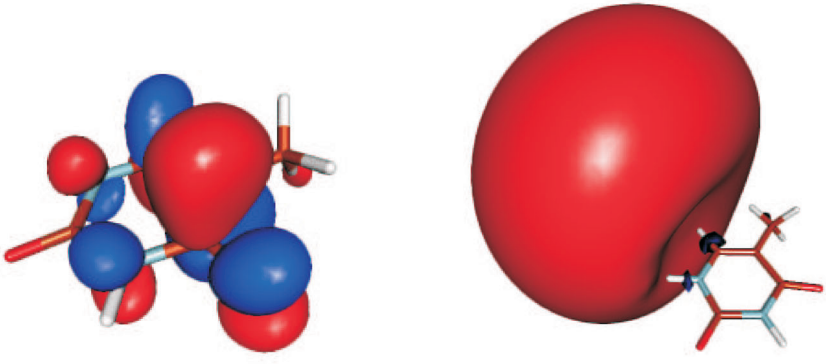

FIG. 2
Highest occupied molecular orbitals (HOMO) in valence-bound and dipole-bound anions of thymine. Dipole-bound orbital plotted with the 0.005 contour surface, valence-bound orbital plotted with the 0.02 contour surface

dispersion-bound anions, where the main contribution to the electron binding energy comes from dispersion interactions, has been predicted[60,61]. Moreover, external fields add significantly to the variety of anions as well as to the richness of their properties. The so-called magnetically induced anions existing exclusively due to the presence of external magnetic field[62] can serve as an example.

2. EXPERIMENTAL STUDIES OF NUCLEOBASE ANIONS

2.1. Experimental Methods

Despite significant experimental effort, the values of the electron affinities of DNA bases are still a matter of debate. In some cases, not only the magnitude but even the sign of the valence molecular electron affinities have not been well established.

The two most common experimental methods used for the characterisation of gas-phase anions are negative ion photoelectron spectroscopy (PES)[63,64] and Rydberg electron transfer (RET)[53,65]. PES is conducted by crossing a mass-selected beam of negative ions, usually generated in a supersonic expansion nozzle, with a fixed-frequency laser beam, followed by an energy analysis of the photodetached electrons. The presence of a DB anion is indicated by a sharp narrow peak at very low electron binding energies (VDE usually being below 0.1 eV) in the photoelectron spectra, while a VB anion is characterised by a broad band at a relatively high electron binding energy. It should be pointed out here that a supersonic expansion source usually tends to create the most stable form of a given anion. An example is the nitromethane anion, where the supersonic expansion ion source makes only the more stable conventional anion[66]. Another example is uracil, where the DB form is more stable than the VB form. Only the DB anion is detected, though both forms coexist[67].

In the RET technique, a pulsed beam of molecules seeded in helium crosses a pulsed supersonic beam of Rydberg-excited Xe atoms. The highly excited Rydberg electrons are transferred via collisions to the neutral molecules of the studied system. The determination of DB electron affinities relies on the observed anion formation rate as a function of the principle quantum number n of the Rydberg electrons. The formation rate usually shows a strong n-dependence and sharply peaks at the certain value of n_{max} [52]. The electron affinity is then derived from an empirical relation[54]

$$EA = \frac{23}{n_{max}^{2.8}} . \qquad (6)$$

In contrast to PES experiments, the EA values for valence-bound anions cannot be deduced from the RET spectra as the presence of covalent anions corresponds to a background shift in all n values[68].

2.2. Uracil and Thymine

Most experimental work has been done on uracil and thymine anions (see Table I for valence-bound adiabatic electron affinities).

We will start by focusing on the electron attachment to those two nucleobases, the results for other nucleobases being summarised in the subsequent section.

Experimentally based estimates of the VB AEAs of nucleobases were first derived from the AEAs of pyrimidine and purine using substitution and replacement rules[69]. Both uracil and thymine anions were predicted to be strongly bound with the estimated values of AEA 0.75 and 0.65 eV, respectively. Later studies by Wentworth et al.[70,71] used cyclic voltammetry to measure the reversible half-wave reduction potentials of nucleobases in an aprotic solvent (dimethyl sulfoxide). The AEAs (0.80 eV for uracil, 0.79 eV for thymine) were estimated using scaling factors based on the known EAs of acridine and anthracene. These values were supported by semiempirical multiconfiguration calculations (AM1-MCCI)[72,73].

TABLE I
Experimental valence-bound adiabatic electron affinities of thymine and uracil reported in literature (in eV)

Reference	Uracil	Thymine
Wentworth et al.[69]	0.75	0.65
Wentworth et al.[70,71]	0.80	0.79
Weinkauf et al.[76]	0.15 ± 0.12	0.12 ± 0.12
Schermann et al.[74]	>30–60 and <93	–
Desfrancois et al.[77]	≈0	≈0
Sanche et al.[78]	–	>0

The existence of a valence-bound state of gas-phase uracil anion has been observed by Schermann et al. using Rydberg electron transfer spectroscopy[74]. The valence-bound anions were prepared by attaching electrons to uracil–argon clusters (the presence of argon stabilises the valence state) followed by the evaporation of the argon atoms. The RET method is generally not able to directly provide accurate values of VB electron affinities, but, based on the route of anion formation, the authors concluded that VB AEA must be greater than the binding energies of argon–uracil clusters (30–60 meV) and smaller than the DB AEA of 93 meV [75]. They supported this conclusion by a DFT calculation which provided a positive VB AEA equal to 70 meV. Moreover, a dipole-bound anion was also detected. The issue of dipole and covalent bound coupling, e.g. known in the case of nitromethane molecule[66], has been raised as well. This is the only simultaneous experimental observation of both valence and dipole-bound states of free non-solvated uracil found in literature.

Weinkauf et al.[76] took advantage of the almost linear relationship between AEA and the number of solvent molecules and estimated the VB AEAs of free nucleobases by extrapolation. They obtained a VB AEA value for uracil equal to 0.15 ± 0.12 eV, and for thymine equal to 0.12 ± 0.12 eV. These estimates and the work of Desfrancois et al.[77] (uracil and thymine VB AEAs were roughly zero) and Sanche et al.[78] (VB AEA of thymine was somewhat larger than 0) are the only experimentally-based values complementing studies using reduction potentials. However, the values of the VB electron affinities obtained in those studies remain far from those obtained by cyclic voltammetry or semiempirical calculations[70–73]. The main assumption of the cyclic voltammetry method is that the solvation energies are, within a family of similar molecules, constant or at least linearly dependent on the electron affinities. This is, however, questionable[79], and estimates based on reduction potentials are generally considered to be unreliable[80]. To the best of our knowledge there are no direct measurements of adiabatic electron affinities of nucleobases valence anions in the gas phase, all the above described techniques representing only indirect measurements.

Negative electron affinities can be experimentally measured by electron transmission spectroscopy ETS [81]. These types of measurements detect negative ion resonance states, which are formed by the temporary (typically 10^{-15} s) capture of an electron by a molecule. Resonance states are energetically unstable with respect to electron autodetachment. The negative vertical electron affinities of conventional valence-bound states were reported by Burrow et al.[82], who obtained values of –0.22 eV for uracil, and of –0.29 eV for thymine, respectively. Another approach, an intermediate between gas-

phase ETS experiments and solution cyclic voltammetry, was developed by Desfrancois et al.[77], who determined the electron attachment properties of nucleic acid bases embedded inside clusters of different solvent species (noble gases, water, ammonia, toluene or methanol) as a function of the cluster size. The determination of the cluster size threshold above which valence anions were observed (by means of RET spectroscopy) provided the estimated value of the valence vertical electron affinities of thymine and uracil (–0.30 eV). The VEA of thymine (–0.53 eV) and of uracil (–0.24 eV) were also estimated using the enthalpy of formation[83].

The DB anions of uracil and thymine were experimentally observed for the first time by Bowen et al.[75] (PES), and Schermann et al.[54] (RET). The estimated values of AEA for thymine are 69 ± 7 meV (PES) and 68 ± 20 meV (RET). Only the DB anions of thymine and uracil were observed. These results were verified by PES studies by Weinkauf et al.[76], yielding a DB AEA value for thymine equal to 62 ± 8 meV.

Bowen et al.[67] reported an observation of a transformation from a dipole-bound state to a valence-bound state due to solvation effects. In a series of negative-ion photoelectron spectroscopic experiments, uracil anions were microsolvated with various numbers of water molecules, and the evidence for the dipole-bound-to-covalent state transformation was looked for. Surprisingly, a single molecule of water was found to be sufficient for the dipole-bound-to-covalent transition. This conclusion was verified in another PES experiment reported by Weinkauf et al.[76] The valence form is stabilised by interaction with water since the excess electron density of the valence-bound uracil anion is much higher than that of the dipole-bound anion, and the water interaction is stronger with a more compact electron distribution. This stabilisation is just another example of a molecular form unstable in gas phase being stabilised by solvation. Bowen et al.[67] further performed PES experiments with weaker noble gas solvents observing dipole-bound anions in $(\text{uracil}\cdots\text{Ar})^-$ and $(\text{uracil}\cdots\text{Kr})^-$ clusters, and a coexistence of both dipole- and valence-bound anions in the $(\text{uracil}\cdots\text{Xe})^-$ system.

The influence of N-methylation on the dipole-bound electron affinities of uracil and thymine has been studied both theoretically[84,85] and experimentally by RET spectroscopy[84]. The change of molecular size with N-methylation leads to a reduction of the electron affinity. This conclusion can be extended to nucleosides, which should be less susceptible to free electron attachment than the isolated bases.

From experimental studies, the following picture concerning the excess electron attachment to uracil emerges:

• The valence-bound anion of uracil in gas phase has a negative vertical electron binding energy[72,82,83], so it cannot be created spontaneously by electron attachment. On the other hand, its adiabatic values are positive[74,76–78] meaning that once the anion is formed, it is stable with respect to electron detachment. The valence-bound anion can be created by electron attachment to uracil–argon cluster, followed by the evaporation of argon atoms[74].

• The dipole-bound state is both vertically and adiabatically stable[54,67,74–76], thus it can be formed by an electron attachment to bare uracil in the gas phase. The geometry of the anion is only slightly distorted from the geometry of the neutral molecule; consequently, the VDE and AEA are very close to each other. The dipole-bound electron affinity is reduced by methylation[84].

• The presence of solvent stabilises the valence-bound state. The coexistence of both DB and VB anions has been observed[67] for uracil–xenon clusters, while the addition of just a single water molecule switches the stable state from the dipole-bound to the valence-bound state[67,76].

2.3. Other Nucleobases

Leaving aside the rather unreliable results based on reduction potential measurements (see Section 2.2), additional information is available for electron attachment to cytosine, guanine, and adenine. Electron transmission spectroscopy (ETS) measurements have provided[82] negative values of valence vertical electron affinities for cytosine (–0.524 eV), adenine (–0.794 eV), and two tautomeric forms of guanine (amino-oxo –1.191 eV, and amino-hydroxy –0.908 eV). The cluster solvation method combined with RET spectroscopy used by Desfrancois et al.[77] (see also Section 2.1) provided estimates of the valence vertical electron affinities of adenine of –0.45 eV and cytosine of –0.55 eV. Also, the enthalpy of formation was used[83] to estimate the VEA of adenine (–0.56 eV), cytosine (–0.40 eV), and guanine (–0.79 eV).

The amino-oxo and amino-hydroxy tautomers of cytosine were studied by Weinkauf et al. in a PES study[76]. The photoelectron spectrum showed two peaks: a narrow, intense peak at 85 ± 8 meV, and a broad, much less intense band at 230 meV. Those peaks were assigned to the dipole-bound states of the amino-hydroxy and amino-oxo forms. The remarkable difference in the intensity between those two bands was explained by the fact that the amino-hydroxy anion was enhanced during the formation process in the source. Those results were later refined theoretically by Ortiz et al.[86],

who assigned the narrow peak to the dipole-bound anion of the canonical amino-oxo form, and the broader band to the valence-bound anions of amino-oxo and two imino-oxo tautomers (those forms are stable only with respect to vertical electron detachment, but not adiabatically).

The dipole-bound anion of adenine was observed in RET experiments by Schermann et al.[54], and its adiabatic electron affinity was estimated to be 12 ± 5 meV. There is no direct experimental observation of guanine anion(s) due to the difficulty of obtaining sufficiently high pressure of this species without isomerization or decomposition[77].

3. Ab initio CALCULATIONS OF NUCLEOBASE ANIONS

3.1. Theoretical Methods

Experimental results obtained from photoelectron spectroscopy, Rydberg electron-transfer spectroscopy, and electron transmission spectroscopy studies present a challenge to theoreticians. The problem of accurate electron affinity calculations is still a matter of controversy, essentially due to the very small energy values involved. There is even a lack of a reliable determination of the sign of valence electron affinity for adenine and guanine, which are notorious for their resistance to attachment of an excess electron.

The simplest qualitative theoretical approach to estimate electron affinity is via Koopman's theorem. Electron affinity is taken as the negative of the Hartree–Fock lowest unoccupied molecular orbital (LUMO).

$$EA_{KT} = -\varepsilon_{LUMO} \qquad (7)$$

This approximation is very rough, as it assumes that the orbitals in the ion are the same as in the neutral system, i.e. orbital relaxation is neglected and orbitals are "frozen". Additionally, the Hartree–Fock method does not include the effects of electron correlation. While orbital relaxation and electron correlation almost cancel each other out for ionization potentials that are approximated as the negative of the highest molecular occupied orbital (HOMO), they add up in the case of electron affinities. Note also that orbital relaxation is typically small for dipole-bound anions[43].

Strictly speaking, for standard quantum chemistry methods only stable bound states are accessible. Since the negative ion resonance states detected by ETS are unbound (lying in the continuum), they should be rigorously calculated by the scattering theory. However, it has been demonstrated by a

number of authors, including Jordan and Falceta[87,88] and Staley and Strnad[89], that a finite basis set approach provides reasonable estimates of the position of resonances if certain basis sets are employed. For example Staley and Strnad[89] used the standard D95V basis set to obtain results close to the experimental values. They also demonstrated that adding polarisation or diffuse orbitals destroys the agreement between the ETS results and energies obtained with the use of Koopman's theorem. The use of small basis sets results in confining the electron to the molecule[90] and results in reasonable relative valence electron affinities[80].

For bound anionic states, one should not impose any restrictions on the form of the anionic wave function and allow for a maximal spatial and angular flexibility of the basis functions. To characterise valence-bound anions with positive electron affinities accurately, atomic orbital basis sets flexible enough to describe both the spatial distributions of electrons and their dynamical correlations must be used. Basis sets augmented with functions decaying slowly with the radial distance r (diffuse atomic orbitals) are required.

The excess electron in VB states causes reorganisation of the molecular framework, thus affecting the zero point vibrational energy (ZPVE). ZPVE, therefore, plays a decisive role in determining the absolute values of the adiabatic electron affinities of the VB anion. The negative electron affinities cannot be appropriately corrected for ZPVE since the calculated species are not in their relaxed states. Dipole-bound states do not usually require the inclusion of a ZPVE correction since the geometry difference between the neutral and anion tends to be small. The gas phase ZPVE difference between the anion and the neutral molecule can be used as a measure of electron localisation[90].

Theoretical studies of valence EAs, which present a difficult task requiring the inclusion of electron correlation and the use of well-defined basis sets, have provided contradictory results for nucleobases. In addition to ab initio electronic structure methods such as the Møller–Plesset (MP) perturbation theory or coupled cluster, the density functional theory (DFT) has become a standard tool for predicting electron affinities over the last several years[91–94].

The orbital occupied by a DB electron is very diffuse and centred away from the molecule on the positive end of its dipole[95] (see Fig. 2). It was long believed that electron correlation effects played a minor role in determining the electron binding energies[96–98] due to the the small overlap between the dipole-bound electron and the molecular orbitals of the neutral molecule. However, it is now well established that electron correlation effects can significantly change the properties of dipole-bound anions[99]. The main

correlation contribution is the dispersion interaction between the excess electron and the electrons of the neutral molecule. The inclusion of correlation also leads to a change (typically a reduction) of the dipole moment of the neutral precursor. Additionally, the supermolecular approach used to calculate binding energies necessitates the use of size-extensive methods. Therefore, the description of the dipole-bound anions requires treating electron correlation effects by the MP perturbation theory or, better, by using coupled cluster (CC) methods together with large flexible basis sets. The description of a dipole-bound state using density functional methods can be problematic since the use of very diffuse electron distributions creates problems of numerical integration when computing the matrix elements of the exchange-correlation potentials. Moreover, density functional methods notoriously fail for dispersion interactions.

The diffuse character of the orbital describing the dipole-bound electron demands the use of extra diffuse functions with very low orbital exponents that are combined with standard valence-type basis sets. The results are rather insensitive to the position of the diffuse orbitals provided that they are located close to the positive end of the molecular dipole[95]. The diffuse orbitals can be placed on the atom closest to the positive end of the molecular dipole moment[84], at a certain distance (possibly optimised[100]) from this atom[101], or the position of the centre carrying the extra functions can be fully optimised. Interestingly, Ortiz et al.[101] obtained reasonable results even without these kinds of diffuse functions, using a valence basis set augmented with diffuse functions close to saturation. However, this might not be the most economical approach.

To properly describe the dipole-bound electron, both diffuse *s* and *p* functions must be added, while the higher angular-momentum diffuse functions usually do not significantly contribute to excess electron binding[102,103]. The value of the lowest exponents in the additional *s* and *p* set is related to the dipole moment of the neutral system[102]; the lower the dipole moment, the smaller the exponents that should be used. An even-tempered sequence of diffuse functions is generated according to the following formula:

$$\alpha_n = \alpha_1 q^{n-1}, \qquad n = 1, \ldots , \tag{8}$$

where α_1 is the value of the lowest exponent, q is the geometrical progression parameter, and n is the length of the sequence (i.e. the number of additional *sp* sets). The extra *s* and *p* functions usually share the same exponents. A detailed study of the role of the valence and extra-diffuse basis sets

has been published by Simons et al.[103] The authors suggest determining the additional diffuse set by monitoring the SCF coefficients of the singly occupied virtual orbital (the coefficients of the most diffuse *s* and *p* basis functions must not be dominant for this molecular orbital, otherwise more functions have to be added), and using the largest exponent in the diffuse set which is smaller by at least a factor of two than the most diffuse exponent in the valence basis set. When even-tempered diffuse functions were used, the optimal geometric progression parameter was found to be only slightly dependent on the dipole moment of the neutral system[102]. Simons et al. propose[103], based on the calculations on small molecules, to use a geometric progression parameter *q* in the range of 3.0–5.0. Another approach, used by Adamowicz[104–106], varies the values of parameters in Eq. (*8*) so that the lowest LUMO energy of a neutral system is reached.

3.2. Valence-Bound Anions

In direct contrast to experimental results, most early ab initio computations of nucleobases predicted negative valence adiabatic electron affinities[107–112] (Tables II–VI).

TABLE II
Theoretically computed valence electron affinities of canonical uracil reported in literature (in eV). The notation describes the level of theory of energy calculation//level of theory of structure optimisation

Reference	Method	Vertical	Adiabatic
Sevilla et al.[107]	scaled Koopman/D95V	–0.19	0.4
Sevilla et al.[107]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	–0.25
Burrow et al.[82]	not given/6-31G*//not given/3-21G	–0.216	–
Boyd et al.[110]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	–0.4
Boyd et al.[113]	B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p)	–0.26	0.18
Russo et al.[114]	B3LYP/6-311++G//B3LYP/6-311++G**	–0.11	0.215
Schaefer et al.[80]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.19
Wiest at al.[167]	B3LYP/6-31+G*//B3LYP/6-31+G*	–0.35	0.18
Sevilla et al.[90]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	–0.32	0.20

TABLE III
Theoretically computed valence electron affinities of canonical thymine reported in literature (in eV)

Reference	Method	Vertical	Adiabatic
Sevilla et al.[107]	scaled Koopman/D95V	–0.32	0.3
Sevilla et al.[107]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	–0.30
Burrow et al.[82]	not given/6-31G//not given/3-21G	–0.364	–
Boyd et al.[110]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	–0.64
Boyd et al.[113]	B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p)	–0.30	0.14
Russo et al.[114]	B3LYP/6-311++G//B3LYP/6-311++G**	–0.34	0.179
Schaefer et al.[80]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.16
Rösch et al.[117]	AM1//averaged experimental coords[118]	–	0.254
Sevilla et al.[90]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	–0.28	0.22
Walch[119]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	–	0.34

TABLE IV
Theoretically computed valence electron affinities of canonical cytosine reported in literature (in eV)

Reference	Method	Vertical	Adiabatic
Sevilla et al.[107]	scaled Koopman/D95V	–0.4	0.2
Sevilla et al.[107]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	–0.46
Eriksson et al.[109]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	–0.6
Adamowicz et al.[124]	MP4/6-31++G**(6d)//UMP2/6-31++G**(6d)	–	–0.51
Russo et al.[114]	B3LYP/6-311++G//B3LYP/6-311++G**	–0.31	0.006
Ortiz et al.[86]	UMP2/6-311++G(2df, 2p)//UMP2/6-31++G**	–	–0.38
Schaefer et al.[80]	B3LYP/TZ2P++//B3LYP/DZP++	–	–0.02
Rösch et al.[117]	AM1//averaged experimental coords[118]	–	0.087
Sevilla et al.[90]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	–0.63	–0.05
Walch[119]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	–	0.20
Schmidt et al.[120]	DFT-GGA	0.84	0.84

TABLE V
Theoretically computed valence electron affinities of canonical guanine reported in literature (in eV)

Reference	Method	Vertical	Adiabatic
Sevilla et al.[107]	scaled Koopman/D95V	–1.23	–0.7
Sevilla et al.[107]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	–0.75
Boyd et al.[111]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	–0.69
Russo et al.[114]	B3LYP/6-311++G//B3LYP/6-311++G**	–0.08	–0.004
Schaefer et al.[80]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.07
Rösch et al.[117]	AM1//averaged experimental coords[118]	–	–0.071
Sevilla et al.[90]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	–1.25	–0.75
Walch[119]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	–	0.25
Schmidt et al.[120]	DFT-GGA	0.84	0.85

TABLE VI
Theoretically computed valence electron affinities of canonical adenine reported in literature (in eV)

Reference	Method	Vertical	Adiabatic
Sevilla et al.[107]	scaled Koopman/D95V	–0.74	–0.3
Sevilla et al.[107]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	–1.19
Boyd et al.[112]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	–0.9
Russo et al.[114]	B3LYP/6-311++G//B3LYP/6-311++G**	–0.34	–0.264
Schaefer et al.[80]	B3LYP/TZ2P++//B3LYP/DZP++	–	–0.17
Rösch et al.[117]	AM1//averaged experimental coords[118]	–	–0.056
Sevilla et al.[90]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	–0.80	–0.35
Walch[119]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	–	0.08
Schmidt et al.[120]	DFT-GGA	0.74	0.79

In 2000 Boyd et al.[113] obtained, without any scaling, the first positive adiabatic electron affinities for uracil and thymine (see Tables II and III). Those results contradict the theoretical work of Adamowicz et al.[104,105], who failed to locate stable valence ions; however, the predicted existence of both dipole and valence-bound anions of uracil is in accord with experimental work[74]. Boyd et al. also determined valence vertical electron affinities, all of which were negative, which is in agreement with experimental findings[82].

Russo et al.[114] evaluated electron affinities (both vertical and adiabatic) at the DFT level using different functionals and basis sets. The vertical affinities were again all negative. It has been shown that the choice of basis set is crucial for getting the correct sign. While recent computations with varying basis set quality confirmed the positive values of thymine and uracil AEAs, the stability of conventional guanine and cytosine anions is less certain, as the sign of electron affinity depends on the chosen level of theory. For adenine, a negative valence electron affinity was found[114] irrespective of the functional and basis set used, which is in agreement with experimental results[54]. The same conclusions were drawn from DFT calculations made by Schaefer et al.[80] The computed VB AEAs of cytosine and guanine oscillate between small positive and negative values and it remains unclear if a covalent anion is bound. Furthermore, the lack of experimental information for guanine and the uncertainty of the measurements for cytosine[76,77,115] do not allow any conclusive statements.

The suitability of a semiempirical AM1 scheme[116] for adiabatic electron affinity calculations was addressed by Rösch et al.[117] The structures of the four bases adenine, cytosine, guanine, and thymine were taken from a statistical survey of small molecules in the Cambridge Structural Database for which high-resolution X-ray and neutron crystal structures are available[118]. Adiabatic electron affinities were calculated using the energy difference between the molecule and its anion using the HOMO orbital energy of the radical anion, and by using the LUMO of the neutral closed-shell system. While AEA values obtained by these three approaches differed considerably, their relative values were found to be very similar because systematic errors were eliminated. This suggests using estimates based on LUMO orbital energies of neutral species as the best strategy for evaluating the reaction energies of electron transfer in DNA by semi-empirical calculations on closed-shell systems.

To better understand the cause of the diversity in the values of EAs, Sevilla et al.[90] performed a series of density functional (B3LYP) calculations with different basis sets. Examination of the singly-occupied molecular orbitals and spin distributions of the anions revealed that the inclusion of a

diffuse basis set could result in contamination of the valence-bound state with the dipole-bound state. Guanine anion was most susceptible to state mixing. For this reason the authors called the earlier reported values for guanine[80,111,113] into question, as they believed they were not representative for neither the valence nor the dipole-bound states. Naturally, the question arises whether the mixing of valence and dipole-bound characters represents the real physical situation, or if it is only an artefact of the employed methodology.

Walch[119] evaluated adiabatic electron affinities using the B3LYP functional with the 6-31++G basis set augmented with atom-centred Rydberg 3s, 3p, 3d, 4s, and 4p functions. He compared his results with those of Schaefer et al.[80] and concluded that they are "of the same order, but the extra electron is more weakly bound in each case". As a matter of fact, the AEA of adenine was, in contrast to Schaefer's value of –0.28 eV, slightly positive, being very close to the experimental value of 12 ± 5 meV[54] assigned to the adenine dipole-bound state. The nature of the anion states was not investigated (e.g. using a plot of anion HOMO), and it is possible that the identified anions were not valence-bound, but correspond to mixed, or even to dipole-bound, states. Schmidt et al.[120] used the DFT method with the generalised gradient approximation (GGA)[121,122] for the exchange and correlation potential in conjunction with a plane-wave basis and ultrasoft non-norm-conserving pseudopotentials[123]. Doubt can be cast upon the applicability of this approach, as those calculations completely failed to find nearly vanishing or negative EAs.

The covalent anions of two cytosine tautomers, amino-oxo and amino-hydroxy, were characterised by Adamowicz et al.[124] Only the covalent anion of the canonical amino-oxo form was found to be vertically stable (VDE = 0.102 eV), while both amino-oxo and amino-hydroxy anions were predicted to be unstable with respect to adiabatic electron detachment. Another study of the valence-bound anions of five cytosine tautomers (amino-oxo, *trans*- and *cis*-amino-hydroxy, and *trans*- and *cis*-imino-oxo) was done by Ortiz et al.[86] It was found that none of the cytosine tautomers produced an adiabatically stable VB anion, and that only valence-bound anions of oxo-forms displayed positive VDE values in accord with Adamowicz's results[124]. Furthermore, when the influence of correlation effects beyond the MP2 level was studied for the amino-oxo form, VDE increased from 0.141 eV (MP2/6-311+G**) to 0.296 eV (CCSD(T)/6-311+G**). Ortiz assigned the experimentally observed broad band[76] of the photoelectron spectrum to the electron detachment from the valence-bound anions of all three oxo-forms.

The polarizable continuum model (PCM) model was also used[90] to obtain EA values for solvated DNA radical anions[90]. All AEAs of solvated anions were found to be positive, and PCM calculations resulted in the same relative order of EAs as in the gas phase.

3.3. Dipole-Bound Anions

All canonical forms of nucleic acid bases (Fig. 3) possess[125] dipole moments higher than the critical value 2.5 D (Fig. 4). As a result, those systems can form stable dipole-bound anions. The electron binding energy is smallest in adenine, which has only a moderate dipole moment close to the critical value.

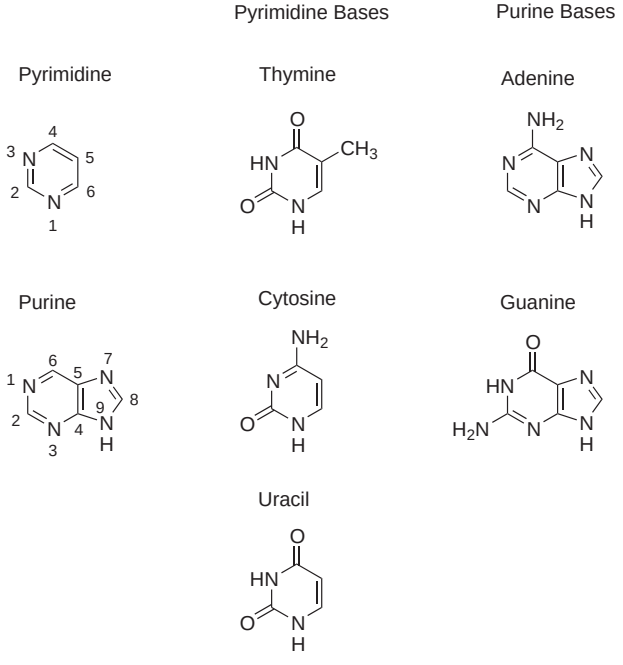

FIG. 3
Chemical structures and atom numbering for purine and pyrimidine nucleic acid bases: thymine (T), cytosine (C), adenine (A), guanine (G) in DNA and uracil (U), cytosine (C), adenine (A), guanine (G) in RNA. Sacharide (deoxyribose in DNA and ribose in RNA) is bonded to the nitrogen atom number 1 (in pyrimidines), or to the nitrogen atom number 9 (in purines)

3.3.1. Uracil, Thymine

In the early nineties, Adamowicz et al. first predicted the existence of an adiabatically stable, dipole-bound anion for uracil[104]. In this work, the geometry of neutral uracil was optimised at the HF/3-21G level. The anion geometry was optimised at the UHF/3-21G level with the additional diffuse functions (X) centred on a "ghost atom" located 1 Å away from the C6 atom (see Fig. 4). With these geometries, neutral and anionic total energies were recalculated at the MP2/6-31+G*X level. A small positive AEA of 0.086 eV was obtained for uracil. A very similar procedure was also used to determine the electron affinity of thymine[105]. The AEA for the excess electron attachment was estimated to be 0.088 eV. Another theoretical calculation of thymine AEA, made again by Adamowicz, was published[84] in 1999. The equilibrium geometry of neutral thymine was determined at the RHF/6-31++G** level. Six additional diffuse sp Gaussian orbitals were placed at the hydrogen atom bound to the C6 atom (see Fig. 4). Optimisation was performed at the UHF/6-31++G**X level, and the total energies of both the neutral and anion species were determined at the MP2/6-31++G**X level.

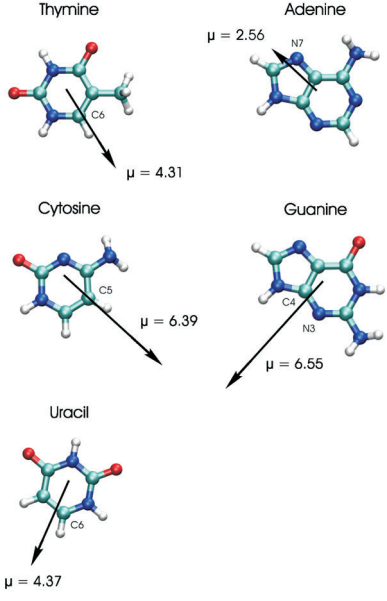

FIG. 4
Magnitudes and vectors of dipole moments μ (in D) of nucleic acid bases calculated at the MP2/aug-cc-pVDZ level. Oxygen is red, nitrogen dark blue, carbon light blue, and hydrogen white. Adopted from[125]

Only the dipole-bound anion of thymine with AEA equal to 0.032 eV was found. In the same work, the AEA of a DB anion of uracil was calculated to be equal to 0.047 eV. Similar values (VEA = 0.031 eV and AEA = 0.040 eV) for uracil were found in[85]. The thermodynamic instability of the valence-bound uracil anion relative to the dipole-bound form was disclosed by Ortiz et al.[100] The dipole-bound AEA of 0.025 eV and VDE of 0.054 eV were determined at the MP2/6-311++G**+B2//MP2/6-311++G**+B2 level, where B2 denotes a basis set containing additional diffuse *s* and *p* functions placed on each atom. No similar calculations (i.e. without employing a "ghost" atom) were performed for thymine anion. An uracil anion dipole-bound EA of 0.063 eV obtained at the MP4(SDQ)//CCSD/6-31+G**(+4sp) level was also reported by Gutowski et al.[43] The most recent theoretical results obtained at the CCSD(T) level with the aug-cc-pVDZ basis set provided a VDE value for uracil of 0.073 eV [126].

Three isomers of uracil$\cdots H_2O$ complexes and their anions were studied with the MP2 method and the 6-31+G* basis set augmented with extra diffuse functions centred on a "ghost" atom at the positive end of the molecular dipole[106]. Only dipole-bound anions of the uracil$\cdots H_2O$ system were found and these appeared to be less stable with respect to electron detachment than dipole-bound uracil anions[104]. No conventional stable valence anionic states were found by the theoretical procedure used in this work (MP2/6-31+G*X//HF/6-31+G*X). These results are in direct contradiction with the photoelectron experiments in which Bowen et al.[67] and Weinkauf et al.[76] demonstrated the valence-bound character of the $(\text{uracil}\cdots H_2O)^-$ anion. The disagreement was attributed to an insufficient level of theory at which optimisation was performed. This conclusion was supported by the work of Ortiz et al.[127], where several isomeric structures of the uracil$\cdots H_2O$ complex and their covalent bound anions were studied at the MP2/6-31++G(2df,2p)//MP2/6-311++G** level of theory. The valence-bound VDEs of all anions lay between 0.3 and 0.9 eV, the VDE of the most stable anion structure (0.9 eV) coincided with the experimentally observed maximum in the broad spectral feature[67], and at least four structures had positive AEAs. The valence-bound states of four uracil$\cdots H_2O$ isomers were also found and characterised at the B3LYP/6-31++G** level[128]. The calculated values of VDE span the range 0.76–0.99 eV. A valence-bound $(\text{uracil}\cdots(H_2O)_3)^-$ cluster with a positive VDE of 0.89 eV was found by Adamowicz[129] in calculations similar to those of lit.[106]. However, this cluster was predicted to have a negative adiabatic electron affinity. Apart from the valence anion, the uracil$\cdots(H_2O)_3$ complex was found[129] to be able to form a stable dipole-bound anion with a very small adiabatic electron affin-

ity equal to 13 meV. Needless to say, the authors themselves admit that "without higher order calculations we still recommend considering our results as the first approximation"[129].

In the study of the interaction of an excess electron with a small cluster of three HF molecules[130], Gutowski and Adamowicz described a new type of anion with two H bonded HF molecules on one side of the excess electron and one HF on the other side. This anion could coexist with a dipole-bound anion of the $(HF)_3$ cluster under certain experimental conditions in the gas phase. Theoretical calculations performed by Adamowicz et al. on the uracil···HF and uracil···H_2O systems revealed[131] a similar form of anion labelled by the authors as anions with internally suspended electrons (AISE). AISE belong to a broader category of anions called solvated electrons, where the excess electron is localised inside the cluster and not on the surface as in the case of DB anions. The formation of AISE probably proceeds in two steps. First, a dipole-bound anion U^- is formed, and next, the second subunit (HF or H_2O) attaches to the DB electron on the side opposite to where the first unit is connected. The excess electron is suspended between the two monomers and mediates a bond between them. Due to its similarity to H-bond, the authors called this interaction e-bond[131]. The orbital occupied by the excess electron in AISE is less diffuse than the orbital occupied in the dipole-bound state of the first monomer. In both cases, the adducts have higher energies than the neutral complexes, therefore, AISE are metastable systems with finite lifetimes that transform either to the neutral system and a free electron or to another type of anion (dipole- or valence-bound). The authors also suggested the possibility that the broad band in the PES spectrum by Bowen[67] corresponds to an AISE state. The calculated value of VDE 0.24 eV is, however, much smaller than the experimental value ≈0.9 eV.

In the above described complexes, the second monomer unit (solvent molecule) possesses a nonzero dipole moment and, consequently, the charge-dipole interaction is the predominant attractive force. Adamowicz et al.[132] also described systems where a dipole-bound electron attached to uracil molecule interacts with noble gas atoms such as He and Ne. The interaction in such systems is dominated by charge-induced dipole effects, as well as by dispersion interactions. AISE were also studied for the uracil–uracil[133], uracil–glycine[134], uracil–adenine[135], and thymine–adenine[136] systems.

3.3.2. Cytosine

Ab initio calculations were performed by Adamowicz et al.[124] to determine the stability of covalent and dipole-bound anions of two tautomers of cyto-

sine, amino-hydroxy (two conformers, cis and trans, were considered) and canonical amino-oxo. The geometries of the dipole-bound anions were determined at the UMP2/6-31++G**(5d)X level, where X denoted the diffuse Gaussian *sp* set centred at the hydrogen atom located closest to the positive end of the molecular dipole (see Fig. 4). Adiabatic electron affinities were obtained at the MP4/6-31++G**X level. The calculated AEAs were 58, 22, and 6 meV for the amino-oxo cytosine and the two conformers of the amino-hydroxy cytosine. These values are considerably smaller than the two experimental values 85 ± 8 and 230 ± 8 meV [76], but the authors left this issue open relying on more refined calculations and experimental measurements in future.

The anions of five isomers (amino-oxo Cy0, *trans*- Cy1 and *cis*-amino-hydroxy Cy2, and *trans*- Cy3 and *cis*-imino-hydroxy Cy4) of cytosine were also studied by Ortiz et al.[86] The structures of the anions were optimised at the UMP2 level with the 6-311++G** basis augmented with the nearly saturated, diffuse basis set B2 [100]. This basis set has already been described in Section 3.3.1. Only the amino-oxo form produced an adiabatically stable dipole-bound anion with an AEA equal to 0.046 eV and VDE to 0.058 eV. There were two other anions, $Cy1^-$ and $Cy2^-$, with positive VDE (0.009 eV for $Cy1^-$ and 0.024 eV for $Cy2^-$), but those anions were adiabatically unstable. These values are in close agreement with the values found by Adamowicz et al.[124] $Cy3^-$ and $Cy4^-$ were both vertically and adiabatically unstable. Ortiz et al. assigned the experimentally observed narrow peak[76] at 0.085 ± 0.0008 eV to the dipole-bound anion of the Cy0 canonical form.

3.3.3. Adenine

The thermodynamic equilibrium of adenine is known to depend very strongly on its environment. In solution, adenine exists as a mixture of canonical N9H, N3H, and N7H tautomers[137,138], while in the gas phase the canonical N9H form strongly dominates. The environmentally-induced shift in the tautomeric equilibrium results from interaction of the dipole moment of adenine with molecules of the solvent and a similar effect can be expected from the interaction of an electron with the adenine molecule. The alteration of the thermodynamic tautomeric equilibrium caused by electron attachment to adenine isomers was studied by Adamowicz et al.[101] The most stable neutral tautomer identified at the MP2//6-31++G**//UHF/6-31++G** level was, as expected, the canonical N9H form with a moderately sized dipole moment of 2.5 D (see Fig. 4). The second most stable N7H form was estimated to be higher in energy by

≈0.1 eV, but it possesses a rather large dipole moment (7.02 D). The electron affinities were determined at the MP2//6-31++G**X//UHF/6-31++G**X level, where X was the additional set of three diffuse *sp* functions. For the N7H tautomer, both the VEA (≈0.1 eV) and AEA (0.12 eV) were calculated, while for the N9H form only the VEA (very small, probably positive) was obtained. The energy gap between these two tautomers decreased upon electron attachment, the situation being somewhat similar to adenine in polar solvents, where the two forms N7H and N9H also coexist.

The configurational topology of the dipole-bound anions of adenine$\cdots(H_2O)_N$ clusters for N = 1, 2, 3 was examined by Adamowicz and Jalbout[139]. The electron affinities were evaluated at the MP2/6-31++G**(5d)X//UHF/6-31++G**(5d)X level of theory, where the additional basis functions X consisted of six diffuse Gaussian *sp* shells centred on the hydrogen atom closest to the positive direction of the dipole moment vector of the complex. Of the three adenine$\cdots H_2O$ complexes, only one was found to form a dipole-bound anion with a small adiabatic electron affinity of 13 meV. The number of possible structures for the adenine$\cdots(H_2O)_2$ system is much higher; ten different complexes were investigated. Five configurations possessed sufficient dipole moments to form dipole-bound anions with positive AEA. Furthermore, one configuration that had no neutral counterpart was found to be stabilised by the excess electron attachment. The adenine$\cdots(H_2O)_3$ complex had a dipole moment of 3.75 D, which was large enough to form a dipole-bound state. The binding of the excess electron was reduced by the size of the system; the AEA calculated for the system was only 3 meV. Adamowicz and Jalbout related their results to the experimental observation by Desfrancois et al.[77], who found that the presence of two molecules of water was sufficient to observe a stable valence anion, concluding that (adenine$\cdots H_2O)^-$ was probably the only stable dipole-bound anion of hydrated adenine which could be formed in the gas phase. For the complexes with two and three water molecules, the dipole-bound anions were very likely to be intermediate species, which after formation rearranged to form the more stable valence anions.

Similar complexes of adenine$\cdots(CH_3OH)_N$, where N = 1, 2, 3, were studied by Adamowicz and Jalbout[140] as well. The threshold to stabilise a covalent anion equals to three molecules of methanol in this case as was observed by Desfrancois et al.[77] The computational methodology employed was the same as in the case of the adenine$\cdots(H_2O)_N$ clusters[139]. Of the three configurations of the adenine$\cdots CH_3OH$ system, only one was found to form a dipole-bound anion (with AEA = 11.4 eV). Such a configuration did not ex-

ist for the adenine···$(CH_3OH)_2$ complexes, the adenine···$(CH_3OH)_2$ cluster did not form DB anions at low temperatures. Only one configuration was considered for the adenine···$(CH_3OH)_3$ complex and a DB anion with a very small AEA (equal to 1.0 meV) was found. In addition, a covalent anion of the adenine···$(CH_3OH)_3$ complex was also investigated, but the calculations at the MP2/6-311++G** and B3LYP/6-311++G** levels failed, in contrast to the experiment[77], to demonstrate adiabatic stability. The failure was attributed to computational limitations, which did not allow the application of more accurate ab initio techniques.

3.3.4. Guanine

Guanine is the nucleic acid base for which high concentrations of the "rare" non-canonical amino-hydroxy tautomer have been found to occur (together with the canonical amino-hydroxy form) in the gas phase[141–144]. The question whether the two major tautomers form stable anions and whether the thermodynamic equilibrium in the mixture of anions is similar to that for the neutral molecules, was addressed by Adamowicz et al.[145] The calculations were performed at the MP2/6-31+G*X//UHF/3-21+GX level, X denoting the extra three diffuse sp shells. Both tautomers were found to be vertically and adiabatically stable, the adiabatic values being 0.034 and 0.00038 eV for the amino-oxo and amino-hydroxy forms. Although the magnitudes of these affinities were very small, they were significantly different from each other. As a result, the tautomeric equilibrium for the neutral system should have been different than that for the anions.

4. CONCLUSION

Quasi-free excess electrons induced in water by UV radiation influence many important biological processes. The response of nucleic acid to the capture, removal or transfer of an electron plays an important role in such phenomena as radiation damage, DNA strand repair, or electric conductivity of nucleic acids. The initial step of high-energy radiation damage to DNA and RNA is suspected to be the formation of transient charged nucleobase radicals within the strand[78]. Such radical anions participate in chemical reactions leading to alterations in their original structure and to loss of genetic information. In this context the determination of electron affinities of DNA and RNA bases is of great significance.

The negative values of the vertical electron affinities of the valence-bound anions of isolated nucleobases preclude direct attachment of an ex-

cess electron. While the electron attachment process in the gas phase is dominated by dipole binding, in the condensed media the vertical electron affinity of nucleobases is raised and the valence state becomes energetically favoured. A model system of uracil···H_2O can serve as an example here; the valence electron attachment[67,76] is a result of the energy gain that occurs when weaker hydrogen bonds in the complex rupture creating electron-deficient areas where the excess electron can attach and form a stationary state. The energy gain due to electron attachment is sufficient to compensate for the energy loss due to H-bond stretching[129]. Moreover, the effect of the solvent dielectric is to lower the energy of antibonding orbitals[79], which are generally very high, so that the valence binding becomes energetically favoured.

The stabilisation of the valence-bound state by a solvent molecule allows the experimental observation of valence anions for bare nucleobases. If a nucleobase has a positive valence AEA (e.g. thymine or uracil), its conventional anion may be prepared by attaching an electron to the solvated molecule followed by the evaporation of solvent molecules[74]. The AEAs of the conventional anions of thymine and uracil are in ranges close to those of their dipole-bound counterparts[74,80,90,114].

In the gas-phase various tautomers of nucleobases, obtained by considering the different positions of hydrogen around the base, coexist. For cytosine there is an agreement[146] that besides the canonical form, two enol and two imino forms are energetically similar and, therefore, should coexist in the gas phase. Consequently, all relevant tautomers must therefore be considered[86] when interpreting the photoelectron spectra[76]. Furthermore, the stability of the conventional anion of cytosine is less certain, as the sign of electron affinity of its canonical form depends on the chosen level of theory[80,114], and it is unclear whether a covalent anion is bound. On the other hand, the stability of the dipole-bound anion of canonical cytosine has been confirmed with high confidence[76,86].

A similar situation occurs in the case guanine covalent anion. The non-canonical amino-hydroxy tautomer has been found to coexist with the canonical amino-hydroxy form in the gas phase[144]. The lack of experimental information for guanine and the fact that guanine has been shown[90] to be very susceptible to the mixing of its dipole and valence states does not allow us to draw a final conclusion regarding its valence-state stability. The thermodynamic equilibrium of individual tautomers is known to depend very strongly on their environment. The environment induced shift in guanine tautomeric equilibrium results from interaction of the dipole moment of the nucleobase with the molecules of the solvent. A similar effect can be

expected from the dipole-bound interaction of an excess electron with guanine[145], where both tautomers were found to be adiabatically and vertically stable with a large difference between adiabatic electron affinities.

The thermodynamic equilibrium of adenine has also been studied[101]. The bound states of its tautomers have only the dipole-bound character, which is in agreement with experimental findings[54]. Moreover, negative valence electron affinity has been found[114] irrespective of the used functional and basis set; so the adenine covalent anion is not a stable species.

5. FUTURE DEVELOPMENT

Clearly, more theoretical work remains to be done to improve our understanding of nucleobases anions. In most of the previous theoretical studies, the central problem was to establish the nature of the anion species that originate from the neutral DNA and RNA bases. In particular, two interpretations that postulate the existence of valence or dipole binding of electrons to bases, have been proposed. Schermann et al.[74], on the basis of a RET experiment and a DFT computation on uracil, have underlined that both interpretations lead to results that are only marginally different and represent two complementary aspects of reality. According to the employed quantum chemistry methodologies or experimental techniques, valence or dipole binding of the excess electron can be favoured. Valence or dipole-bound anions can be observed according to the design and operation conditions of the anion sources. In parallel, depending on whether very diffuse orbitals are included in the anion basis set or not, whether the neutral molecule geometry is used as a starting point for geometry optimisation or not, and whether the neutral molecule orbitals are used as an initial guess or not, ab initio calculations can predict the existence of dipole-bound or valence-bound anions. Clearly, much progress can be made in computing EAs as differences between anion and neutral total energies[147] to firmly establish the VB, DB, or mixed nature of the observed anions. It is fortunate that with increasing computing power more accurate ab initio calculations (such as CCSD(T)) are becoming accessible for larger systems including purine and pyrimidine bases.

In addition, to obtain reasonable accuracy for small electron affinities, electronic energies have to be calculated with as high precision as possible. This criterion includes sustaining the accuracy in calculating the atomic integrals, tightening the convergence criteria in the SCF and post-SCF calculations, etc. Obviously, the challenge of evaluating accurate electron af-

finities becomes more and more difficult as the size of the molecule or complex grows.

In the late 60s and early 70s, the so-called equations-of-motion (EOM) quantum chemistry methods were developed[148–151]. The EOM methods offer a route to calculating the EA directly as eigenvalues of a set of working equations. The fundamental working equations of any EOM theory are derived by writing the Schrödinger equations for the neutral and anion states of interest and subtracting the two equations as a first step toward obtaining a single equation that yields the EA. That is, the EOM theory produces the energy difference directly as an eigenvalue of the working equation. The same framework can also be used to compute molecular ionization potentials. The wave function of the neutral molecule can be based on the MP expansion[152], multiconfiguration self-consistent field (MC-SCF) form[153], or coupled-cluster wavefunction[154]. Such techniques have already been used successfully for small molecular systems. For example, the coexistence of both VB and DB anions has been experimentally demonstrated for the nitromethane CH_3NO_2 molecule[66,155–158]. Both states were also successfully studied[159] by the Hartree–Fock density functional theory (HFDFT) for the valence state and by the electron attached equation of motion coupled cluster (EA-EOMCC) method for the dipole-bound state. Unfortunately, the EA-EOMCC method is still too computationally expensive to be applied to nucleobases and larger systems, but hopefully it will become feasible for these systems in the near future.

We conclude by stressing that all the reviewed studies represent only the first step towards understanding the relevant biological problems mentioned in the introduction, which will also require treatment of base pairs[90,160–165], stacking, nucleosides[166] and nucleotides, as well as solvation effects.

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, the Centre for Complex Molecular Systems and Biomolecules (grant LN00A032) and by the research project Z4 055 905. We especially want to acknowledge P. Hobza for valuable and helpful comments.

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