In search for an optimal methodology to calculate the valence electron affinities of temporary anions†

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Recently, we have proposed an approach for finding the valence anion ground state, based on the stabilization exerted by a polar solvent; the methodology used standard DFT methods and relatively inexpensive basis sets and yielded correct electron affinity (EA) values by gradually decreasing the dielectric constant of the medium. In order to address the overall performance of the new methodology, to find the best conditions for stabilizing the valence state and to evaluate its scope and limitations, we gathered a pool of 60 molecules, 25 of them bearing the conventional valence state as the ground anion and 35 for which the lowest anion state found holds the extra electron in a diffuse orbital around the molecule (non valence state). The results obtained by testing this representative set suggest a very good performance for most species having an experimental EA less negative than −3.0 eV; the correlation at the B3LYP/6-311+G(2df,p) level being $y = 1.01x + 0.06$, with a correlation index of 0.985. As an alternative, the time dependent DFT (TD-DFT) approach was also tested with both B3LYP and PBE0 functionals. The methodology we proposed shows a comparable or better accuracy with respect to TD-DFT, although the TD-DFT approach with the PBE0 functional is suggested as a suitable estimate for species with the most negative EAs (*ca.* −2.5 to −3.5 eV), for which stabilization strategies can hardly reach the valence state. As an application, a pool of 8 compounds of key biological interest with EAs which remain unknown or unclear were predicted using the new methodology.

Introduction

When a neutral, closed shell substrate suffers a single-electron transfer (SET) reduction, the electron can be received either by a σ^* orbital or by a π^* acceptor in the substrate; in the latter case the reduction generally leads to the formation of a radical anion (RA), an open shell reactive species which controls the reactivity of further chemical processes. Such processes have a remarkable relevance in organic and biological chemistry, ranging from its synthetic interest in the case of nucleophilic substitution reactions by SET[1–3] to the understanding of DNA damage/repair promoted by RAs.[4] The accurate knowledge of energetics of the RA states is the most difficult and crucial key required for the modeling of these reactions.[5,6]

The electron affinity (EA) is defined as the difference in the energies of the RA and its neutral precursor in gas phase. Although a gas phase property by definition, the EA is a key magnitude for understanding the reactivity in polar organic solvents or water, since the modeling of the SET reactions requires knowledge of the actual difference in the energies of the neutral and anionic potential energy surfaces of the isolated systems.[5,7] Moreover, EAs are also required for calculating chemical potential, hardness and electrophilicity;[8] all of them useful quantities for understanding the reactive behavior of these compounds.

EAs can be positive or negative, depending on whether the anion state lies at lower or higher energies than the neutral substrate, respectively.[9,10] Experimental EAs are intrinsically difficult to reproduce, even in the simplest case of stable anion states (positive EAs).[7,11] In the case of negative EAs, the problem is even more complex, since the anionic species is short lived and then unstable with respect to the spontaneous electron detachment to its ground neutral state. For these elusive RAs, called temporary anions,[5,9,10] some authors suggested that standard (bound-electron) DFT methods could fail in predicting their electron affinities.[12] However, most groups concerned with reactivity studies of RAs in organic or biological systems have successfully used standard DFT methods, regardless of the positive or negative EAs of the compounds.[3,11,13–21]

The understanding of SET reaction mechanisms requires the combination of both gas phase and solution theoretical data, as well as different species having either positive or negative EAs. In this context, a suitable computational model should be able to reasonably reproduce the EA of all

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† Electronic supplementary information (ESI) available: Charts with the chemical structures of all compounds under study. Computational details as total energies and zero point energy correction. Supplementary figures of the ΔE *versus* $(1/\varepsilon)$ profiles obtained for the "blank" trial subset and for the "work" subset. Details regarding the extrapolation in different solvents. Details on the calculations with aug-cc-VDZ and aug-cc-VTZ bases and the B3PW91 and B1B95 functionals. Total energies, excitation energies and details concerning the TD-DFT calculations with PBE0 and B3LYP functionals. Details concerning the calculations of compounds in Table 4, and *xyz* coordinates of all compounds. See DOI: 10.1039/b908870a

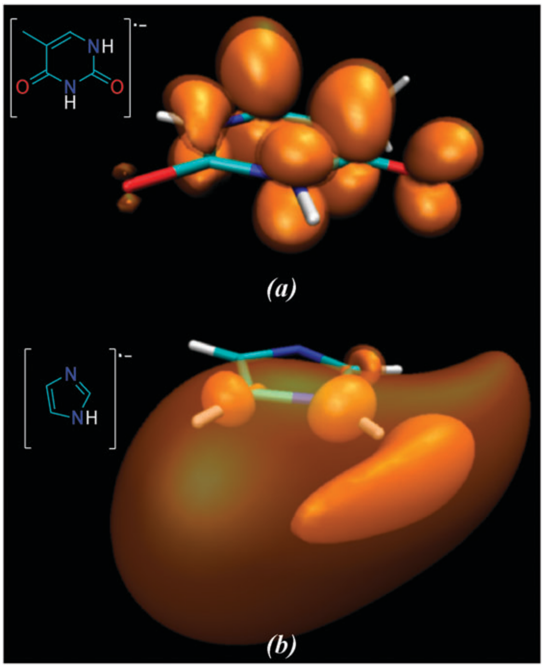

Fig. 1 A typical valence and non-valence RA for thymine (a) and imidazole (b), respectively. Spin density distribution: the solid and faded isosurfaces correspond to isodensity values of 0.0025 and 0.0010 a.u., respectively.

compounds involved in these reactions, preferably using the same or compatible computational techniques.[5]

With this aim, we have distinguished two possible cases for temporary anions: (i) when the calculated state is of valence type (V), as shown in Fig. 1a for thymine, the EA can be reproduced accurately; (ii) when the ground anion state is non-valence (N), *i.e.* with the unpaired electron in a diffuse orbital around the molecule (as shown in Fig. 1b for imidazole), the EA is not comparable to the lowest valence state, generally obtained from electron transmission spectroscopy (ETS),[9] and most importantly, it is not the state of reference when dealing with organic or biological reactions in solution. The more negative the EA is (roughly more negative than -1 eV), the more likely a DFT computation on the RA will yield an N anion.[5,22]

However, and even when the anion state obtained is not a valence one, it has been shown that it is still possible to extend standard DFT formalisms to address the right valence EA by means of different approaches and strategies. Recently, Tozer and de Proft,[23] have proposed a methodology based on standard DFT methods, for obtaining the correct valence EA, based on the application of an external wall potential; previously, they have also developed methodologies for estimating the negative EAs based on a definition of absolute hardness and Koopmans' theorem,[24,25] and, further, using the values of the ionization potential.[24–26] Other authors advocated improving the predictions of EAs and ionization potentials, as well as other properties, by ensuring the proper long-range asymptotic behavior of the functionals,[27] among other efforts.[12] However, we will focus our discussion on obtaining EA by means of the computation of total energies (instead of orbital energies, *i.e.* Koopmans')[28] and to standard methods with regard to the specific problem of negative valence EAs.

Independently, a few months later, we have proposed an approach based on the stabilization exerted by a polar solvent; the methodology yielded correct EA values by gradually decreasing the dielectric constant of the medium and extrapolation to the gas phase.[6] However, the strategy proposed has only been tested with a set of 16 molecules, 8 of them within the most difficult case of non-valence anion states, which is not enough for determining its actual scope and accuracy. In order to address the overall performance of the new methodology, to find the best conditions for stabilizing the valence state and to evaluate its scope and limitations, we here applied the procedure to 44 new species, gathering a wider set of 60 molecules, most of them with the lowest anion state found as N type; all of them with known experimental EAs in the range of $0 \sim -3.5$ eV.[29] As an application example, we will also predict the EA of 8 biological compounds, most of them with EAs which have not (as yet) been measured.

In addition, we also explored the possibility of finding the valence state as one of the excited anion states, by using the time dependent DFT (TD-DFT) approach. Even though TD-DFT is not expected to be as accurate as ground DFT, which is virtually variationally exact (within the exchange correlation formula used), its use is becoming widespread.[30,31] However, to our knowledge, it has not yet been applied to systematically calculating negative EAs. The feasibility of determining very unstable anion states is an open question, and one which is worth addressing, since stabilization by other means seems to be harder to obtain with progressively negative EAs.

Methodology

Direct EA computation

The vertical EAs (VEAs) were first computed as the difference between the electronic energy of the anion and the neutral at the frozen geometry of the latter (eqn (1a)) and the adiabatic electron affinities (AEA, eqn (1b)) were obtained as the corresponding difference in the total energies with full geometry optimization of both species, including the zero point energy (ZPE) corrections.[5,6,7,11,13]

$$\begin{aligned}\mathrm{VEA} = {} & E(\text{optimized neutral}) \\ & - E(\text{anion on the optimized geometry of the neutral})\end{aligned} \tag{1a}$$

$$\begin{aligned}\mathrm{AEA} = {} & E(\text{optimized neutral}) \\ & - E(\text{optimized anion}) + \mathrm{ZPE}(\text{neutral}) - \mathrm{ZPE}(\text{anion}).\end{aligned} \tag{1b}$$

Since, in this work, we are mainly concerned with species which have the most unstable RAs (or most negative EAs), most experimental values are vertical values and, thus, EA will hereafter refer to VEA, unless otherwise indicated.

By simply applying eqn (1), we have shown that the standard B3LYP DFT functional,[34] one of the most widely used, with relatively inexpensive basis sets, reproduces experimental EA values within a few meV of error in the case of V anions. On the other hand, it is not possible to address the valence EA by directly applying eqn (1) when the lowest anion state found is of N type.[5]

EAs obtained by extrapolation

When studying RAs in solution,[3,18,19] we learnt that the charge localization of a given electronic state strongly determines the further stabilization exerted by a polar solvent. Indeed, the procedure outlined in ref. 6 mainly relies upon the fact that N anions are much more delocalized than V ones (see Fig. 1), and thus a polar solvent should exert a much stronger stabilization on the valence anions, which have their charge condensed on the molecule. Thus, due to the effect of an even slightly polar solvent, a V state is expected to experience a stabilization drastic enough to become the ground anion state. This fact will be used in order to overcome the impossibility of calculating EAs by directly using eqn (1).[5,6]

The overall free energy of the process

$$\mathrm{A(sol)} + \mathrm{e}^- \rightarrow \mathrm{A}^{\bullet -}\mathrm{(sol)} \tag{2}$$

can be obtained by desolvating the species, ionizing in the gas phase and re-solvating:

$$\Delta G = -\mathrm{EA} + \Delta\Delta G_{\mathrm{solv}}, \tag{3}$$

where $\Delta\Delta G_{\mathrm{solv}}$ is the difference in the solvation free energies (ΔG_{solv}) of the neutral and anionic species:

$$\Delta\Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{solv}}(\mathrm{anion}) - \Delta G_{\mathrm{solv}}(\mathrm{neutral}). \tag{4}$$

If the solvent is modeled as a polarized continuum, as in Tomasi's self consistent reaction field (SCRF) IEF-PCM[32] used in this work, the solvation energies can be easily separated into their electrostatic (reaction field) and non-electrostatic (cavitation entropic term, dispersion and repulsion van der Waals terms) contributions.[32,33] Thus, by splitting up the solvation energy difference into electrostatic ($\Delta\Delta G_{\mathrm{solv;elect}}$) and non-electrostatic components ($\Delta\Delta G_{\mathrm{solv;non\text{-}elect}}$),

$$\Delta\Delta G_{\mathrm{solv}} = \Delta\Delta G_{\mathrm{solv;non\text{-}elect.}} + \Delta\Delta G_{\mathrm{solv;elect}}, \tag{5}$$

we can define the difference between the neutral and anionic species in solution due to the electrostatic contribution as ΔE:

$$\Delta E = \mathrm{EA} - \Delta\Delta G_{\mathrm{solv;elect}}. \tag{6}$$

Note that we defined ΔE with the opposite sign to the energy change of eqn (2), in order to have the same sign as the electron affinities (ΔE would be "EA in solution", although we prefer to avoid this label, since EA is, by definition, a gas phase magnitude).

For a given species, the electrostatic contribution, $\Delta\Delta G_{\mathrm{solv;elect}}$, will mainly depend on the dielectric constant of the medium, ε, being most negative for larger values of ε [mainly due to the ΔG_{solv}(anion) term]. It has been shown that $\Delta\Delta G_{\mathrm{solv;elect}}$ has a smooth variation with ε, since we are computing the same molecular geometry with M or $M + 1$ electrons (or a very similar structure in the case of adiabatic EA, see below). $\Delta\Delta G_{\mathrm{solv;elect}}$ will vanish as ε approaches 1.[6] Although a rather complex SCRF quantum model has been used in the present calculations, the fact could be easily illustrated by considering the much simpler Poisson–Boltzman result for a classical solute in a spherical cavity immersed in a dielectric continuum:[6,33]

$$\Delta G_{\mathrm{solv;elect}} = -\frac{1}{2}\frac{q^2}{a}\frac{\varepsilon-1}{\varepsilon} - \frac{|\mu|^2}{a^3}\frac{\varepsilon-1}{2\varepsilon+1} - \frac{|\Theta|^2}{a^5}\frac{\varepsilon-1}{3\varepsilon+2} + \cdots, \tag{7}$$

where a is the radius and q, μ, Θ..., correspond to the charge (monopole, dipole, quadrupole, *etc*). The first two terms correspond to the simple Born and Onsager models.[32] All terms of the expansion tend to zero as ε tends to 1, thus $\Delta G_{\mathrm{solv;elect}}$ and $\Delta\Delta G_{\mathrm{solv;elect}}$ also vanish. Owing to its electrostatic nature, $\Delta\Delta G_{\mathrm{solv;elect}}$ will always vanish, regardless of the complexity of the continuum model used to compute the solvation energies.[33]

With this definition, ΔE can be considered as a function of ε. The value $\Delta E(\varepsilon = 1)$ will not be the valence EA when dealing with species for which the lowest anion state found in gas phase is of N type. However, if the valence state has been obtained for a given range of ε values, the valence EA can be obtained by a suitable extrapolative procedure as a limiting value, as shown in ref. 6.

$$\lim_{\varepsilon \to 1} \Delta E(\varepsilon) = \mathrm{EA}. \tag{8}$$

In order to extrapolate eqn (8), $\Delta E(\varepsilon)$ is computed in a set of 15 solvents of decreasing polarity. For convenience, ΔE is plotted against $1/\varepsilon$, which varies from 0.012 (water) to 0.7 (argon),

$$\mathrm{EA} = \lim_{\varepsilon \to 1} \Delta E(1/\varepsilon). \tag{9}$$

EA can be readily obtained from plots of ΔE *vs.* $1/\varepsilon$ using eqn (9).[6]

EAs obtained using TD-DFT

When the V state is not the anion ground state, it could still be found as an excited state using TD-DFT. The energy of the first V state was obtained as the ground energy plus the vertical excitation energy to the corresponding state (vertical energy of the anion in eqn (1a)).

Computational setup

The general setup has already been described in ref. 5 and 6. The main results were obtained at the B3LYP/6-311+G(2df,p) level of theory,[34] as implemented in the Gaussian 03 package,[35] optimization and frequency calculations with the 6-31+G* basis. The results obtained with this basis set for the direct EA and extrapolations are available in the ESI.† The ZPE corrections were calculated for all neutrals and for those anions having known experimental values of the adiabatic electron affinity; the ZPE was included in the adiabatic EAs. The continuum solvation model used was the IEFPCM as implemented in Gaussian 03.[32]

Besides the above procedure applied to all molecules in the set, which allows for comparing the new extrapolated values with those obtained in ref. 5, other functionals, basis sets and solvation models were tested in smaller subsets. Essays were performed in a subset of ten compounds with other hybrid funcionals: B1B95[36] and B3PW91.[37] Correlation-consistent bases aug-cc-VTZ on the geometries obtained with aug-cc-VDZ[38] were tested on a subset of twenty compounds.

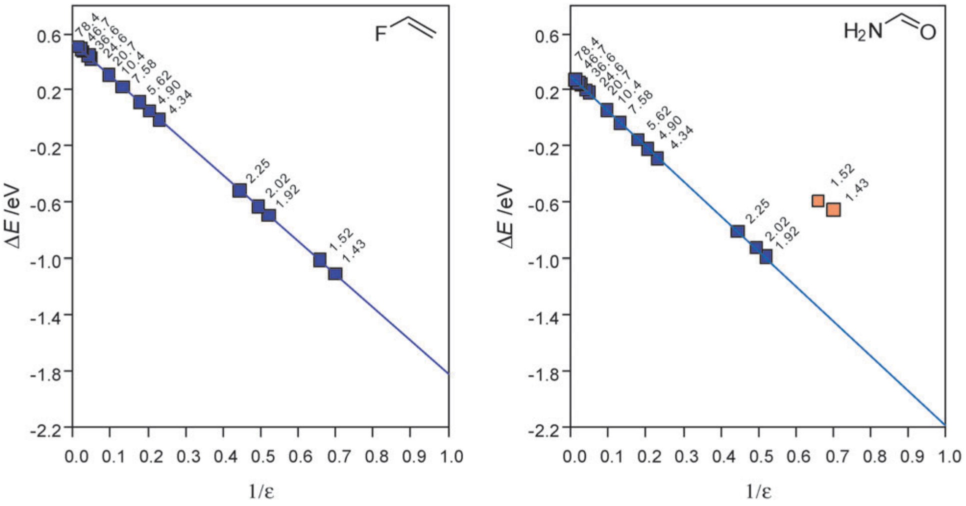

Fig. 2 $\Delta E(1/\varepsilon)$ profile obtained for fluorethylene (a, left) and formamide (b, right). The blue points correspond to the solvents where the ground anion is a V-type RA, whereas the orange ones correspond to N-type RAs; the dielectric constant of each model solvent is indicated on the corresponding point.

In order to evaluate the error introduced by the extrapolation and to judge the best way of obtaining the EA from the ΔE *vs.* $1/\varepsilon$ profiles, three different extrapolation options were tested with the subset of molecules for which the V state was already found in the gas phase. The extrapolations are referred as (i) linear: a linear fit was used, including the ΔE points corresponding to *V* anions; the EA limiting value was obtained by finding the abscissa for the ordinate $1/\varepsilon = 1$ (this is illustrated in Fig. 2 for fluorethylene and formamide, plots for other species and the complete data used for extrapolations of the whole set of species under study are available in the ESI†); (ii) quadratic: a quadratic term is also included, and (iii) rational: a rational function, with the same shape as eqn (7) (all parameters of the second order fit are adjustable, no experimental or calculated multipole included).

The package of solvents used for scanning ε were (ε in parenthesis): water (78.4), dimethylsulfoxide (46.7), acetonitrile (36.6), ethanol (24.5), acetone (20.7), 1,2-dichloroethane (10.4), tetrahydrofuran (7.60), chlorobenzene (5.60), chloroform (4.90), ether (4.33), benzene (2.25), cyclohexane (2.02), heptane (1.92), krypton (1.52) and argon (1.43).

In cases where the ground is not the valence state for the anions studied, TD-DFT calculations were performed by computing 12 excited states and selecting the valence state using both the B3LYP[34] and PBE0[39] functionals. The latter was included since it is expected to yield better excitation energies[30,31] than B3LYP, which is mostly used so far.[5,6,40] All geometries obtained with the B3LYP functional were re-optimized with PBE0, only results with the 6-311+G(2d,p) bases are shown in main text and tables, results with 6-31+G(d) are available in the ESI†. Except for oxazole (**18**), all compounds for which the valence anion state appears as the ground state with B3LYP were also V type with PBE0.

Orbitals, electrostatic potential and spin density visualization and molecular graphics were made using Molden 4.6[41] and VMD 1.8.6,[42] using the cube files of the state of interest obtained with the formchk and cubegen utilities of Gaussian 03 as input.

Results and discussion

Most species having N-type RAs in the gas phase were successfully stabilized by the whole set of solvents, as shown for fluorethylene, represented in Fig. 2a. Even in those cases were the valence state is not stabilized enough in some of the less polar solvents, shown by formamide, as an example, in Fig. 2b, the smooth and almost linear dependence of ΔE with $1/\varepsilon$ allows for extrapolation of the EA as ΔE at $\varepsilon = 1$. This smooth variation is ascribed to the fact that there are no changes on the atomic positions and then on the external potential exerted by the nuclei between the neutral and its anion. Thus, if the key difference is the net charge, the variation on the differences between their solvation energies will be mainly controlled by ε. It is also noted that there is no need to reproduce accurate experimental solvation energies, only the differences between them for a couple of closely related species (anyway, the procedure can be checked at any time against experimental solvation energies, where available). Moreover, when computing adiabatic EAs (anion and neutral have slightly different geometries), the profiles were not sensitively different; also, for these cases, the profiles were smooth enough to allow successful extrapolation (ΔE *vs.* $1/\varepsilon$ profiles for the whole set of molecules are available in the ESI†).

The trial set of 60 molecules was built up by including different heteroatoms in the π systems, including third row elements, open and closed shell species, as well as a few adiabatic EAs (chemical structures of all compounds are available as Chart S1 in the ESI). Since we are mainly interested in those cases where the ground anion appears as a N-type, we searched for species having the most negative EAs, and checked the nature of the calculated ground anion, gathering 35 compounds (including eight tested in ref. 6) with gas phase N anions; as in ref. 6 we called these species the "work" subset. Once a new compound was found to have a V type ground anion, it became part of the control subset, or "blank" subset. Compounds in this "blank" set were

Table 1 Experimental and calculated EA for compounds which have a gas phase valence state ("blank" subset)[a]

Species		Anion type	EA calculated, eqn (1) Uncorrected	EA calculated, eqn (9) Linear	Quadratic	Rational	EA experim.[c]
1	1,1-Dichloroethylene	V	−0.87	−0.91	−0.87	−0.88	−0.75
2	2-Bromo-1-propene	V	−1.12	−1.20	−1.11	−1.13	−1.31
3	3-Bromo-1-propene	V	−0.44	−0.50	−0.43	−0.44	−0.60
4	Adenine	V	−0.74[b]	−0.80	−0.72	−0.74	−0.64
5	Bromoethylene	V	−1.17	−1.22	−1.17	−1.18	−1.17
6	Chloroethylene	V	−1.32[b]	−1.36	−1.31	−1.32	−1.29
7	*cis*-1-Bromo-2-butene	V	−0.46	−0.55	−0.44	−0.46	−0.68
8	*cis*-1,2-Dichloroethylene	V	−1.21[b]	−1.23	−1.20	−1.21	−1.12
9	Cyclobutanone	V	−1.06	−1.16	−1.02	−1.05	−1.00
10	Cyclopentadiene	V	−1.19	−1.22	−1.17	−1.18	−1.19
11	Cyclopropene	V	−1.64	−1.71	−1.63	−1.65	−1.73
12	Cytosine	V	−0.55[b]	−0.57	−0.54	−0.54	−0.36
12a	Cytosine (adiabatic)	V	−0.07[b]	−0.07	−0.06	−0.06	−0.06
13	Ethyl radical (adiabatic)	V	−0.25[b]	−0.34	−0.23	−0.25	−0.26
14	Ethylene	V	−1.71[b]	−1.75	−1.70	−1.71	−1.78
15	Isopropyl radical (adiabatic)	V	−0.30[b]	−0.35	−0.25	−0.28	−0.32
16	Isothiazole	V	−0.77	−0.82	−0.76	−0.77	−0.63
17	Isoxazole	V	−1.16	−1.22	−1.15	−1.17	−1.09
18	Oxazole	V	−1.38	−1.47	−1.38	−1.40	−1.44
19	*t*-Butyl radical (adiabatic)	V	−0.15[b]	−0.26	−0.07	−0.11	−0.16
20	Thiazole	V	−0.90	−0.94	−0.89	−0.90	−0.80
21	Thiophene	V	−1.24	−1.29	−1.22	−1.24	−1.17
22	Thymine	V	−0.30[b]	−0.34	−0.32	−0.32	−0.31
23	*trans*-1-Bromo-2-butene	V	−0.62	−0.65	−0.54	−0.56	−0.68
24	*trans*-1,2-Dichloroethylene	V	−0.98[b]	−1.01	−0.98	−0.98	−0.82
25	Uracil	V	−0.27[b]	−0.27	−0.27	−0.27	−0.21
25a	Uracil (adiabatic)	V	0.17[b]	0.16	0.23	0.22	0.15
Mean absolute deviation			0.08	0.09	0.09	0.08	

[a] B3LYP/6-311+G(2df,p), all energies in eV. [b] From ref. 5. [c] From ref. 29.

calculated using the proposed protocol in order to test if it adds further errors, and to determine the best way of extrapolating eqn (9). These checks are possible since, in these cases, both the experimental and the "conventional" EA (*i.e.* that calculated using eqn (1)) are well known. Results obtained for the blank set (compounds **1–25**) with the standard Pople's basis and B3LYP are summarized in Table 1. In addition to the linear extrapolation, each pool of solvent calculations was extrapolated with a quadratic and with a rational function (see Computational setup). The agreement between extrapolated and experimental results was good and similar for the three extrapolations (colored points and lines in Fig. 3); none of them visibly departs from the results obtained without extrapolation (black circles in Fig. 3). The rational extrapolation yielded a correlation with the experimental values of $y = 0.98x - 0.01$, with some little improvement in the calculated EAs of a few compounds which have profiles with a slight curvature; however, the slopes varied from 0.98 to 1.00 and the intercepts from −0.01 to 0.05, with all correlation indexes around 0.98 for the three extrapolation procedures. Thus, for simplicity (and because it could potentially be faster, since fewer points are required) we continued using the linear extrapolation, which yielded $y = 0.99x + 0.05$, and a correlation index of 0.983. This is not distinguishable from the correlation obtained without extrapolation, (eqn (1)): $y = 1.00x + 0.01$, taking into account the dispersion and the standard errors expected in correlating negative[5,43] EAs (compare the four correlations shown in Fig. 3). As practical considerations, no particular functional form is required for extrapolating eqn (9) and the smoother the shape of the profile, the smaller the number of points (solvent calculations) required in order to have a successful extrapolation.

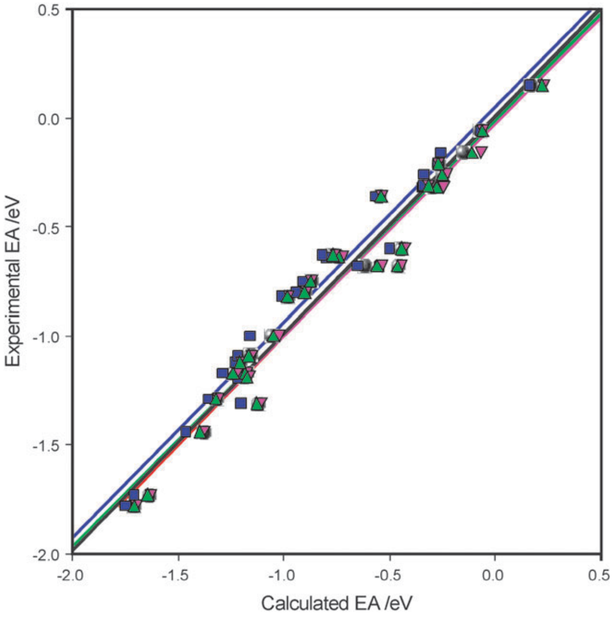

Fig. 3 Experimental *vs.* calculated correlation obtained for the blank set by performing a linear (■), quadratic (▼) and rational (▲) extrapolation of eqn (9). The ideal prediction (—) and values calculated with eqn (1) (●) are also included.

Since eqn (1) is expected to fail in predicting the EAs of the molecules having N anions in the gas phase (those in the work set), these compounds (**26–60**), are our main target. The results obtained for these species are summarized in Table 2 and Fig. 4, together with the uncorrected values. Most compounds in this subset have clearly overestimated EAs (light triangles on Fig. 4) by the conventional evaluation (eqn (1)); after extrapolating eqn (9) a good agreement is obtained between the right anion states and the experimental EAs (compare blue squares and line with the ideal prediction, *i.e.* $y = x$, red line in Fig. 4).

As expected, some of the compounds with very negative EAs were problematic. For some of them, their valence states were not stabilized in the less polar solvents as, for example, acetylene (experimental EA of −2.6 eV, Table 2) and formamide (shown on Fig. 2b), though this fact did not prevent successful extrapolations. In the case of compounds **56–60** (experimental EAs from ∼−2.5 to −3.5 eV), it was not possible to find the V state in most solvents and, in these cases, the procedure failed.

However, despite the problems encountered when approaching −3 eV, and the slightly higher dispersion with respect the compounds in the blank set (correlation index of 0.90, which is not surprising since these values are harder to obtain both experimental and theoretically), the methodology succeeded in predicting most negative EAs. The prediction is clearly unbiased; this meaning the straight has a slight intercept and a slope very close to 1 ($y = 0.96x + 0.06$).

Briefly, a few considerations about the basis set will be given. Previously, it has been checked that when dealing with this kind of anion, the aug-cc-VDZ and aug-cc-VTZ basis showed the trend of giving N type states, yielding, in general, results which were not as good as the corresponding double- and triple-ζ standard Pople's bases 6-31+G* and 6-311+G(2df,p).[5] We tried 20 compounds of the overall set

Table 2 Experimental and calculated EA for compounds which have gas phase non-valence state ("work" subset)[a]

Species	Anion type (gas phase)	EA, calc. (eqn (1)), uncorrected	Deviation	EA, extrapolated. (eqn (9))[b]	Deviation	Anion type after extrapolation	EA, experimental[d]
26 1,4-Cyclohexadiene	N	−1.10	(−0.65)	−1.84	(0.09)	V	−1.75
27 2-Methyl-2-butene	N	−1.12[c]	(−1.12)	−2.11	(−0.13)	V	−2.24
28 Acetic acid	N	−1.02	(−0.78)	−2.11	(0.31)	V	−1.80
29 Acetone	N	−1.05[c]	(−0.46)	−1.46	(−0.05)	V	−1.51
30 Acetylene	N	−1.33	(−1.27)	−2.40	(−0.20)	V	−2.60
31 Allene	N	−1.37	(−0.51)	−1.60	(−0.28)	V	−1.88
32 Butyrolactone	N	−0.96	(−0.97)	−1.93	(0.00)	V	−1.93
33 *Cis*-1-bromo-1-propene	N	−1.01	(−0.48)	−1.88	(0.39)	V	−1.49
34 *Cis*-1,2-difluorethylene	N	−1.14	(−1.04)	−2.02	(−0.16)	V	−2.18
35 *Cis*-2-butene	N	−1.19[c]	(−1.03)	−2.42	(0.20)	V	−2.22
36 Cyclobutene	N	−1.42	(−0.58)	−2.12	(0.12)	V	−2.00
37 Cyclopentene	N	−1.26	(−0.88)	−2.42	(0.28)	V	−2.14
38 di-*tert*-butyl-peroxide	N	−0.99	(−1.01)	−1.80	(−0.20)	V	−2.00
39 Ethylene carbonate	N	−0.88	(−2.05)	−2.85	(−0.08)	V	−2.93
40 Fluorethylene	N	−1.57	(−0.34)	−1.82	(−0.09)	V	−1.91
41 Formamide	N	−1.11	(−0.94)	−2.19	(0.14)	V	−2.05
42 Furan	N	−1.23[c]	(−0.53)	−1.75	(−0.01)	V	−1.76
43 Guanine	N	−0.40[c]	(−1.00)	−1.41	(0.01)	V	−1.40[e]
44 Imidazole	N	−0.90	(−1.23)	−2.15	(0.02)	V	−2.13
45 Methyl vinyl ether	N	−1.25	(−1.05)	−2.30	(0.00)	V	−2.30
46 Propene	N	−1.33[c]	(−0.66)	−1.90	(−0.09)	V	−1.99
47 Propiolactone	N	−1.02	(−0.88)	−1.93	(0.03)	V	−1.90
48 Propyne	N	−1.12	(−1.68)	−2.67	(−0.13)	V	−2.80
49 Pyrrole	N	−0.97[c]	(−1.41)	−2.21	(−0.17)	V	−2.38
50 Tetramethylethylene	N	−1.08	(−1.19)	−2.65	(0.38)	V	−2.27
51 *Trans*-1-bromo-1-propene	N	−0.93	(−0.37)	−1.52	(0.22)	V	−1.30
52 *Trans*-1-chloro-1-propene	N	−1.14	(−0.35)	−1.63	(0.14)	V	−1.49
53 *Trans*-1,2-difluorethylene	N	−1.14	(−0.70)	−1.85	(0.01)	V	−1.84
54 *Trans*-2-butene	N	−1.40[c]	(−0.70)	−2.20	(0.10)	V	−2.10
55 Trifluorethylene	N	−1.17	(−1.23)	−2.15	(−0.25)	V	−2.40
56 2-Butyne	N	−1.15	(−2.28)	Not available		N	−3.43
57 Acetonitrile	N	−0.88	(−1.94)	Not available		N	−2.82
58 Dimethylformamide	N	−2.31	(−0.09)	Not available		N	−2.40
59 Ethyl isocyanate	N	−0.85	(−1.78)	Not available		N	−2.63
60 Tetrafluoroethylene	N	−1.12	(−1.88)	Not available		N	−3.00
Compounds **25–60** (this table)							
Mean deviation			−1.00		0.02		
Mean absolute deviation			1.00		0.14		
Compounds **1–60** (see also Table 1)							
Mean deviation			−0.56		0.04		
Mean absolute deviation			0.60		0.12		

[a] B3LYP/6-311+G(2df,p), all energies in eV. [b] Linear extrapolation. [c] From ref. 6. [d] From ref. 29. [e] Other values in ref. 6 and references cited therein.

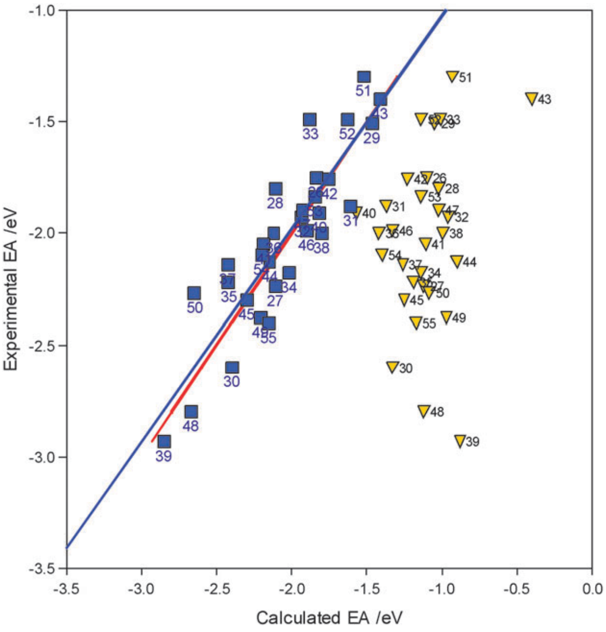

Fig. 4 Experimental *vs.* calculated correlation obtained for the work set by eqn (9) (■) and eqn (1) (▼). Ideal fit ($y = x$, —).

(most of them from the work subset) and compared them with the results summarized in Table 2 and Fig. 4. Some compounds were found as N anions in the gas phase with aug-cc-VTZ whilst they were of V type with 6-311 + G(2df,p). Although in most cases the V anion was successfully obtained by means of eqn (9), yielding a good correlation with experimental results, the fit with the standard Pople's basis was better. The results are summarized in Fig. 5 (details in Table S5 and the whole summary of results in Table S6 in the ESI†). In addition, four compounds: 1,4-cyclohexadiene, imidazole, propiolactone and *trans*-butene, for which good results were obtained with Pople's bases (Table 2), were not sufficiently stabilized to obtain a suitable extrapolation with aug-cc-VTZ.

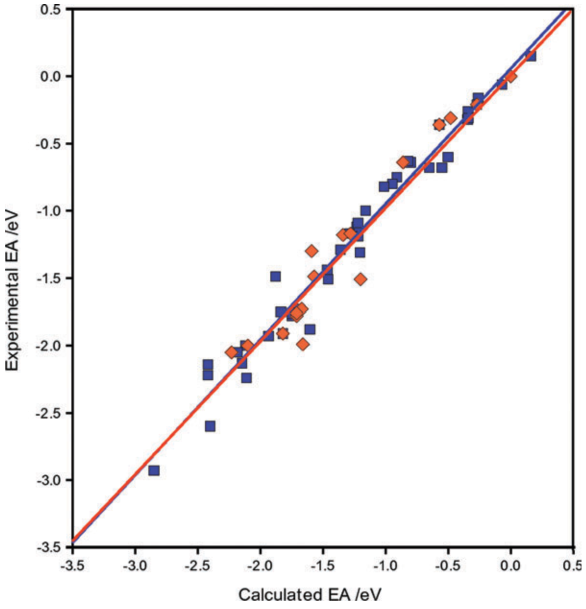

Fig. 5 Comparison between cc-aug-VTZ (◆) and 6-311 + G(2df,p) (■) basis sets.

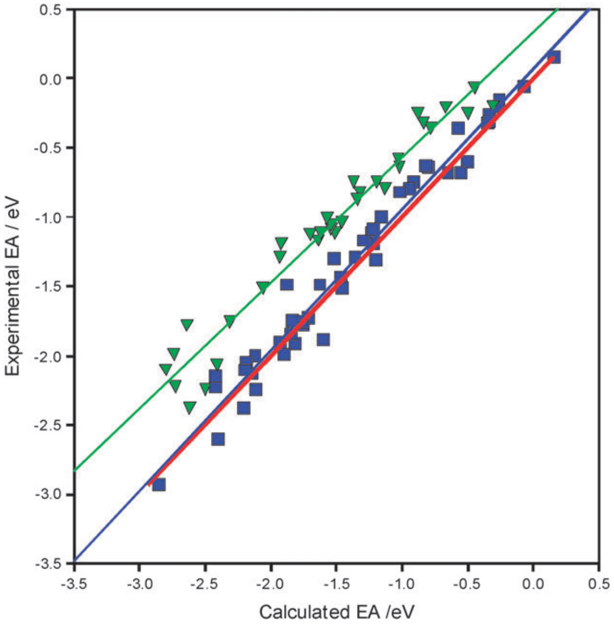

Fig. 6 Comparison between the correlation obtained in ref. 23 (-▼-), this work (-■-) and an ideal prediction (—).

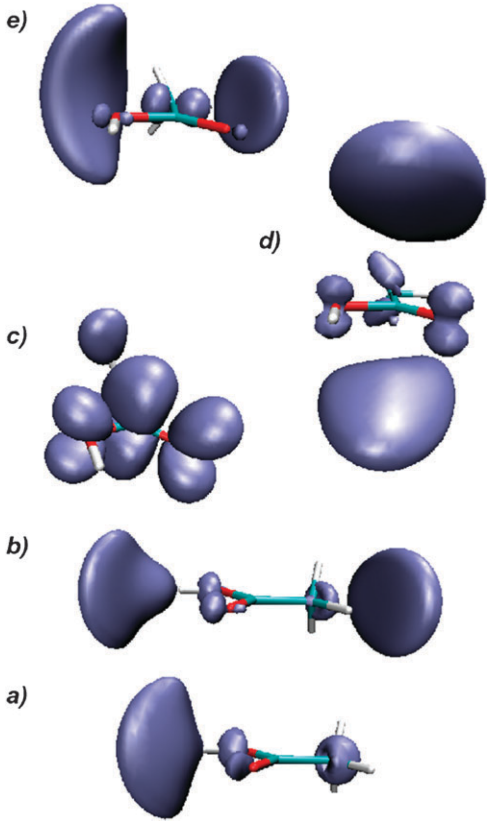

Fig. 7 Spin density of the ground state RA of acetic acid, (a), which is of N type, and the first 4 excited anionic states (b–e). The second state ((c), root 2) is the lowest valence anion state, selected for the calculation of the EA; all surfaces plotted with an isodensity value of 0.0015 a.u.

As an alternative to the IEFPCM solvation model, the SCIPCM[44] was also tested. It showed a convergence which was too slow and, in some solvents, failed. For this reason it was not tested further (results not shown).

In order to test other hybrid functionals, the electron affinities of a subset of 10 compounds, with experimental EAs ranging from −1.5 to −2.5 eV were obtained by extrapolating eqn (9) with the standard Pople's basis and the B3PW91 and B1B95 functionals (overall comparison plotted in Fig. S3, details on the calculation as Table S7 in the ESI†). The values calculated with B3PW91 were poorer than those with B3LYP, with a systematic underestimation of about 0.3 eV. The B1B95 functional yielded a prediction of $y = 0.98x + 0.09$, close to B3LYP, although with more dispersion. Although the number of points is not significantly large, there is no indication of a sensitive improvement over B3LYP by using these functionals. The whole blank set has also been tested with the PBE0 functional, which was further used for time-dependent DFT calculations, as an alternative strategy for finding the valence state (see below). Slight differences were found between the performances of PBE0 and B3LYP for these compounds, the correlation obtained being available as Fig. S4 in the ESI†.

At this point, we considered it worthwhile to compare the overall performance of these results for the whole set (Tables 1 and 2) with the new method proposed in ref. 23. This is because (i) the authors of ref. 23 have used several compounds computed in ref. 5, which gives the opportunity to compare against the same experimental results; (ii) both methodologies have been proposed within a few months, (iii) both are based on standard DFT methods and could be used and implemented by any chemist without, or practically without, modifying the existing codes currently used by researchers involved in organic/biological reactivity and mechanisms; (iv) both are beyond the Koopmans' theorem approximation,[45] and expected to yield accurate thermodynamic EAs (*i.e.* using the total energies of neutral and anion species instead of the one-electron orbital energies). The performance of our whole set (blue squares on Fig. 6) is characterized by a correlation index of 0.984, with an overall linear correlation $y = 1.01x + 0.06$, close to an ideally unbiased correlation ($y = x$ shown as a red line in Fig. 6). On the other hand, the

Table 3 Summary of results obtained by TD-DFT. Experimental and calculated EA for compounds which have ground non-valence state ("work" subset)[a]

Species		EA, TD-B3LYP/6-311+G(2df,p)//B3LYP/6-31+G*	Deviation	EA, TD-PBE0/6-311+G(2df,p)//PBE0/6-31+G*	Deviation	EA, experimetnal[b]
18	Oxazole[c]	−1.38	(−0.06)	−1.34	(−0.10)	−1.44
26	1,4-Cyclohexadiene	−1.63	(−0.12)	−1.76	(0.01)	−1.75
27	2-Methyl-2-butene	−1.77	(−0.47)	−1.82	(−0.42)	−2.24
28	Acetic acid	−1.76	(−0.04)	−1.79	(−0.01)	−1.80
29	Acetone	−1.07	(−0.44)	−1.43	(−0.08)	−1.51
30	Acetylene	−2.02	(−0.58)	−2.12	(−0.48)	−2.60
31	Allene	−1.57	(−0.31)	−1.62	(−0.26)	−1.88
32	Butyrolactone	−1.62	(−0.31)	−1.61	(−0.32)	−1.93
33	*Cis*-1-bromo-1-propene	−1.48	(−0.01)	−1.58	(0.09)	−1.49
34	*Cis*-1,2-difluorethylene	−1.84	(−0.34)	−2.03	(−0.15)	−2.18
35	*Cis*-2-butene	−1.94	(−0.28)	−2.08	(−0.14)	−2.22
36	Cyclobutene	−1.86	(−0.14)	−2.01	(0.01)	−2.00
37	Cyclopentene	−1.97	(−0.17)	−2.12	(−0.02)	−2.14
38	Di-*tert*-butyl-peroxide	−1.97	(−0.03)	−2.31	(0.31)	−2.00
39	Ethylene carbonate	−2.16	(−0.77)	−2.40	(−0.53)	−2.93
40	Fluorethylene	−1.74	(−0.17)	−1.78	(−0.13)	−1.91
41	Formamide	−1.91	(−0.14)	−2.09	(0.04)	−2.05
42	Furan	−1.58	(−0.18)	−1.75	(−0.01)	−1.76
43	Guanine	−0.83	(−0.57)	−1.03	(−0.37)	−1.40
44	Imidazole	−1.76	(−0.37)	−1.89	(−0.25)	−2.13
45	Methyl vinyl ether	−1.59	(−0.71)	−1.81	(−0.49)	−2.30
46	Propene	−1.70	(−0.29)	−1.79	(−0.20)	−1.99
47	Propiolactone	−1.43	(−0.47)	−1.61	(−0.29)	−1.90
48	Propyne	−2.67	(−0.13)	−3.13	(0.33)	−2.80
49	Pyrrole	−2.09	(−0.29)	−2.20	(−0.18)	−2.38
50	Tetramethylethylene	−2.04	(−0.23)	−2.04	(−0.23)	−2.27
51	*Trans*-1-bromo-1-propene	−1.31	(0.01)	−1.65	(0.35)	−1.30
52	*Trans*-1-chloro-1-propene	−1.31	(−0.18)	−1.44	(−0.05)	−1.49
53	*Trans*-1,2-difluorethylene	−1.42	(−0.42)	−2.01	(0.17)	−1.84
54	*Trans*-2-butene	−2.02	(−0.08)	−2.02	(−0.08)	−2.10
55	Trifluorethylene	−1.96	(−0.44)	−2.14	(−0.27)	−2.40
56	2-Butyne	−3.24	(−0.19)	−3.62	(0.19)	−3.43
57	Acetonitrile	−2.42	(−0.40)	−2.57	(−0.25)	−2.82
58	Dimethylformamide	−2.31	(−0.09)	−2.44	(0.04)	−2.40
59	Ethyl isocyanate	−2.94	(0.31)	−2.94	(0.31)	−2.63
60	Tetrafluoroethylene	−2.95	(−0.05)	−3.02	(0.02)	−3.00
Mean deviation			−0.13		−0.01	
Absolute mean deviation			0.18		0.17	

[a] All energies in eV. [b] From ref. 29. [c] Oxazole ground anion is of V type with B3LYP.

correlation from data in ref. 23 is $y = 0.90x + 0.33$ with a correlation index of 0.977 (green triangles, Fig. 6). The overall quality of both correlations is remarkably good (the fact that our correlation index is better is compensated, in part, because the number of points used in ref. 23 is smaller). Three observations can be made from this comparison: (i) some points (corresponding to the same compound), which show a visibly greater deviation in this work, also appear deviated in ref. 23 (which could be addressed either to the quality of each experimental datum or to the fact that the same B3LYP functional has been used in both cases); (ii) the small offset in this work against a systematic underestimation of 0.33 eV in ref. 23;[46] (iii) in both cases, a higher dispersion appears at more negative EAs.

Finally, it is interesting to find an alternative strategy for obtaining at least an estimate of the valence EA, when any stabilization fails. To this end, we have tested the possibility of finding the valence state as an excited state of the anion by means of time dependent DFT, as shown for acetic acid, as an example, in Fig. 7. For the TD-DFT calculations, the PBE0 functional was included since it is expected to yield better excitation energies[30,31] than the B3LYP mostly used so far.[5,6] Table 3 summarizes the results obtained for all compounds for which the valence state appears as an excited state using both TD-B3LYP and TD-PBE0 models. In addition, all compounds in the blank set, for which the valence state appears as the anion ground, were also calculated again with PBE0 (results available in the ESI†, Part 5) and the correlations were taken by gathering the whole 60 compounds in order to detect or to discard either a systematic under- or overestimation of the energies of the states, which could be introducing additional error, besides the error in the calculations of the EAs themselves. The correlations obtained with both B3LYP and PBE0/6-311 + G(2df,p) are compared to the ones obtained by means of the extrapolation technique (eqn (9)) in Fig. 8. The slopes obtained by fitting only excited valence states, fitting only the blank set (ground valence states, available in the ESI†) and fitting the whole 60 compounds were not significantly different, and were close to unity, especially for the PBE0 results.

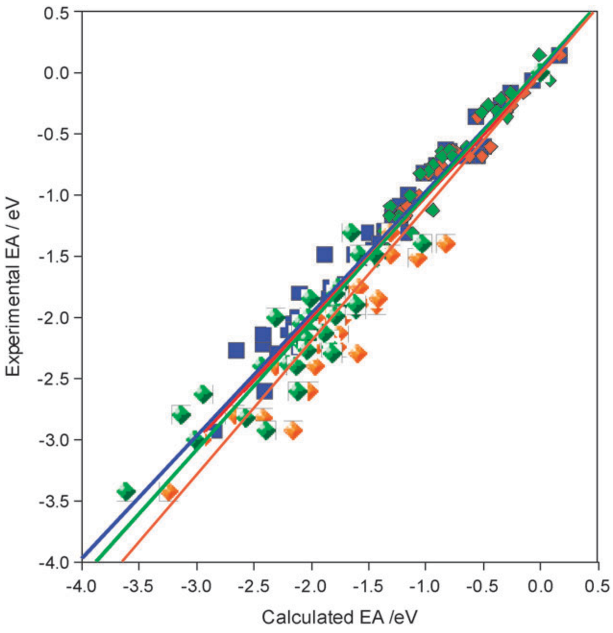

Fig. 8 Comparison between the correlations obtained with experimental EAs obtained by extrapolating eqn (9) (■) and by means of TD-DFT (◆ shaped diamonds for valence states found as excited states, plain diamonds for valence anion found as ground). --- : Ideal prediction $y = x$; -■- : Extrapolation of eqn (9): $y = (1.01\ x + 0.06) \pm 0.07$; -◆-: TD-PBE0: $y = (1.04\ x + 0.05) \pm 0.20$; -◆-: TD-B3LYP: $y = (1.10\ x - 0.01) \pm 0.21$.

The correlation obtained using TD-PBE0 ($y = 1.05x + 0.06$, correlation index of 0.969, green on Fig. 8) was slightly better than the corresponding TD-B3LYP results (orange on Fig. 8) and closer to our stabilization procedure (blue on Fig. 8). Even though the reliability of the TD-DFT predictions is better than Koopmans' theorem, and although even the most negative EAs were reasonably well reproduced, a greater dispersion and a higher standard error (0.2 eV) is obtained in comparison with the extrapolation strategy. Nevertheless, after reviewing hundreds of molecules, Rienstra-Kirakofe *et al.*,[7] have proposed that a reasonable DFT prediction for a positive EA will have a precision of 0.1–0.2 eV, and it is clear that those cases are more amenable from both the experimental and the theoretical point of view than the case of negative EAs.

Further applications

At revision time, a reviewer suggested that we predict a small set of unknown or not unambiguously known EAs of compounds which could be of interest in different areas of chemistry and potential targets for future measurements. Thus, we present in Table 4 the predicted valence EAs of ten compounds of considerable interest in chemistry and biology. The ground anions of these species are also the most challenging N type case with considerably negative EAs (the chemical structures of all these compounds are given in Chart S2 in the ESI†).

Table 4 Prediction of the EAs of some compounds of biological interest[a]

Species	Anion type (ground gas phase)	Anion type after extrapolation	EA extrapolated eqn (9)
61 α-(L)-Alanine	N	V	−1.73[b]
62 α-(L)-Glycine	N	V	−2.05[b]
63 α-(L)-Tyrosine	N	V	−0.78
64 Ascorbic acid (vitamin C)	N	V	−0.99
65 β-Alanine	N	V	−1.94[b]
66 Carbonyl fluoride	N	V	−1.92
67 Succinic acid	N	V	−1.43
68 Urea	N	N	−3.36, −3.46[c]

[a] Using B3LYP/6-311 + G(2df,p)//6-31 + G(d) unless indicated. All energies in eV, all amino acids in neutral form. [b] Valence EAs of −1.8 and −1.93 eV have been given in ref. 50 for alanine and glycine respectively; however N type anions have been obtained for them in ref. 51. [c] Values calculated with TDDFT using B3LYP and PBE0 functionals respectively, as in Table 3.

Surprisingly, among the compounds in Table 4, vitamin C (**66**),[47] a cofactor and probably the best known natural antioxidant, succinic acid (**67**) and urea (**68**), which are two highly widespread biological metabolites, have no measured EAs.[48] Carbonyl fluoride ($C(O)F_2$, **65**) would also be a candidate for further experimental interest, since it is a known sink compound for the decomposition of many fluorinated atmospheric pollutants and thus a probe of anthropogenic activity.[49]

The simplest amino acids, **61**, **62** and **64**, are the subject of experimental[50] and theoretical[51] concern by themselves and as models for more complex residues and peptidic chains under ionizing radiation exposure and electron transfer processes in proteins.[4,52] Tyrosine (**63**) (which, to our knowledge, has not already been measured), has an additional interest because the side chain bears a π acceptor apart from the carbonyl of the backbone; the electron can go to either of these moieties or can delocalize between them. This leads *a priori* to different possibilities for the lowest valence anion state. As shown in Fig. S5 of the ESI†, the coupling between the carboxylic carbonyl and the phenol moeity is strong. The EA of this compound (−0.78 eV) is also far away from the one observed for either phenol (−1.01 eV)[29e] or glycine (−2 eV).

Concluding remarks

We explored different alternatives for obtaining negative EAs, even for compounds with a very unstable anion, with especial emphasis on cases where the direct evaluation (eqn (1)) of the EA with standard DFT methods is more problematic, *i.e.* the anion ground is not a valence state.

The methodology based on the stabilization in a series of solvents was tested with the cc-AUG-VTZ basis, which did not improve the results with standard double- and triple-ζ basis (see Methodology: Computational setup), although a little offset (intercept) appears in the results with double-ζ, the triple-ζ is recommended. Linear extrapolation suffices in most cases, although a rational function could improve the fitting to $\varepsilon = 1$. The B1B95 and PBE0 are expected to work as good as B3LYP, which was used extensively.

In most cases, the valence EA was obtained, although in some cases the procedure could fail in stabilizing the anion; this can occur when treating the most unstable anions. However, this can be easily checked by inspecting the orbitals and spin density to ensure that the right anion state has been obtained. Despite this limitation, it should be remarked that most compounds considered interesting in organic ET reactions have EAs less negative than −3 eV and they were indeed successfully stabilized. It is noted that compounds **56–60** (not stabilized) are very poor electron acceptors; acetonitrile and dimethylformamide, **58** and **59**, respectively, are not thought of as reactives (electron acceptors) since they are inert enough to be used as solvents in many organic processes involving single ET reactions.

Although the TD-DFT procedure is inherently less accurate than ground DFT, it has been proven as a suitable alternative for obtaining reasonable values of EAs, especially for very unstable anions. The PBE0 functional, in combination with standard triple-ζ basis is recommended.

The values of the valence EAs obtained by means of extrapolation of eqn (9) are in remarkably good agreement with the experimental data in a representative set of compounds, the correlation being given by an unbiased line $y = (1.01x + 0.06) \pm 0.07$ eV, with a correlation index of 0.982. Neither external parameters nor experimental information is required. Although the idea of stabilizing the valence in some artificial way has already been proposed for dealing with such anions,[53] in this particular case, the stabilization is done using a medium which has full physical meaning, since it represents a solvent. In this framework, all data calculated in order to stabilize the valence anion state have a fully chemical significance. The computational methods used in this aim involve the same formalisms and computational codes used for studying the mechanisms and chemical reactivity of the species in solution, and the results obtained are fully comparable to any other energetic magnitudes measured or calculated for other species, as, for example, ionization potentials or even positive electron affinities.

Finally, a set of 8 interesting compounds, most of them with unknown and very negative EAs have been predicted. Due to the relevance of some of these species, we hope any experimental group would be interested in determining their experimental EAs in the near future, hopefully giving additional evidence to reinforce the predictive reliability of the present proposal.

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