

# Ab Initio Electronic Structure of Thymine Anions

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*Dedicated to Prof. Vladimir Bondybey on the occasion of his 65th birthday.*

Dipole-bound and valence-bound anions of thymine were characterised by means of state-of-the-art ab initio calculations. The dipole-bound anion of thymine is both vertically and adiabatically stable with adiabatic electron affinity of 51 meV. The valence-bound anion is also adiabatically stable, albeit less than the dipole-bound anion. Its adiabatic electron affinity is only 30 meV, however, its vertical stability of 553 meV is higher than that of the dipole-bound anion. All these values agree well with experimental findings.

**Keywords:** thymine, anion, dipole-bound, valence-bound, vertical detachment energy, adia-

## 1 Introduction

The attachment of an excess electron to a polar molecule can produce two different types of anions [1, 2]: a valence-bound (VB) anion (also called covalent or conventional anion), or a dipole-bound (DB) anion. In VB anions the extra electron occupying a valence molecular orbital is strongly bound. This leads to a considerable alteration of the molecular structure of the neutral precursor. DB electrons are weakly bound to polar molecules primarily due to electrostatic charge-dipole interactions [3–5] and dispersion interactions between the loosely bound electron and the neutral molecule [6–9]. Therefore, a dipole-bound attachment affects the intramolecular structural parameters less than a valence-bound one. The existence of a DB anions has been predicted for the first time in the seminal paper of Fermi and Teller [10]. An interesting analysis of their work can be found in Ref. [11]. The critical dipole moment for binding an excess electron depends on the molecular moment of inertia [12–14], but, as a rule of thumb, a value of 2.5 D is usually used [15, 16].

Electron attachment to a molecule is described by properties such as vertical detachment energy (VDE), adiabatic electron affinity (AEA), or vertical electron affinity (VEA) (see Figure 1). Generally, the geometry of a neutral system changes upon electron attachment. If there is no time for the neutral molecule to adjust its geometry, the transition is called vertical. If the molecule is allowed to relax, the transition is called adiabatic. If the VEA is positive, the molecule acts as a trap for an excess electron, the attachment of the electron is energetically advantageous, and the anion can be created spontaneously. Positive AEA means that once the

electron is trapped “inside” the molecule, it does not undergo autodetachment. If the VDE is positive, the anion is stable with respect to vertical electron autodetachment. The VDE and the VEA represent the upper and lower bounds to the AEA, respectively. VDE, AEA, and VEA of DB anions are very close each to other due to very small difference in geometry of anion and its neutral precursor, which is generally not true for VB anions.

A detailed knowledge of an excess electron binding mechanism to nucleobases is essential for understanding the influence of radiation damage on biological function of the nucleic acids [17]. Moreover, the current interest in charge transfer in DNA is not restricted to its role in biology, since the advent of molecular electronics has stimulated interest in the possibility to exploit this molecule in functional mesoscopic electronic devices [18]. A key structural feature, which makes DNA a promising candidate for applications in nanometer-scale electronics, is the array of  $\pi$ -stacked base pairs [19,20]. To elucidate the mechanism of electron transfer the determination of the charge distribution in DNA is essential, and nucleic acid bases anions (both dipole-bound and valence-bound) have been the subject of many experimental and theoretical studies [21–27].

The existence of nucleic acid base dipole-bound anions was first predicted theoretically for uracil by Adamowicz et al. [25] and subsequently confirmed experimentally by photoelectron spectroscopy (PES) [23] and Rydberg electron transfer spectroscopy (RET) [22]. Similar calculations for thymine yielded [28] the AEA of 88 meV. In 1999 Adamowicz published [29] a new study of thymine DB anion, where the thymine AEA was estimated to be equal to 32 meV. These values correlate with the RET experimental results of Schermann et al. [22] (AEA =  $68 \pm 20$  meV) and PES studies of Bowen et al. [23] (AEA =  $69 \pm 7$  meV) and Weinkauff et al [30] (AEA =  $62 \pm 8$  meV). The influence of N-methylation on the dipole-bound electron affinities of uracil and thymine has also been studied both theoretically [29,31] and experimen-

tally by RET spectroscopy [29]. The change of molecular size with N-methylation leads to a reduction of the electron affinity; the EA of uracil was reduced from  $75 \pm 20$  meV to  $40 \pm 10$  meV [29] by methylating both N1 and N3 hydrogens.

Negative valence-bound VEAs, corresponding to the temporary negative ion resonance states, obtained by electron transmission spectroscopy experiments [32] indicate that dipole-bound electron attachment to isolated nucleic acid bases is preferred over the valence-bound one. An observation of uracil anion dipole-to-valence-bound state transformation due to solvation effects was reported by Bowen et al. [24]. In a series of negative-ion photoelectron spectroscopic experiments, uracil anions were microsolvated with argon, krypton, xenon, and varying number of water molecules, and the evidence for the dipole-to-valence-bound state transformation was looked for. Dipole-bound anions in the  $(\text{uracil} \dots \text{Ar})^-$  and the  $(\text{uracil} \dots \text{Kr})^-$  clusters, as well as a coexistence of both dipole-bound and valence-bound anions in the  $(\text{uracil} \dots \text{Xe})^-$  system, was observed. Interestingly, just a single molecule of water was found to be sufficient for the dipole-to-valence-bound transition. This conclusion was verified by another PES experiment reported by Weinkauff et al. [30].

The adiabatically stable valence-bound uracil anions were observed by Schermann et al. using Rydberg electron transfer spectroscopy [33]. 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. Generally, the RET method is not able to provide very accurate values of VB electron affinities directly, however, 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 [23]. Their conclusion was supported by a DFT (B3LYP/6-311G++(2d)) calculation providing a positive

VB AEA equal to 70 meV. Although their value does not include zero-point vibrational energy (ZPVE) correction, the authors note a significant nuclear rearrangement of the anion relative to the neutral. The valence-bound anion formation was also observed for thymine [34]. This is the only direct experimental observation of stable valence-bound anions of non-solvated uracil or thymine found in literature.

Apart from Schermann's observation of VB anion of isolated uracil [33] and a brief remark concerning thymine anion [34], thymine VB AEA was evaluated indirectly based on different experimental approaches. Weinkauff et al. [30] took the 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 thymine equal to  $0.12 \pm 0.12$  eV. Studying a stepwise solvation of DNA bases, Desfrancois et al. [34] observed the threshold number of solvent species which can stabilise the negative ions, and using a semi-empirical intermolecular potential they estimated AEAs to be approximately equal to zero. However, as authors themselves admit, their method leads to electron affinities that are intermediate between adiabatic and vertical values. Theoretical electron affinities calculations still present a difficult task [35], basically due to very small energy values involved. Computed valence electron affinities of canonical thymine reported in literature so far are summarised in Table 1. The first positive VB AEA of thymine was calculated by Sevilla et al. [36] from scaled Koopman's values. Most other VB AEAs estimates are based on the DFT theory [26, 27, 37–40].

## 2 Computational Methods

Absolute energies, equilibrium structures, harmonic vibrational frequencies, and zero-point energies were determined for the neutral and anion forms of the canonical DNA base thymine (see Figure 2). All calculations for DB anions and projected MP2 and CCSD(T) calculations for VB anions were performed using the Gaussian03 code [41]. The RI-MP2 optimisation was carried out using Turbomole 5.6 [42] and some of the CCSD(T) calculations were done using the Molpro 2002.6 program suite [43]. Analytic gradient techniques were utilised to obtain optimum geometry structures. The frozen core approximation was used for correlated calculations throughout the work. VEA, AEA and VDE were calculated from the supramolecular approach using the following relationships:

$$\text{VEA} = E_{\text{T}}^{\text{T}} - E_{\text{T}^-}^{\text{T}} \quad (1)$$

$$\text{AEA} = E_{\text{T}}^{\text{T}} - E_{\text{T}^-}^{\text{T}^-} \quad (2)$$

$$\text{VDE} = E_{\text{T}^-}^{\text{T}^-} - E_{\text{T}^-}^{\text{T}^-} \quad (3)$$

where E stands for energy, the subscript denotes thymine anion or neutral, while the superscript defines at what geometry the energy is evaluated. Since very small energy differences must be determined, it is essential to maintain high precision at each computational step. In Gaussian, large integration grid was used for the computation of two-electron integrals

(“Int=(NoXCCTest,UltraFine)” keyword), and the convergence problems in SCF procedure were avoided using the “SCF=(NoVarAcc, Tight)” keyword.

## 2.1 Dipole Bound Anion

The high value of the dipole moment of thymine ( $\mu > 4.0$  D (see Table 2)) suggests the existence of a stable dipole-bound anion [28]. To describe a dipole-bound electron, the core valence basis set must be augmented with a set of diffuse functions with very small exponents. At least  $S$  and  $P$  functions are needed to describe the non-spherical character of the orbital occupied by the excess electron. An even-tempered sequence of close-to-saturation diffuse functions was generated according to the following formula [9, 44]:

$$\alpha_n = \alpha_1 q^{n-1}, \quad n = 1, \dots \quad (4)$$

where  $\alpha_1$  is the value of the lowest exponent,  $q$  is the geometry progression parameter, and  $n$  is the length of the sequence (i.e., the number of additional  $SP$  sets). The extra diffuse functions share the same exponents. A detailed study of the valence and extra-diffuse basis sets influence on the dipole-bound electron binding energies has been published by Gutowski et al. [9] and by Simons et al. [44]. In our work we follow their procedure for determining the diffuse set: the SCF orbitals of the neutral molecule with the diffuse set present are calculated and the atomic orbital coefficients of the virtual orbital (occupied by the excess electron in the anion) are then monitored. The most diffuse  $SP$  functions coefficients should not be dominant for this molecular orbital. The largest exponent in the supplemental diffuse set should be smaller by at

least a factor of two than the most diffuse exponent in the valence basis set in order to avoid linear dependencies in the final basis set. The value of the progression parameter  $q$  depends on the size of the dipole moment of the neutral molecule. For molecules with dipole moments in the 3.0 – 4.5 D range  $q$  adopts values between 3.0 and 5.0 [9, 44].

The orbital occupied by a DB electron (see Figure 3) is centered outside the molecule towards the positive end of its dipole [45]. Electron correlation effects significantly change the properties of DB anions [6, 9, 44], therefore, state-of-the-art electron correlation treatment should be employed. Moreover, as the values of electron affinities are obtained by subtracting the energies of anion and neutral, the use of size-extensive methods, such as Møller-Plesset (MP) or coupled cluster, is imperative. In our dipole-bound anion calculations we employed the spin unrestricted MP2 and CCSD(T) methods with an aug-cc-pVDZ basis set [46] augmented by different diffuse  $SP$ -sets. To avoid convergence problems in anion calculations, the HF/aug-cc-pVDZ orbitals of neutral were used as a starting orbital guess.

## 2.2 Valence Bound Anion

The presence of a single unpaired electron dictates that the wave function should be a pure doublet having the expectation value of  $\langle S^2 \rangle$  equal to 0.75. Using the unrestricted HF reference for MP2 calculations (termed UMP2) leads to a non-negligible amount of spin contamination ( $\langle S^2 \rangle \approx 0.80$ ) making the energies somewhat unreliable. To address this problem, two methods can be used: either restricted open-shell MP2 method (ROMP2), or spin-projected MP2 method (PMP2). Different ROMP2 methods giving different energies exist, because the canonical MOs used in the perturbation expansion are not unique [47], and there is no firm theoretical ground



for choosing one over the other. Therefore, we used the PMP2 method, that reduced the spin contamination very close to zero. Finally, the coupled cluster method is substantially better in reducing spin contamination relative to UMP2 [48], and unrestricted CCSD(T) was used in our calculations.

To find the optimum valence-bound anion geometry is technically complicated. Anion optimisation at the UMP2/aug-cc-pVDZ level typically ends up in the planar geometry corresponding to the DB-VB state mixture. In our calculations, the correct, non-planar VB anion geometry was obtained by the following approach: i) the dihedrals of the planar neutral molecule geometry were perturbed by small randomly chosen values ii) this geometry was used as a starting point for the UMP2/6-31G optimisation iii) and the optimised geometry from the previous step was used as a starting geometry for RI-MP2/aug-cc-pVTZ optimisation. In this way the geometry remains non-planar (see Figure 4) and corresponds to the VB anion.

To achieve high accuracy in VB AEAs, Dunning’s augmented correlation consistent basis sets of double and triple zeta quality [46] were utilised and complete basis set (CBS) M2P energies were estimated using the extrapolation scheme developed by Helgaker et al. [49–51]. In this two-point procedure, total HF [51–53] energy and MP2 [49, 50] correlation contribution are extrapolated using the following formulas:

$$E_X^{HF} = E_\infty^{HF} + Be^{-\alpha X} \quad (5)$$

$$E_X^{corr} = E_\infty^{corr} + AX^{-3} \quad (6)$$

where  $X$  is the splitting number of the valence basis set,  $E_\infty$  is the complete basis set limit,  $\alpha$  is equal to 1.43 for extrapolation from double to triple basis set [51], and constants  $A$  and  $B$  are evaluated from known  $E_X$  energies (where  $X = 2$  and  $3$  in our case). Evaluating Equations 5 and 6 for two unknowns  $E_\infty$  and  $A$  or  $B$ , respectively, yields

$$E_\infty^{HF} = E_{aug-cc-pVDZ}^{HF} - (E_{aug-cc-pVDZ}^{HF} - E_{aug-cc-pVTZ}^{HF})/0.760691 \quad (7)$$

$$E_\infty^{MP2} = E_{aug-cc-pVDZ}^{MP2} - (E_{aug-cc-pVDZ}^{MP2} - E_{aug-cc-pVTZ}^{MP2})/0.703704 \quad (8)$$

The applicability of the MP2 method with large basis sets of double, triple and higher zeta quality to DNA bases and their complexes is limited due to computational demands. The approximate resolution of identity MP2 (RI-MP2) method [54–56] offers a very attractive and efficient alternative [57–59] and was employed in our calculations. The results for thymine VB anion obtained with the RI-MP2 method differ only marginally (AEA changes by  $\approx 1$  meV) from those evaluated with the exact MP2 method, while computational time savings are as large as one order of magnitude.

Assuming the difference between CCSD(T) and MP2 energies ( $E^{CCSD(T)} - E^{MP2}$ ) exhibits only a small basis set dependence [60, 61], the CBS CCSD(T) energy can be approximated as

$$E_\infty^{CCSD(T)} = E_\infty^{MP2} + (E_{SBS}^{CCSD(T)} - E_{SBS}^{MP2}) \quad (9)$$

where  $SBS$  is a small basis set at which CCSD(T) energy is not prohibitively expensive to

calculate. We used the 6-31+G\* basis for this purpose. The CBS extrapolation and CCSD(T) correction were calculated for MP2/aug-cc-pVTZ geometry.

The excess electron in the VB state causes a significant change in the molecular geometry affecting the zero point vibrational energy. It is well known, that the calculated frequencies generally overestimate fundamental frequencies, due to the incomplete treatment of electron correlation, neglect of vibrational anharmonicity, and basis set truncation effects. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies [62,63] and zero-point vibrational energies [62,64,65] are sometimes scaled by a factor between 0.9 and 1.0 . Since there is no systematic way how to scale both frequencies of neutral molecules and their corresponding anions [66,67], and since scaling in the above margins results in very small (less than 5 meV) changes in electron binding energies, we employed unscaled zero point energies.

## 3 Results and Discussion

### 3.1 Dipole Bound Anion

In this work we started with refining the results of Adamowicz et al. which are based on UHF geometries [28,29]. We used the UMP2/aug-cc-pVDZ method for geometry optimisation and UCCSD(T)/aug-cc-pVDZ method for single point calculations. Moreover, we systematically studied the influence of the choice of the progression parameter  $q$  (see Table 3) and of the sequence length  $n$  of the extra diffuse  $SP$  set (see Tables 4 and 5), the influence of the presence of  $D$  functions in this set (see Table 6), the influence of the position of additional diffuse

functions (see Table 7), and the influence of zero point vibrational energy correction.

VDE, AEA and VEA were calculated for sequence length up to 5 functions and progression parameter ranging from 3.0 to 5.0 (see Table 3). The optimal diffuse basis set composition is 5 *SP* functions with a progression parameter  $q = 3.5$  [9, 44, 68], but the energies are rather insensitive within reasonable margins, to exact values of the diffuse basis set parameters. The difference between VDE, AEA, and VEA is very small, which is a clear indication of only a slight geometry change of DB anion with respect to its neutral precursor (see Figure 4). From the same reason, zero-point vibrational energy correction does not significantly change the calculated AEA; AEA changes from 33.49 meV to 35.21 meV upon the inclusion of ZPVE correction.

The influence of higher angular momentum diffuse functions (*D* functions) on the excess electron binding is relatively unimportant (see Table 6). AEA increases only by about 2% after four *D* functions were added.

The extent to which the *SP* sets can be truncated was also tested. *SP* set with progression parameter  $q = 3.5$  can be trimmed to a four-term sequence without a significant loss of accuracy in electron affinities (see Table 4). The *SP* set with a progression parameter  $q = 5.0$  can be truncated even more up to a three-term sequence (see Table 5). The highest coefficient of the most diffuse *SP* set slightly dominates the  $q = 5.0$  three-term sequence, and we suggest to always closely inspect cases, where the LCAO coefficients of the diffuse functions are roughly of the same magnitude. A smaller *SP* diffuse set is an advantage from the point of view of numerical stability and efficiency.

The dependence of AEA on the position of the extra diffuse set was also explored. The diffuse

set was always placed close to the positive end of the molecular dipole, either on a hydrogen atom H15, or on a carbon atom C6, or on a ghost atom that was located 1Å away from the H15 hydrogen (see Table 7). The position of the ghost atom was kept either fixed, or optimised along the molecular dipole moment axis. The fact that electron affinity does not significantly depend on the diffuse basis set position is an additional evidence of the *SP* set saturation.

Our best estimate of thymine DB anion AEA, calculated at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level, is 51.40 meV. Inclusion of CCSD(T) correlation correction leads to 53% increase of the calculated electron affinity with respect to the MP2 result; this conclusion is consistent with the observation made by Gutowski et al. [6] and by Gutsev and Bartlett [69]. Our estimated AEA value agrees reasonably well with the experimental AEA of Bowen et al. [23], Weinkauff et al. [30], and Schermann et al. [22] (see Table 8).

### 3.2 Valence Bound Anion

Most of the theoretical estimates of thymine valence AEA are based on the DFT method (see Table 1), since other ab initio methods failed so far [37, 70] to predict a stable VB anion. Unfortunately, DFT suffers from the self-interaction error (SIE), due to the inexact nature of the exchange-correlation and, consequently, an incomplete cancellation of the electron-electron self-repulsion terms. In spite of this problem it has been shown that DFT can be applied for qualitative predictions of electron affinities [71–73]. This issue has been discussed in a great detail by Schaefer et al. [74]. The SIE significantly reduces the accuracy of DFT, and the average absolute error in electron affinities for B3LYP calculations can be as large as 300 meV [74]. The best theoretical estimates from DFT theory have been shown to be reliable in

terms of relative order of different nucleic acid bases valence electron affinities [26, 27], but no definite conclusions should be drawn about their absolute values.

Computed zero-point vibrational frequencies are summarized in Table 9. We stress the necessity of including ZPVE correction and CBS extrapolation for obtaining reliable electron binding energies. After including the ZPVE and higher order CCSD(T) correlation corrections to the MP2 CBS limit, the adiabatic electron affinity reached 30.15 meV, which is our best estimate of thymine VB AEA. This result is consistent with the experimental detection of a stable valence bound anion of uracil [33]. In this study, Schermann et al. concluded that the valence AEA must lie in the range of 30 – 90 meV. Moreover, the AEA of thymine is supposed to be somewhat lower than that of uracil [22, 23, 29, 31].

As of the reliability of the CBS limit and CCSD(T) correction approach for the VB anion of thymine, we can, based on the studies of CBS interaction energies [75], reaction enthalpies [76] and dipole moments [75], only roughly estimate the error bars to be  $\pm 30$  meV. Despite this error bounds we can conclude, that a stable (albeit weakly bound) VB anion of thymine with positive AEA is very likely to exist. This conclusion is further supported by the large positive CBS value of VDE equal to 553 meV, and by the puckered geometry of this anion, which is very different from the planar geometry of the neutral molecule, and which does not become planar when the basis set is increased from aug-cc-pVDZ to aug-cc-pVTZ, or even aug-cc-pVQZ.

## 4 Summary

In the present work, the gas phase electron binding energies of both dipole-bound and valence-bound anions of thymine were calculated. The main findings can be summarised as follows:

1. Thymine dipole-bound anion is both vertically and adiabatically stable and the calculated adiabatic electron affinity of 51 meV is close to the experimental values [22, 23, 30] (see also Table 8).
2. The valence-bound anion of thymine lies higher in energy than the dipole-bound one, and it is adiabatically stable by only 30 meV. The valence-bound anion formation of thymine [34] and uracil [33] were observed experimentally, and the valence AEA of uracil was estimated to lie in the range  $AEA = 30 - 90$  meV [33]. Experiments also suggest that thymine electron affinity is somewhat lower than that of uracil [22, 23, 29]. Our valence AEA value is consistent with these experimental observations and significantly smaller than previous DFT estimates.
3. The computational procedure for dipole-bound anions is discussed extensively in the literature [9, 44]; additional steps are required for the calculation of the thymine VB anion. The low values of the valence-bound AEA require the use of highly accurate ab-initio methods. Both anion and neutral molecule energies were calculated as follows:
  - (a) the initial estimate of the VB anion geometry was obtained by the MP2/6-31G optimization,
  - (b) the geometry of the VB anion was obtained from the initial estimate by the RI-MP2/aug-cc-pVTZ optimization,

- (c) using the aug-cc-pVTZ geometry, both the PMP2 aug-cc-pVDZ and aug-cc-pVTZ energies were calculated,
- (d) the complete basis set (CBS) limit MP2 energy was obtained for both HF energy and MP2 correlation contribution [49–51], and
- (e) the CBS energy was corrected by the non-scaled zero point vibrational energy (ZPVE) calculated at the MP2/aug-cc-pVDZ level
- (f) the CCSD(T) correction [60, 61], obtained by subtracting CCSD(T)/6-31+G\* and MP2/6-31+G\* energies calculated at the aug-cc-pVTZ geometry, was added to the CBS limit of the MP2 energy.

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## References

- [1] J. Simons and K. Jordan, *Chemical Reviews*, 1987, **87**(3), 535.
- [2] J. Simons, *Encyclopedia of mass spectrometry: Vol. 5. Theory and Ion Chemistry 2. Theory (energies and potential energy surfaces)*., 2002, **5**, 55.
- [3] C. Desfrancois, H. AbdoulCarime, and J. Schermann, *International Journal of Modern Physics B*, 1996, **10**(12), 1339.
- [4] M. Gutowski and P. Skurski, *Recent Research Developments in Physical Chemistry*, 1999, **3**, 245.
- [5] K. Jordan and F. Wang, *Annual Review of Physical Chemistry*, 2003, **54**, 367.
- [6] M. Gutowski, P. Skurski, A. Boldyrev, J. Simons, and K. Jordan, *Physical Review A*, 1996, **54**(3), 1906.
- [7] M. Gutowski and P. Skurski, *Journal of Physical Chemistry B*, 1997, **101**(45), 9143.
- [8] M. Gutowski, P. Skurski, K. Jordan, and J. Simons, *International Journal of Quantum Chemistry*, 1997, **64**(2), 183.
- [9] M. Gutowski, K. Jordan, and P. Skurski, *Journal of Physical Chemistry A*, 1998, **102**(15), 2624.
- [10] E. Fermi and E. Teller, *Physical Review*, 1947, **72**, 406.
- [11] J. E. Turner, *American Journal of Physics*, 1977, **45**, 758.
- [12] O. H. Crawford, *Chemical Physics Letters*, 1968, **2**, 461.

- [13] W. R. Garrett, *Chemical Physics Letters*, 1970, **5**, 393.
- [14] W. R. Garrett, *Physical Review A*, 1971, **3**, 961.
- [15] H. O. Crawford, *Proceedings of The Royal Society: London*, 1967, **91**, 279.
- [16] H. O. Crawford and A. Dalgarno, *Chemical Physics Letters*, 1967, **1**, 23.
- [17] S. Loft and H. Poulsen, *Journal of Molecular Medicine-JMM*, 1996, **74**(6), 297.
- [18] Y. Ito and E. Fukusaki, *Journal of Molecular Catalysis B-Enzymatic*, 2004, **28**(4-6), 155.
- [19] D. M. Eley and D. I. Spivey, *Transactions of The Faraday Society*, 1962, **58**, 411.
- [20] N. Robertson and C. McGowan, *Chemical Society Reviews*, 2003, **32**(2), 96.
- [21] D. Svozil, P. Jungwirth, and Z. Havlas, *Collection of Czechoslovak Chemical Communications*, 2004, **69**(7), 1395.
- [22] C. Desfrancois, H. AbdoulCarime, and J. Schermann, *Journal of Chemical Physics*, 1996, **104**(19), 7792.
- [23] J. Hendricks, S. Lyapustina, H. deClercq, J. Snodgrass, and K. Bowen, *Journal of Chemical Physics*, 1996, **104**(19), 7788.
- [24] J. Hendricks, S. Lyapustina, H. de Clercq, and K. Bowen, *Journal of Chemical Physics*, 1998, **108**(1), 8.
- [25] N. Oyler and L. Adamowicz, *Journal of Physical Chemistry*, 1993, **97**(42), 11122.
- [26] S. Wesolowski, M. Leininger, P. Pentchev, and H. Schaefer, *Journal of The American Chemical Society*, 2001, **123**(17), 4023.

- [27] X. Li, Z. Cai, and M. Sevilla, *Journal of Physical Chemistry A*, 2002, **106**(40), 9345.
- [28] N. Oyler and L. Adamowicz, *Chemical Physics Letters*, 1994, **219**(3-4), 223.
- [29] C. Desfrancois, H. Abdoul-Carime, S. Carles, V. Periquet, J. Schermann, D. Smith, and L. Adamowicz, *Journal of Chemical Physics*, 1999, **110**(24), 11876.
- [30] J. Schiedt, R. Weinkauff, D. Neumark, and E. Schlag, *Chemical Physics*, 1998, **239**(1-3), 511.
- [31] D. Smith, J. Smets, Y. Elkadi, and L. Adamowicz, *Journal of Physical Chemistry A*, 1997, **101**(43), 8123.
- [32] K. Aflatooni, G. Gallup, and P. Burrow, *Journal of Physical Chemistry A*, 1998, **102**(31), 6205.
- [33] C. Desfrancois, V. Periquet, Y. Bouteiller, and J. Schermann, *Journal of Physical Chemistry A*, 1998, **102**(8), 1274.
- [34] V. Periquet, A. Moreau, S. Carles, J. Schermann, and C. Desfrancois, *Journal of Electron Spectroscopy and Related Phenomena*, 2000, **106**(2-3), 141.
- [35] K. Jordan and P. Burrow, *Chemical Reviews*, 1987, **87**(3), 557.
- [36] M. Sevilla, B. Besler, and A. Colson, *Journal of Physical Chemistry*, 1995, **99**(3), 1060.
- [37] S. Wetmore, R. Boyd, and L. Eriksson, *Chemical Physics Letters*, 2000, **322**(1-2), 129.
- [38] N. Russo, M. Toscano, and A. Grand, *Journal of Computational Chemistry*, 2000, **21**(14), 1243.

- [39] A. Voityuk, M. Michel-Beyerle, and N. Rösch, *Chemical Physics Letters*, 2001, **342**(1-2), 231.
- [40] S. Walch, *Chemical Physics Letters*, 2003, **374**(5-6), 496.
- [41] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, , and J. A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh PA, U.S.A., 2003.
- [42] R. Ahlrichs, M. Bar, M. Haser, H. Horn, and C. Kolmel, *Chemical Physics Letters*, 1989, **162**(3), 165.
- [43] H.-J. Werner, P. J. Knowles, R. Lindh, M. Schütz, et al., Molpro, version 2002.6, a package of ab initio programs, 2003.
- [44] P. Skurski, M. Gutowski, and J. Simons, *International Journal of Quantum Chemistry*, 2000, **80**(4-5), 1024.

- [45] K. D. Jordan and W. Luken, *Journal of Chemical Physics*, 1976, **64**, 2760.
- [46] R. Kendall, T. Dunning, and R. Harrison, *Journal of Chemical Physics*, 1992, **96**(9), 6796.
- [47] P. Kozłowski and E. Davidson, *Journal of Chemical Physics*, 1994, **100**(5), 3672.
- [48] J. Stanton, *Journal of Chemical Physics*, 1994, **101**(1), 371.
- [49] T. Helgaker, W. Klopper, H. Koch, and J. Noga, *Journal of Chemical Physics*, 1997, **106**(23), 9639.
- [50] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, H. Koch, J. Olsen, and A. Wilson, *Chemical Physics Letters*, 1998, **286**(3-4), 243.
- [51] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, and J. Olsen, *Chemical Physics Letters*, 1999, **302**(5-6), 437.
- [52] D. Feller, *Journal Of Chemical Physics*, 1992, **96**(8), 6104.
- [53] D. Feller, *Journal of Chemical Physics*, 1993, **98**(9), 7059.
- [54] M. Feyereisen, G. Fitzgerald, and A. Komornicki, *Chemical Physics Letters*, 1993, **208**(5-6), 359.
- [55] O. Vahtras, J. Almlöf, and M. Feyereisen, *Chemical Physics Letters*, 1993, **213**(5-6), 514.
- [56] D. Bernholdt and R. Harrison, *Chemical Physics Letters*, 1996, **250**(5-6), 477.
- [57] P. Jurecka, P. Nachtigall, and P. Hobza, *Physical Chemistry Chemical Physics*, 2001, **3**(20), 4578.
- [58] F. Weigend, A. Kohn, and C. Hattig, *Journal of Chemical Physics*, 2002, **116**(8), 3175.

- [59] D. Feller, E. Apra, J. Nichols, and D. Bernholdt, *Journal of Chemical Physics*, 1996, **105**(5), 1940.
- [60] H. Koch, B. Fernandez, and O. Christiansen, *JOURNAL OF CHEMICAL PHYSICS*, 1998, **108**(7), 2784.
- [61] P. Jurecka and P. Hobza, *Chemical Physics Letters*, 2002, **365**(1-2), 89.
- [62] A. Scott and L. Radom, *Journal Of Physical Chemistry*, 1996, **100**(41), 16502.
- [63] M. Halls, J. Velkovski, and H. Schlegel, *Theoretical Chemistry Accounts*, 2001, **105**(6), 413.
- [64] R. Grev, C. Janssen, and H. Schaefer, *Journal of Chemical Physics*, 1991, **95**(7), 5128.
- [65] J. Delbene, D. Aue, and I. Shavitt, *Journal of The American Chemical Society*, 1992, **114**(5), 1631.
- [66] A. Brouwer, *Journal of Physical Chemistry A*, 1997, **101**(19), 3626.
- [67] A. El-Azhary, H. Suter, and J. Kubelka, *Journal of Physical Chemistry A*, 1998, **102**(3), 620.
- [68] I. Dabkowska, personal communication, 2004.
- [69] G. Gutsev and R. Bartlett, *Journal of Chemical Physics*, 1996, **105**(19), 8785.
- [70] I. Dabkowska, J. Rak, M. Gutowski, J. Nilles, S. Stokes, D. Radisic, and K. Bowen, *PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 2004, **6**(17), 4351.
- [71] J. Galbraith and H. Schaefer, *Journal of Chemical Physics*, 1996, **105**(2), 862.

- [72] N. Rösch and S. Trickey, *Journal of Chemical Physics*, 1997, **106**(21), 8940.
- [73] G. Tschumper and H. Schaefer, *Journal of Chemical Physics*, 1997, **107**(7), 2529.
- [74] J. Rienstra-Kiracofe, G. Tschumper, H. Schaefer, S. Nandi, and G. Ellison, *Chemical Reviews*, 2002, **102**(1), 231.
- [75] A. Halkier, W. Klopper, T. Helgaker, P. Jorgensen, and P. Taylor, *Journal of Chemical Physics*, 1999, **111**(20), 9157.
- [76] K. Bak, P. Jorgensen, J. Olsen, T. Helgaker, and W. Klopper, *Journal of Chemical Physics*, 2000, **112**(21), 9229.
- [77] L. Clowney, S. Jain, A. Srinivasan, J. Westbrook, W. Olson, and H. Berman, *Journal Of The American Chemical Society*, 1996, **118**(3), 509.
- [78] I. Kulakowska, G. M., and L. B., *Biochimica et Biophysica Acta*, 1974, **361**, 119.

Table 1: Calculated valence adiabatic electron affinities of canonical thymine reported in literature.

Reference	Method	AEA [meV]
Sevilla et al. [36]	scaled Koopman/D95V	300
Boyd et al. [37]	B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d,p)	140
Russo et al. [38]	B3LYP/6-311++G//B3LYP/6-311++G**	179
Schaefer et al. [26]	B3LYP/TZ2P++//B3LYP/DZP++	160
Rösch et al. [39]	AM1//averaged experimental coords [77]	254
Sevilla et al. [27]	B3LYP/D95V+(D)//B3LYP/D95V+(D)	220
Walch [40]	B3LYP/6-31++G(Ryd)//B3LYP/6-31++G(Ryd)	340

Table 2: Dipole moments of the canonical DNA base thymine. Theoretical dipole moments were obtained at the MP2 level of theory.

Basis	Dipole moment [D]
6-31G*	4.11
6-31+G*	4.56
6-31++G**	4.50
aug-cc-pVDZ	4.34
cc-pVTZ	4.11
aug-cc-pVTZ	4.30
experimental value [78]	4.13



Table 3: Influence of progression parameter  $q$  on the vertical detachment energy (VDE), adiabatic electron affinity (AEA), and vertical electron affinity (VEA) of thymine dipole-bound anion. Electron binding energies were calculated at the MP2 level of theory using the aug-cc-pVDZ valence basis set augmented with 5 sets of diffuse  $SP$  functions.

Progression param. $q$	VDE [meV]	AEA [meV]	VEA [meV]
3.0	35.13	33.58	32.11
3.5	35.00	33.49	32.04
4.0	34.84	33.35	31.91
4.5	34.61	33.14	31.72
5.0	34.29	32.84	31.42

Table 4: Influence of additional sets of diffuse functions on the vertical detachment energy (VDE), adiabatic electron affinity (AEA) and vertical electron affinity (VEA) of thymine dipole-bound anion. Electron binding energies were calculated at the MP2 level of theory using aug-cc-pVDZ valence basis set augmented with  $n$  sets of diffuse  $SP$  functions with progression parameter  $q = 3.5$ .

$n$	VDE [meV]	AEA [meV]	VEA [meV]
5	35.0	33.49	32.04
4	35.07	33.50	31.07

Table 5: Influence of additional sets of diffuse functions on the vertical detachment energy (VDE), adiabatic electron affinity (AEA) and vertical electron affinity (VEA) of thymine dipole-bound anion. Electron binding energies were calculated at the MP2 level of theory using aug-cc-pVDZ valence basis set augmented with  $n$  sets of diffuse  $SP$  functions with progression parameter  $q = 5.0$ .

$n$	VDE [meV]	AEA [meV]	VEA [meV]
5	34.28	32.84	31.43
4	34.28	32.84	31.46
3	34.28	32.83	31.45
2	33.14	33.11	31.67

Table 6: Influence of the  $D$  functions in the additional diffuse basis set on the adiabatic electron affinity (AEA) of thymine dipole-bound anion. AEA was calculated at the MP2 level using the aug-cc-pVDZ valence basis set augmented with 5 sets of diffuse  $SP$  functions with progression parameter  $q = 3.5$ . The calculation with 5  $D$  functions failed to converge.

Number of D functions	AEA [meV]
1	34.07
2	34.20
3	34.17
4	34.18

Table 7: Influence of the additional diffuse basis set position on the adiabatic electron affinity (AEA) of thymine dipole-bound anion. AEA was calculated at the MP2 level using the aug-cc-pVDZ valence basis set augmented with 5 sets of diffuse  $SP$  functions with progression parameter  $q = 3.5$ . Bq denotes the ghost atom.

Position	AEA [meV]
H15	33.49
C6	30.69
Bq 1 Å from H15	33.66
Bq optimised	33.66

Table 8: Experimental values of thymine dipole-bound adiabatic electron affinity (AEA). PES stands for photoelectron spectroscopy and RET for Rydberg electron transfer spectroscopy.

Reference	Method	AEA [meV]
Bowen et al. [23]	PES	$69 \pm 7$
Weinkauff et al. [30]	PES	$62 \pm 8$
Schermann et al. [22]	RET	$68 \pm 20$

Table 9: MP2/aug-cc-pVDZ zero-point vibrational energies (ZPVE) of thymine valence-bound anion.

Thymine	ZPVE [eV]
neutral	3.12
anion	3.01

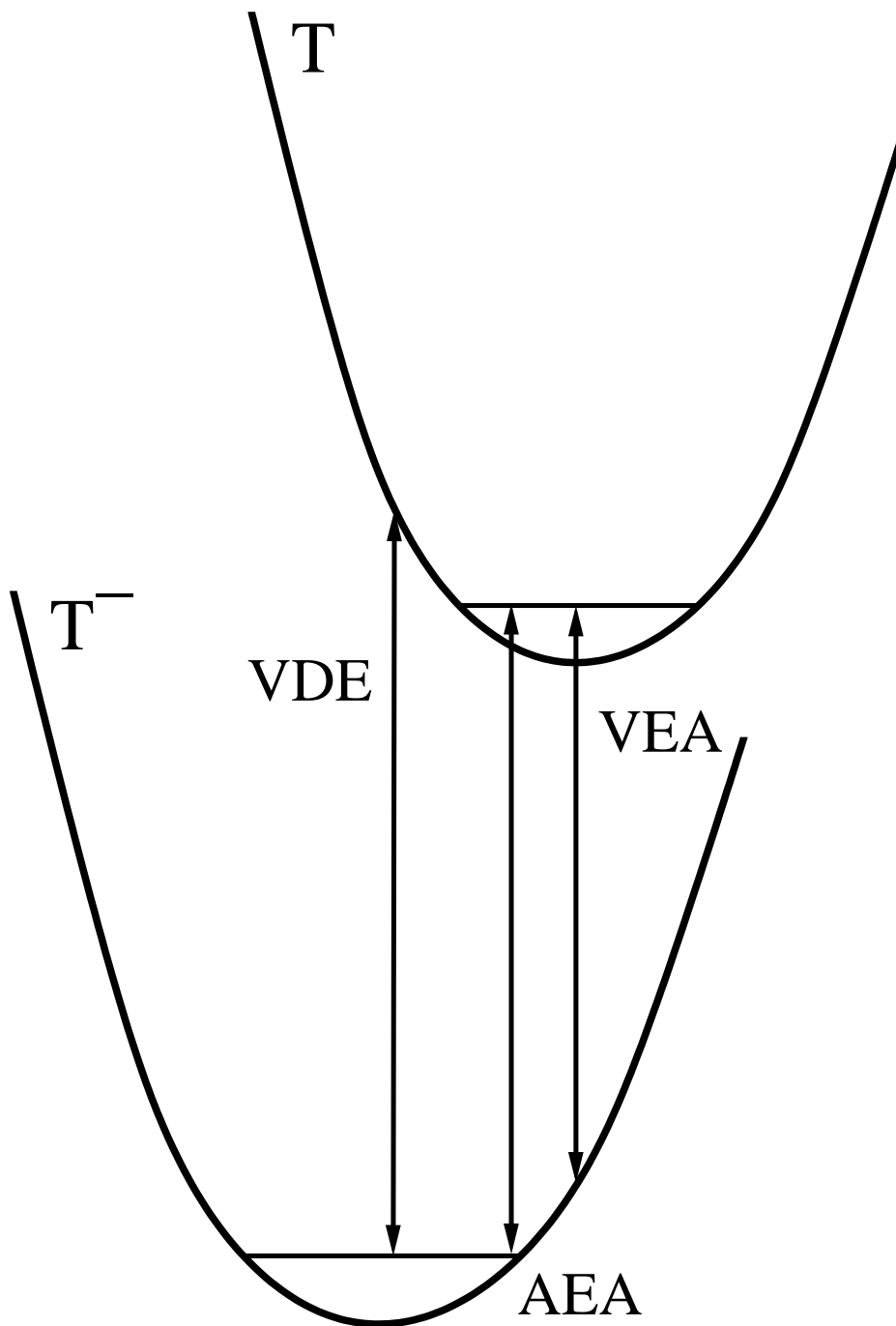


Figure 1: Electron binding energies for molecular anions. The vertical detachment energy (VDE) and the vertical electron affinity (VEA) represent the upper and lower bounds to the adiabatic electron affinity (AEA).

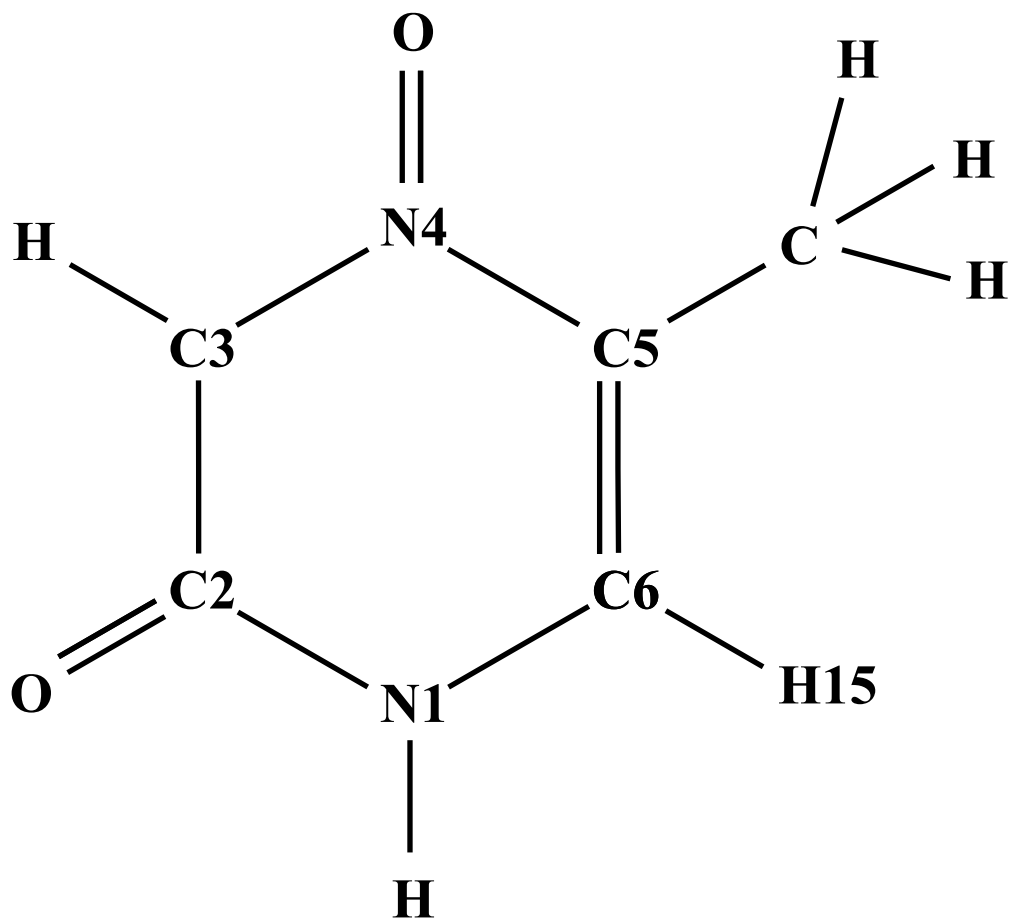
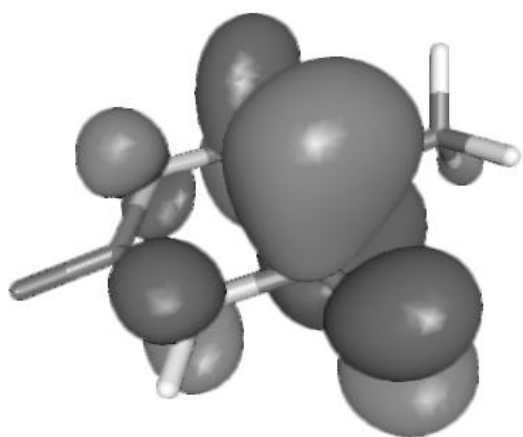
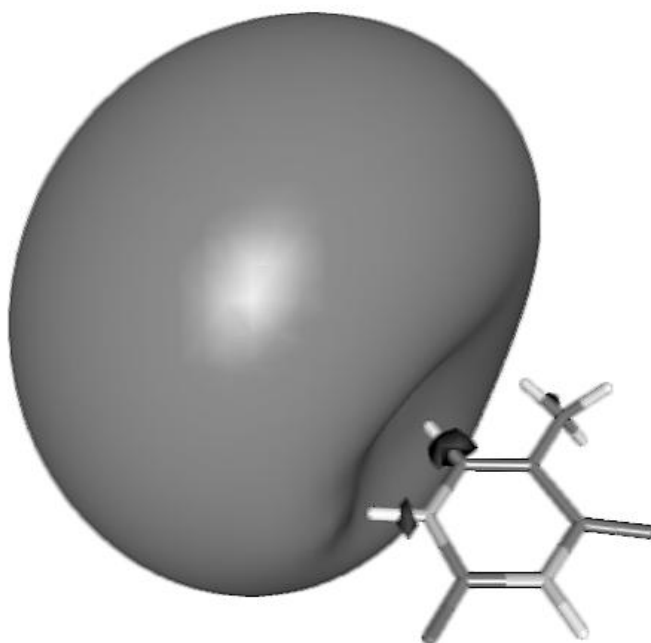


Figure 2: Chemical structure and atom numbering of thymine. The positive end of the molecular dipole moment is close to the hydrogen H15.



valence-bound anion



dipole-bound anion

Figure 3: Highest occupied molecular orbital (HOMO) in thymine valence-bound and dipole-bound anions obtained at the UMP2/aug-cc-pVDZ level. The valence-bound orbital is plotted at the 0.02 isocontour surface, while the dipole-bound orbital is plotted at the 0.005 isocontour value.



Figure 4: UMP2 equilibrium structures of the thymine dipole-bound and valence-bound anions. The deviation from planarity in valence-bound anion is about 16 degrees. Optimised geometry parameters are available from authors upon request.

- Fig. 1** Electron binding energies for molecular anions. The vertical detachment energy (VDE) and the vertical electron affinity (VEA) represent the upper and lower bounds to the adiabatic electron affinity (AEA).
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