Electron Binding to Nucleic Acid Bases

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Abstract

The mechanism of binding of an excess electron to DNA and RNA nucleobases is important for our understanding of the influence of radiation damage on the biological function of nucleic acids. The nature of anions created by the electron attachment to individual nucleic acid bases is discussed in detail. The principles of 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.

Keywords: DNA; RNA; nucleobase; anion; dipole bound; valence bound; ab initio; photoelectron spectroscopy; Rydberg electron transfer; vertical detachment energy; adiabatic electron affinity; vertical electron affinity

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. 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.[1] Radiation damage to DNA can be classified as (a) structural damage leading to a breakage of phosphodiester bonds and subsequent single–strand or double–strand breaks and (b) change in information caused by the chemical modification of individual DNA bases. Both types of damage can be lethal, and both may lead to mutagenic changes causing aging and disease.[1] Radiation triggers[2,3] a release of free electrons and, consequently, single–electron oxidation or reduction initiates a cascade of reactions, the outcomes of which are far reaching.[4,5]

Apart from the physiological importance the electron transport in DNA is also interesting from the technological point of view.[6–8] 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 the electronic device.[9] The use of DNA molecules as wires in molecular electronic circuits[10] offers attractive advantages, which are consequences of its molecular recognition and self-assembly properties.[8]

In 1962, Eley and Spivey proposed[11] that $\pi - \pi$ 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 an efficient transport of electrons.[12–14] 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 about how DNA structure and sequence affects 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 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.

[FIGURE 1 GOES HERE]

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 (see Figure 2), which is discussed in detail below.

[FIGURE 2 GOES HERE]

The transition between a neutral system and a corresponding anion is accompanied by a change in the positions of 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 the 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 given by the negative of the energy change in the reaction:

$$B + e^- \longrightarrow B^- \tag{1}$$

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:

$$\begin{aligned} VEA &= -(E^B_{B^-} - E^B_B) \\ VAE &= -VEA \end{aligned} \tag{2}$$

where E stands for energy, the lower index denotes anion or neutral, while the upper index defines at what geometry the energy is evaluated. If 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 the negative ion resonances do no exist for any chemically significant period of time.

The adiabatic electron affinity AEA is given as:

$$AEA = -(E_{B^-}^{B^-} - E_B^B) \tag{3}$$

If 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:

$$B^- \longrightarrow B + e^- \tag{4}$$

Note, that while the electron affinity is defined as the negative of the energy change in Reaction 4, the detachment energy is defined as the energy change:

$$VDE = E_B^{B^-} - E_{B^-}^{B^-} \tag{5}$$

If 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, VEA and VDE provide lower and upper bounds to AEA (see Figure 2). An exception to this rule is, for example, the ClF_7 molecule,[15] where the addition of an electron significantly changes the geometry and, consequently, VDE (5.57 eV) is lower than 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:[16,17] a valence bound (VB) anion which is also called a covalent or conventional anion, or a dipole bound (DB) anion (see Figure 3).

[FIGURE 3 GOES HERE]

In VB anions the extra electron occupies a valence molecular orbital and is strongly bound, which leads to a 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 intra–molecular structural parameters much less than that of valence bound electron. An overview of the historical development of DB states as well as detailed reviews are given in Refs. 18, 19, and 20. The first treatise on this topic appeared in a seminal paper of Fermi and Teller.[21] An interesting overview of their pioneering work can be found in Ref. 22. The critical dipole moment for binding of an excess electron depends on the moment of inertia of the molecule,[23–25] but, as a rule of thumb, the value of 2.5 D is often adopted.[26,27] 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[28–30] but, up to now, 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 has also been described. Metal surfaces,[31,32] and certain inert–gas clusters (e.g. Xe_n, $n \geq 6$, see Refs. 33–35) possess bound states where the electron binding is dominated by polarisation. Recently, the existence of a so–called dispersion bound anions, where the main

contribution to the electron binding energy comes from dispersion interactions, has been predicted.[36,37] Moreover, external fields add significantly to the variety of anions as well as to the richness of their properties. As an example can serve the so-called magnetically induced anions, existing exclusively due to the presence of external magnetic field.[38]

2 Experimental studies of nucleobases anions

2.1 Experimental methods

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

Two most common experimental methods used for the characterisation of gas phase anions are negative ion photoelectron spectroscopy (PES)[39,40] and Rydberg electron transfer (RET).[29,41] PES is conducted by crossing a mass–selected beam of negative ions, usually generated in 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 being usually 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 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.[42] Another example is uracil, where the DB form is more stable than the VB form. Only DB anion is detected though both forms coexist.[43]

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 transfered 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 certain value of n_{max}.[28] The electron affinity is then derived from an empirical relation:[30]

$$EA = \frac{23}{n_{max}^{2.8}} \tag{6}$$

In contrary 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.[44]

2.2 Uracil, and thymine

Most experimental work has been done on the anions of uracil and thymine (see Table 1 for valence bound adiabatic electron affinities).

[TABLE 1 GOES HERE]

In the first part we focus only on the electron attachment to those two nucleobases, the results for other nucleobases being summarised in the subsequent section.

Experimentally based estimates of VB AEAs of nucleobases were first derived from AEAs of pyrimidine and purine using substitution and replacement rules.[45] Both uracil and thymine anions were predicted to be strongly bound with the estimated values of AEA of 0.75 and 0.65 eV, respectively. Later studies of Wentworth et al.[46,47] used cyclic voltammetry to measure the reversible half wave reduction

potentials of nucleobases in an aprotic solvent (dimethylsulfoxide). 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).[48,49]

The existence of valence bound state of gas phase uracil anion has been observed by Schermann et al. using Rydberg electron transfer spectroscopy.[50] The valence bound anions were prepared by electron attachment to uracil–argon clusters (the presence of argon stabilises the valence state) followed by the evaporation of argon atoms. The RET method is generally not capable to directly provide accurate values of VB electron affinities, but based on the route of anion formation 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.[51] They supported this conclusion by a DFT calculation which provided positive VB AEA equal to 70 meV. Moreover, dipole bound anion was also detected. The issue of the dipole and covalent bound coupling, known e.g. in the case of nitromethane molecule,[42] 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.[52] 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 the value of VB AEA for uracil equal to 0.15 ± 0.12 eV, and for thymine equal to 0.12 ± 0.12 eV, respectively. These estimates and the work of Desfrancois et al.[53] (VB AEAs of uracil and thymine roughly zero) and Sanche et al.[54] (VB AEA of thymine somewhat larger than 0) are the only experimentally based values complementing studies using reduction potentials. However, the values of VB electron affinities obtained in those studies remain far from those obtained by cyclic voltammetry or semiempirical calculations.[46–49] 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,[55] and the estimates based on reduction potentials are generally considered to be unreliable.[56] To the best of our knowledge there are no direct measurements of adiabatic electron affinities of valence anions of nucleobases 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.[57] These types of measurements detect negative ion resonance states, which are formed by temporary (typically 10^{-15} s) capture of an electron by a molecule. Resonance states are energetically unstable with respect to electron autodetachment. Negative vertical electron affinities of conventional valence bound states were reported by Burrow et al.,[58] 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.,[53] who determined electron attachment properties of nucleic acid bases embedded inside clusters of different solvent species (rare gases, water, ammonia, toluene or methanol) as a function of the cluster size. Determination of the cluster size threshold above which valence anions are observed (by means of RET spectroscopy) provides the estimated value of the valence vertical electron affinities of thymine and uracil (-0.30 eV). VEA of thymine (-0.53 eV) and of uracil (-0.24 eV) were also estimated using the enthalpy of formation.[59]

The DB anions of uracil and thymine were experimentally observed for the first time by Bowen et al.[51] (PES) and Schermann et al.[30] (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.,[52] yielding a value of DB AEA of thymine equal to 62 ± 8 meV.

Bowen et al.[43] 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 number 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.[52] The valence form is stabilised by interaction with water, since the excess electron density on the valence bound uracil anion is much higher than that on 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.[43] further performed PES experiments with weaker rare gases solvents observing dipole bound anions in $(\text{uracil}\ldots\text{Ar})^-$ and $(\text{uracil}\ldots\text{Kr})^-$ clusters, and a coexistence of both dipole and valence bound anions in $(\text{uracil}\ldots\text{Xe})^-$ system.

The influence of N–methylation on the dipole bound electron affinities of uracil and thymine has been studied both theoretically,[60,61] and experimentally by RET spectroscopy.[60] The change of molecular size with N–methylation leads to a reduction of the electron affinity. This conclusion can be extended to nucleosides, that 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 negative vertical electron binding energy,[53,58,59] so it cannot be created spontaneously by electron attach-

ment. On the other hand, the adiabatic values are positive[50,52–54] 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.[50]

- The dipole bound state is both vertically and adiabatically stable,[30,43,50–52] 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 neutral molecule, consequently VDE and AEA are very close each to other. Dipole bound electron affinity is reduced by methylation.[60]

- The presence of solvent stabilises the valence bound state. The coexistence of both DB and VB anions has been observed[43] 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 one.[43,52]

2.3 Other nucleobases

Leaving aside the rather unreliable results based on the reduction potentials measurements (see Section 2.2), additional information is available for electron attachment to cytosine, guanine, and adenine. The electron transmission spectroscopy (ETS) measurements provided[58] 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–oxy −0.908 eV). The cluster solvation method combined with RET spectroscopy used by Desfrancois et al.[53] (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[59] to estimate the VEA of adenine (−0.56 eV), cytosine (−0.40 eV), and guanine (−0.79 eV).

Amino–oxo and amino–oxy tautomers of cytosine were studied by Weinkauf et al. in a PES study.[52] 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 dipole bound states of the amino–oxy and amino–oxo forms. The remarkable difference in the intensity between those two bands was explained by the fact that the amino-oxy anion was enhanced during the formation process in the source. Those results were later refined theoretically by Ortiz et al.,[62] 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).

Dipole bound anion of adenine was observed in RET experiments by Schermann et al.,[30] and its adiabatic electron affinity was estimated to be 12 ± 5 meV. There is no direct experimental observation of guanine anion(s) due to a difficulty of obtaining a high enough pressure of this species without isomerization or decomposition.[53]

3 Ab initio calculations of nucleobases 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 calculations of electron affinities is still a matter of controversy, essentially due to 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 the Koopman's theorem. Electron affinity is taken as the negative of the lowest unoccupied Hartree–Fock molecular orbital (LUMO).

$$EA_{KT} = -\varepsilon_{LUMO} \tag{7}$$

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 for ionization potentials that are approximated as the negative of the highest occupied orbital (HOMO), they add up in the case of electron affinities. Note also that orbital relaxation is typically small for dipole bound anions.[19]

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[63,64] and Staley and Strnad,[65] that a finite basis set approach provides reasonable estimates of the positions of resonances if certain basis sets are employed. For example Staley and Strnad[65] used the standard D95V basis set obtaining 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[66] and in reasonable relative valence electron affinities.[56]

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 orbitals basis sets flexible enough to describe both 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, affecting thus the zero point vibrational energy (ZPVE). ZPVE, therefore, plays a decisive role in determining absolute values of adiabatic electron affinities of 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 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.[66]

Theoretical studies of valence EAs, that present a difficult task requiring the inclusion of electron correlation and the use of well-defined basis sets, have provided contradictory results for the nucleobases. In addition to ab initio electronic structure methods, such as Møller–Plesset perturbation theory or coupled cluster, density functional theory (DFT) has become a standard tool for predicting electron affinities over the last several years.[67–70]

The orbital occupied by a DB electron is very diffuse and centred away from the molecule on the positive end of its dipole[71] (see Figure 3). It was long believed that electron correlation effects play a minor role in determining the electron binding energies[72–74] 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.[75] 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 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 Møller–Plesset (MP) perturbation theory or, better, using coupled cluster (CC) methods together with large flexible basis sets. The description of dipole bound state using density functional methods can be problematic since the use of very diffuse electron distributions creates problems of numerical integration in the computation of 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.[71] The diffuse orbitals can be placed on the atom closest at the positive end of the molecular dipole moment,[60] at a certain distance (possibly optimised[76]) from this atom,[77] or the position of the centre carrying the extra functions may be fully optimised. Interestingly, Ortiz et al.[77] obtained reasonable results even without this kind of diffuse functions, using a valence basis set augmented with diffuse functions close to saturation. However, this might not be the most economic 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 the excess electron binding.[78,79] The value of the lowest exponents in the additional s and p set is related to the dipole moment of the neutral system;[78] the lower the dipole moment, the smaller exponents should be used. An even-tempered sequence of diffuse functions is generated according to the following formula:

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

where α_l 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 α_n. A detailed study of the role of the valence and extra diffuse basis sets has been published by Simons et al.[79] The authors suggest to determine 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 should be added), and to use 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 the even tempered diffuse functions are used, the optimal geometric progression parameter was found to be only slightly dependent on the dipole moment of the neutral system.[78] Simons et al. propose,[79] 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 (see, e.g.,[80–82]), varies the values of parameters in the Equation 8 so that the lowest LUMO energy of neutral system is reached.

3.2 Valence bound anions

In direct contrast with experimental results, most early ab initio computations of nucleobases predicted negative valence adiabatic electron affinities[83–88] (see Tables 2, 3, 4, 5, and 6).

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In 2000 Boyd et. al[89] obtained, without any scaling, for the first time positive adiabatic electron affinities for uracil and thymine (see Tables 2 and 3). Those results contradict the theoretical work of Adamowicz et al.,[80,81] 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.[50] Boyd et al. also determined valence vertical electron affinities, all of them being negative, which is in an agreement with experimental findings.[58]

Russo et al.[90] 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

sign correctly. While recent computations with varying basis sets quality confirmed the positive values of AEAs of thymine and uracil, the stability of conventional anions of guanine and cytosine is less certain, as the sign of electron affinity depends on the chosen level of theory. For adenine, negative valence electron affinity was found[90] irrespective on the used functional and basis set, which is in agreement with experimental results.[30] The same conclusions was drawn from DFT calculations made by Schaefer et al.[56] 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[52,53,91] do not allow for any conclusive statements.

To better understand the cause of the diversity in the values of EAs, Sevilla et al.[66] 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 diffuse basis set can result in contamination of the valence bound state with the dipole bound state. The most susceptible to the states mixing is the guanine anion. From this reason authors called the earlier reported values for guanine[56,87,89] in question, as they believed they were neither representative of valence nor dipole bound state. Naturally, the question arises if the mixing of valence and dipole bound character represents the real physical situation, or if it is only an artefact of the employed methodology. Walch[92] 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 to those of Schaefer et al.[56] concluding, 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 now, in contrary to Schaefer's value

of −0.28 eV, slightly positive being very close to the experimental value of 12 ± 5 meV[30] assigned to the adenine dipole bound state. The nature of the anion states was not investigated (e.g. using plot of anion HOMO), and it is possible, that the identified anions are not valence bound but correspond to mixed or even to dipole bound states. Schmidt et al.[93] used the DFT method with the generalised gradient approximation (GGA)[94,95] to the exchange and correlation potential in conjunction with a plane–wave basis and ultrasoft non-norm-conserving pseudopotentials.[96] Doubts can be casted upon the applicability of this approach, as those calculations completely failed to find nearly vanishing or negative EAs.

Covalent anions of two tautomers, amino–oxo and amino–oxy, of cytosine were characterised by Adamowicz et al.[97] 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-oxy anions were predicted to be unstable with respect to adiabatic electron detachment. Another study of valence bound anions of five cytosine tautomers (amino–oxo, trans– and cis–amino–oxy, and trans– and cis–imino–oxo) is due to Ortiz et al.[62] It was found that none of the cytosine tautomers produced an adiabatically stable VB anion, and only valence bound anions of oxo–forms displayed positive VDE values, in accord with results of Adamowicz.[97] Furthermore, the influence of correlation effects beyond the MP2 level was studied for 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[52] of the photoelectron spectrum to the electron detachment from valence bound anions of all three oxo–forms.

The polarizable continuum model (PCM) model was also used[66] to obtain values of EAs for solvated DNA radical anions.[66] 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 possess[98] dipole moments higher than the critical value of 2.5 D (see Figure 4). As a result, those systems can form stable dipole bound anions. The electron binding energy is smallest in adenine, that has only moderate dipole moment close to the critical value.

[FIGURE 4 GOES HERE]

3.3.1 Uracil, thymine

In the early 90s, Adamowicz et al. first predicted the existence of an adiabatically stable dipole bound anion of uracil.[80] 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 C6 atom (see Figure 4). At 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.[81] The AEA for the excess electron attachment was estimated to be 0.088 eV. Another theoretical calculation of AEA of thymine, made again by Adamowicz, was published in 1999.[60] The equilibrium geometry of neutral thymine was determined at the RHF/6–31++G** level. Additional six diffuse sp Gaussian orbitals were placed to hydrogen atom bound to C6 atom (see Figure 4). Optimisation was performed at the UHF/6–31++G**X level, and the total energies of both neutral and anion species were determined

at the MP2/6–31++G**X level. Only the dipole bound anion of thymine with AEA equal to 0.032 eV was found. In the same work, 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 Ref. 61. Thermodynamic instability of the valence bound uracil anion relative to the dipole bound form was disclosed by Ortiz et al.[76] 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. Dipole bound EA of uracil anion of 0.063 eV obtained at the MP4(SDQ)//CCSD/6–31+G**(+4sp) level was also reported by Gutowski et al.[19] The most recent theoretical results obtained at the CCSD(T) level with the aug–cc–pVDZ basis set provided a value of VDE for uracil of 0.073 eV.[99]

Three isomers of uracil...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 a molecular dipole.[82] Only dipole bound anions of uracil...H_2O system were found and these appeared to be less stable with respect to the electron detachment than dipole bound uracil anion.[80] No conventional stable valence anionic states were found with the theoretical procedure used in this work (MP2/6–31+G*X//HF/6–31+G*X). These results are in direct contradiction with photoelectron experiments, in which Bowen et al.[43] an Weinkauf et al.[52] demonstrated the valence bound character of (uracil...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.,[100] where several isomeric structures of the uracil...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. Valence bound VDEs of all anions lied between 0.3 and 0.9 eV, VDE of the most stable anion structure (0.9 eV) coincided with the experimentally observed maximum in the broad spectral feature,[43] and at least four structures had positive AEAs. Valence bound states of four uracil...H_2O isomers were also found and characterised at the B3LYP/6–31++G** level.[101] The calculated values of VDE span the range $0.76 - 0.99$ eV. A valence bound (uracil...$(H_2O)_3)^-$ cluster with a positive VDE of 0.89 eV was found by Adamowicz[102] in calculations similar to those of Ref. 82. However, this cluster was predicted to have a negative adiabatic electron affinity. Apart from the valence anion, the uracil...$(H_2O)_3$ complex was found[102] to be able to form a stable dipole bound anion with very small adiabatic electron affinity equal to 13 meV. Needless to say, authors themselves admit, that "without higher order calculations we still recommend considering our results as the first approximation".[102]

In the study of the interaction of an excess electron with a small cluster of three HF molecules,[103] Gutowski and Adamowicz described a new type of anions with two H bonded HF molecules on one side of the excess electron and one HF on the other side. This anion could coexist under certain experimental conditions in the gas phase with a dipole bound anion of the $(HF)_3$ cluster. Theoretical calculations performed by Adamowicz et al. on uracil...HF and uracil...H_2O systems revealed[104] a similar form of anions 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 the site where the first unit is connected. The excess electron is suspended between the two monomers and it mediates a bonding

between them. Due to a similarity to H–bond, authors called this interaction e–bond.[104] 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). Authors also suggested the possibility that the broad band in the PES spectrum by Bowen[43] corresponds to an AISE state. The calculated value of VDE of 0.24 eV is, however, much smaller than the experimental value of $\approx$ 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.[105] also described systems where a dipole bound electron attached to uracil molecule interacts with rare 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 uracil–uracil,[106] uracil–glycine,[107] uracil–adenine,[108] and thymine–adenine[109] systems.

3.3.2 Cytosine

Ab initio calculations were performed by Adamowicz et al.[97] to determine the stability of covalent and dipole bound anions of two tautomers of cytosine, amino–oxy (two rotamers, 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 denotes the diffuse gaussian sp set centred at the hydrogen atom located closest to the positive end of the molecular dipole (see Figure 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 rotamers of the

amino–oxy cytosine. Those values are considerably smaller than the two experimental values of 85 ± 8 meV and 230 ± 8 meV,[52] but the authors left this issue open relying on more refined calculations and experimental measurements in the future.

The anions of five isomers (amino–oxo Cy0, trans– Cy1 and cis–amino–oxy Cy2, and trans– Cy3 and cis–imino–oxy Cy4) of cytosine were also studied by Ortiz et al.[62] The structures of anions were optimised at the UMP2 level with the 6–311++G** basis augmented with the nearly saturated, diffuse basis set B2.[76] This basis set has already been described in the Section 3.3.1. Only the amino–oxo form produced an adiabatically stable dipole bound anion, with 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 of Adamowicz et al.[97] $Cy3^-$ and $Cy4^-$ were both vertically and adiabatically unstable. Ortiz et al. assigned the experimentally observed narrow peak[52] at 0.085 ± 0.0008 eV to the dipole bound anion of the canonical form Cy0.

3.3.3 Adenine

The thermodynamic equilibrium of adenine is known to very strongly depend on the environment. In solution adenine exists as a mixture of canonical N9H, N3H, and N7H tautomers,[110,111] 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 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.[77] 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 moderate size of dipole moment

of 2.5 D (see Figure 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 is the additional set of three diffuse sp functions. For the N7H tautomer both VEA (≈ 0.1 eV), and AEA (0.12 eV) were calculated, while for the N9H form only VEA (very small, probably positive) was obtained. The energy gap between these two tautomers decreases 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...$(H_2O)_N$ clusters for $N = 1, 2, 3$ was examined by Adamowicz and Jalbout in.[112] 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. From the three adenine...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...$(H_2O)_2$ system is much higher; ten different complexes were investigated. Five configurations possesses sufficient dipole moments and form dipole bound anions with positive AEA. Furthermore, one configuration, that has no neutral counterpart, was found to be stabilised by the excess electron attachment. Adenine...$(H_2O)_3$ complex has dipole moment of 3.75 D which is large enough to form a dipole-bound state. The binding of the excess electron is reduced by the size of the system, the AEA calculated for the system is only 3 meV. Adamowicz and Jalbout related their results with the experimental observation by Desfrancois et al.,[53] who found that the presence of two molecules of water is sufficient to observe a stable valence anion, concluding

that (adenine...H_2O)$^-$ is probably the only stable dipole bound anion of hydrated adenine which can be formed in the gas phase. For the complexes with two and three water molecules, the dipole bound anions are very likely to be intermediate species, which after formation will rearrange to form the more stable valence anions.

Similar complexes of adenine...$(CH_3OH)_N$, where $N = 1, 2, 3$, were studied by Adamowicz and Jalbout[113] 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.[53] The employed computational methodology was similar as in the case of the adenine...$(H_2O)_N$ clusters.[112] From three configurations of the adenine...CH_3OH system, one was found to form a dipole bound anion (with $AEA = 11.4$ eV). There does not exist such a configuration for the adenine...$(CH_3OH)_2$ complexes, the adenine...$(CH_3OH)_2$ cluster does 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,[53] to demonstrate the adiabatic stability. The failure was attributed to computational limitations, that did not allow for 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–oxy tautomer have been found to occur (together with the canonical amino–oxy form) in the gas phase.[114–117] The question whether the two major tautomers form stable anions, and if the thermodynamic equilibrium in the mixture of anions is similar to the equilibrium for the neutral molecules, was addressed by Adamowicz et al.[118] 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–oxy forms. Although the magnitudes of these affinities are very small, they are significantly different from each other. As a result, the tautomeric equilibrium for the neutral system should be different than that for the anions.

4 Summary

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 nucleobases radicals within the strand.[54] 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 a great significance.

The negative values of vertical electron affinities of valence bound anions of isolated nucleobases preclude direct attachment of an excess electrons. The electron attachment process in gas phase is dominated by the dipole binding. On the contrary, 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[43,52] is a result of the energy gain occurring 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 the H–bond stretching.[102] Moreover, the effect of the solvent dielectric is to lower the energies of antibonding orbitals,[55] 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 of bare nucleobases. If a nucleobase has a positive valence AEA (e.g. thymine or uracil), its conventional anion may be prepared by an electron attachment to the solvated molecule followed by an evaporation of solvent molecules.[50] AEAs of conventional anions of thymine and uracil are in ranges close to those of their dipole bound counterparts.[50,56,66,90]

In the gas–phase various tautomers of nucleobases, obtained when considering different positions of hydrogen around the base, coexist. For cytosine, there is an agreement[119] 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[62] when interpreting the photoelectron spectra.[52] 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,[56,90] and it is unclear if a covalent anion is bound. The stability of the dipole bound anion of canonical cytosine has, on the other hand, been confirmed with high confidence.[52,62]

Similar situation occurs in the case of covalent anion of guanine. The non–canonical amino–oxy tautomer have been found to coexist with the canonical amino–oxy form in the gas phase.[117] The lack of experimental information for guanine and the fact, that guanine has been shown[66] to be very susceptible to the dipole and valence states mixing, does not allow to draw a final conclusion regarding the valence state stability. The thermodynamic equilibrium of individual tautomers is known to very strongly depend on the environment. The environmental induced shift in

the tautomeric equilibrium results from interaction of the dipole moment of the nucleobase with the molecules of solvent. A similar effect can be expected from the dipole bound interaction of an excess electron with guanine,[118] 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.[77] Bound states of tautomers have only the dipole bound character, which is in agreement with experimental findings.[30] Moreover, negative valence electron affinity has been found[90] irrespective on the used functional and basis set, so the adenine covalent anion is not a stable species.

5 Future development

Apparently, 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 electron to bases, have been proposed. Schermann et al.,[50] on the basis of a RET experiment and a DFT computation on uracil, have underlined that both the interpretations lead to results that are only marginally different and represent two complementary aspects of the 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 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 EA as differences between anion and neutral total energies[120] to firmly establish the VB, DB or mixed nature of the observed anions. It is fortunate that with the 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 affinities 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.[121–124] 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 Møller–Plesset expansion,[125] multi-configuration self–consistent field (MC–SCF) form,[126] or coupled-cluster wavefunction.[127] Such techniques have already been successfully used 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.[42,128–131] Both states were also successfully studied[132] 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, 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 toward the understanding of the relevant biological problems mentioned in the introduction, which will also require treatment of base pairs, stacking, nucleosides and nucleotides, as well as extended solvation effects.

Acknowledgement

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

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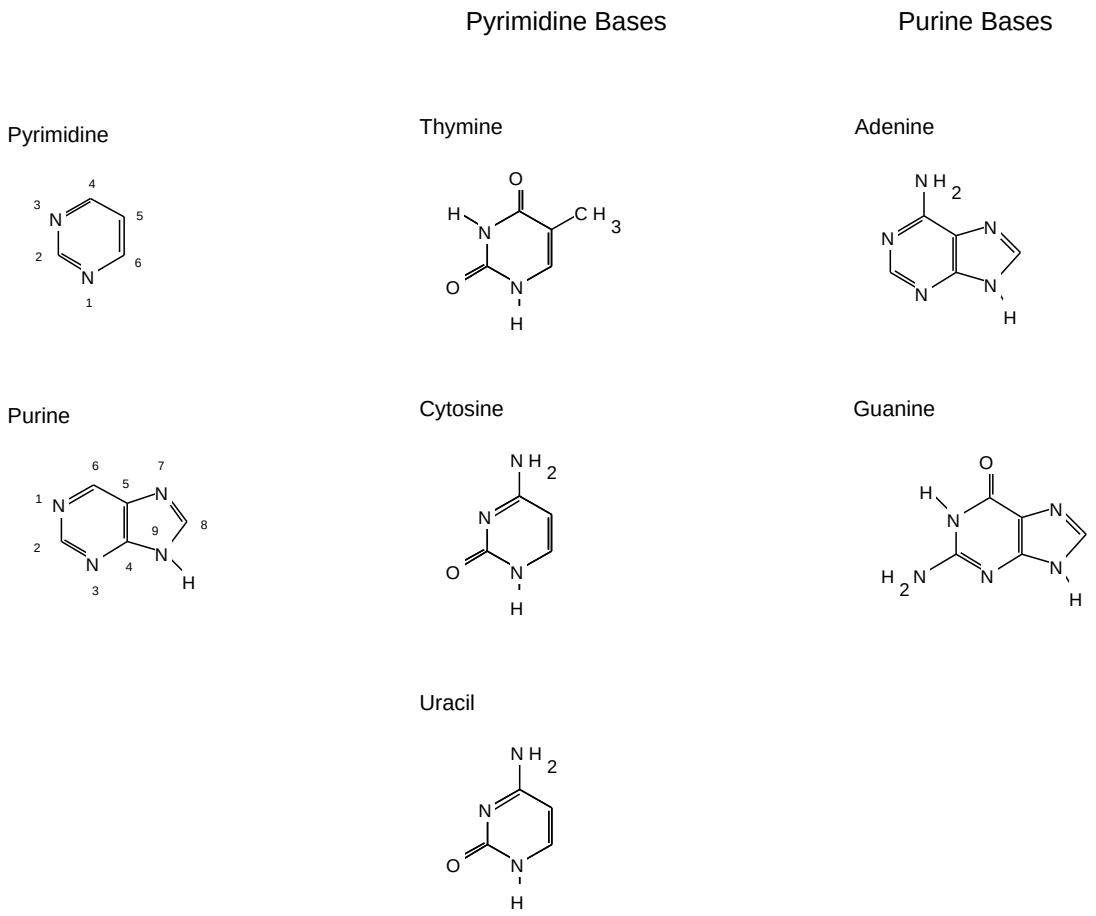

Figure 1: Chemical structures and atomic labels for purine and pyrimidine nucleic acid bases: thymine (T), cytosine (C), adenine (A), guanine (G) in DNA and uracil (U), cytosine (C), adenine (A), guanine (G) in RNA. Sugar (deoxyribose in DNA and ribose in RNA) is bonded to the nitrogen atom number 1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

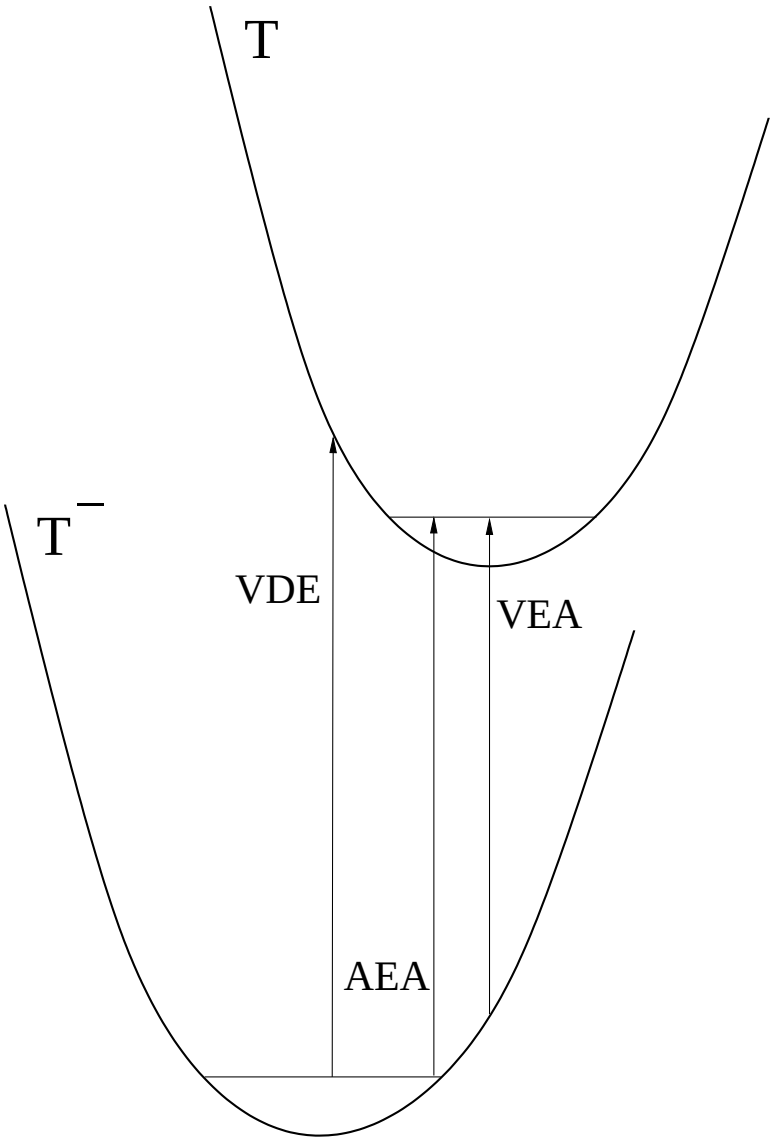

Figure 2: Definition of the energetic quantities for molecular anions. The horizontal axis corresponds to an intermolecular coordinate. Vertical electron affinity VEA is the negative of vertical attachment energy VAE. VDE and VEA represent the upper and lower bounds to AEA, respectively. If VEA is positive, the molecule is able to spontaneously attract the electron. If AEA is positive the anion is stable with respect to the electron autodetachment. VDE is always positive for stable anions.

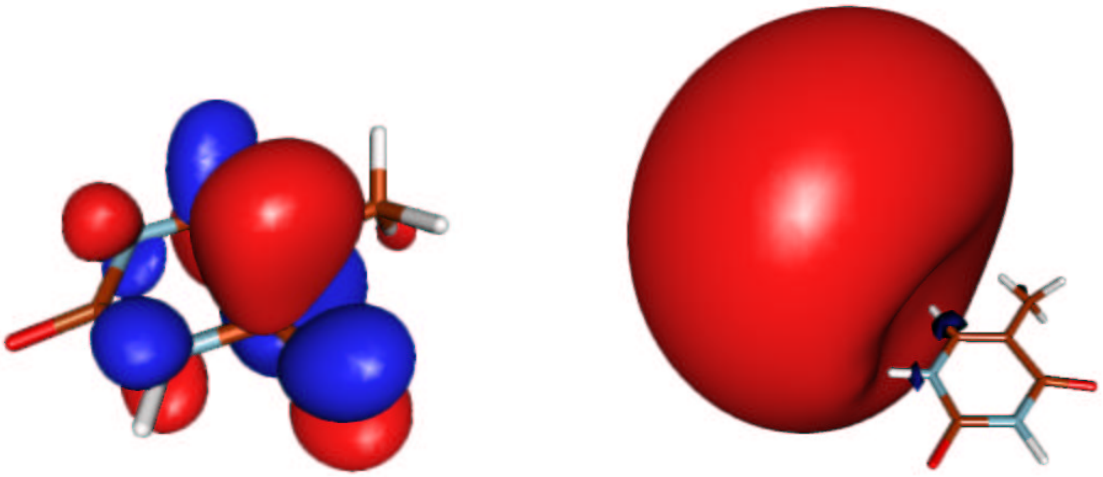

Figure 3: Highest occupied molecular orbitals in valence bound and dipole bound anions of thymine. Dipole bound orbital plotted with the 0.005 contour surface, valence bound orbital plotted with the 0.02 contour surface.

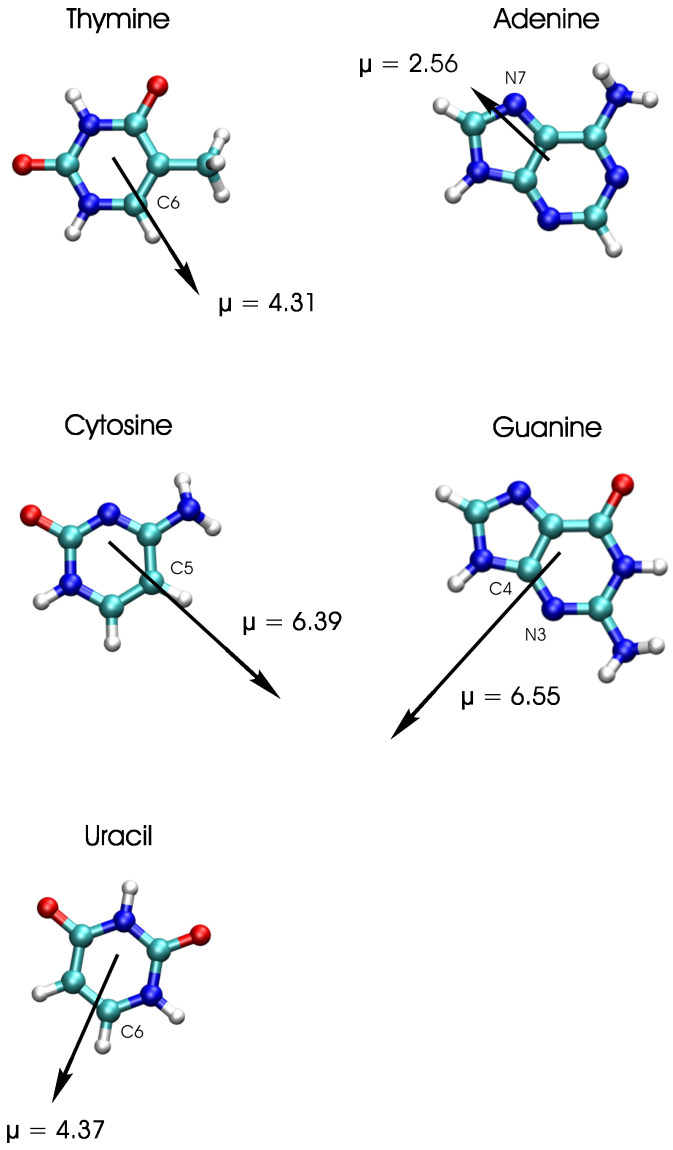

Figure 4: Magnitudes and vectors of dipole moments μ (in D) of nucleic acid bases calculated at the MP2/aug–cc–pVDZ level. Oxygens are red, nitrogens dark blue, carbons light blue, and hydrogens white. Adopted from Ref. 98.

Reference	Uracil	Thymine
Wentworth et al.[45]	0.75	0.65
Wentworth et al.[46,47]	0.80	0.79
Weinkauf et al.[52]	0.15 ± 0.12	0.12 ± 0.12
Schermann et al.[50]	$> 30 - 60$ and < 93	–
Desfrancois et al.[53]	≈ 0	≈ 0
Sanche et al.[54]	–	> 0

Table 1: Experimental valence bound adiabatic electron affinities of thymine and uracil reported in literature (in eV).

Reference	Method	Vertical	Adiabatic
Sevilla et al.[83]	scaled Koopman/D95V	−0.19	0.4
Sevilla et al.[83]	scaled MP2/6–31+G(d)//MP2/6-31G*	–	−0.25
Burrow et al.[58]	not given/6–31G*//not given/3–21G	−0.216	–
Boyd et al.[86]	B3LYP/6–311G(2df,p)//B3LYP/6–31G(d,p)	–	−0.4
Boyd et al.[89]	B3LYP/6–311+G(2df,p)//B3LYP/6–31+G(d,p)	−0.26	0.18
Russo et al.[90]	B3LYP/6–311++G//B3LYP/6–311++G**	−0.11	0.215
Schaefer et al.[56]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.19
Wiest at al.[133]	B3LYP/6–31+G*//B3LYP/6–31+G*	−0.35	0.18
Sevilla et al.[66]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	−0.32	0.20

Table 2: 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.[83]	scaled Koopman/D95V	−0.32	0.3
Sevilla et al.[83]	scaled MP2/6-31+G(d)//MP2/6-31G*	–	−0.30
Burrow et al.[58]	not given/6-31G*//not given/3-21G	−0.364	–
Boyd et al.[86]	B3LYP/6-311G(2df,p)//B3LYP/6-31G(d,p)	–	−0.64
Boyd et al.[89]	B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p)	−0.30	0.14
Russo et al.[90]	B3LYP/6-311++G//B3LYP/6-311++G**	−0.34	0.179
Schaefer et al.[56]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.16
Sevilla et al.[66]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	−0.28	0.22
Walch[92]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	–	0.34

Table 3: Theoretically computed valence electron affinities of canonical thymine reported in literature (in eV).

Reference	Method	Vertical	Adiabatic
Sevilla et al.[83]	scaled Koopman/D95V	−0.4	0.2
Sevilla et al.[83]	scaled MP2/6–31+G(d)//MP2/6–31G*	–	−0.46
Eriksson et al.[85]	B3LYP/6–311G(2df,p)//B3LYP/6–31G(d,p)	–	−0.6
Adamowicz et al.[97]	MP4/6–31++G**(6d)//UMP2/6–31++G**(6d)	–	−0.51
Russo et al.[90]	B3LYP/6–311++G//B3LYP/6–311++G**	−0.31	0.006
Ortiz et al.[62]	UMP2/6–311++G(2df, 2p)//UMP2/6–31++G**	–	−0.38
Schaefer et al.[56]	B3LYP/TZ2P++//B3LYP/DZP++	–	−0.02
Sevilla et al.[66]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	−0.63	−0.05
Walch[92]	B3LYP/6–31++G(Ryd)//B3LYP/6–31++G(Ryd)	–	0.20
Schmidt et al.[93]	DFT-GGA	0.84	0.84

Table 4: Theoretically computed valence electron affinities of canonical cytosine reported in literature (in eV).

Reference	Method	Vertical	Adiabatic
Sevilla et al.[83]	scaled Koopman/D95V	−1.23	−0.7
Sevilla et al.[83]	scaled MP2/6–31+G(d)//MP2/6–31G*	–	−0.75
Boyd et al.[87]	B3LYP/6–311G(2df,p)//B3LYP/6–31G(d,p)	–	−0.69
Russo et al.[90]	B3LYP/6–311++G//B3LYP/6–311++G**	−0.08	−0.004
Schaefer et al.[56]	B3LYP/TZ2P++//B3LYP/DZP++	–	0.07
Sevilla et al.[66]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	−1.25	−0.75
Walch[92]	B3LYP/6–31++G(Ryd)//B3LYP/6–31++G(Ryd)	–	0.25
Schmidt et al.[93]	DFT–GGA	0.84	0.85

Table 5: Theoretically computed valence electron affinities of canonical guanine reported in literature (in eV).

Reference	Method	Vertical	Adiabatic
Sevilla et al.[83]	scaled Koopman/D95V	−0.74	−0.3
Sevilla et al.[83]	scaled MP2/6–31+G(d)//MP2/6–31G*	–	−1.19
Boyd et al.[88]	B3LYP/6–311G(2df,p)//B3LYP/6–31G(d,p)	–	−0.9
Russo et al.[90]	B3LYP/6–311++G//B3LYP/6–311++G**	−0.34	−0.264
Schaefer et al.[56]	B3LYP/TZ2P++//B3LYP/DZP++	–	−0.17
Sevilla et al.[66]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	−0.80	−0.35
Walch[92]	B3LYP/6–31++G(Ryd)//B3LYP/6–31++G(Ryd)	–	0.08
Schmidt et al.[93]	DFT–GGA	0.74	0.79

Table 6: Theoretically computed valence electron affinities of canonical adenine reported in literature (in eV).