A Reliable and Inexpensive Method for Calculating Ionization Potentials and Electron Affinities of Radicals and Molecules

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The ionization potentials and electron affinities of a variety of organic radicals and closed-shell molecules have been calculated with the outer valence Green's function (OVGF) technique, coupled with semiempirical MNDO, AM1 and PM3 calculations. The calculations cover a wide range of energies >11 eV in a variety of radicals and molecules. It is found that the OVGF method gives significantly better agreement with the experimental data than do results obtained with semiempirical calculations using Koopmans' theorem. Of the three semiempirical methods tested (MNDO, AM1, PM3) the OVGF(AM1) method gives the best agreement with experiment (*e.g.*, for the vertical ionization potentials of 38 different organic radicals the mean deviation between experimental data and theoretical values is only 0.35 eV), and thereby can serve as a routine method for the calculation of the above-mentioned molecular properties of a variety of species.

The ionization potentials, electron affinities and reorganization energies of molecules are fundamental physical quantities which are used in a variety of chemical areas[1] ranging from chemical reactivity, to thermochemistry, electrochemistry and spectroscopy. Though current experimental techniques[2] have become sufficiently refined to measure such quantities for a variety of molecules, there is still a basic need for an inexpensive and reliable computational method which can supplement experiment and enable a routine calculation of these quantities for a variety of molecules.

The useful methods for calculating ionization potentials (E_i) can be divided into 'direct' and 'indirect' ones. The 'indirect' E_i values are calculated as the difference in the total energies of the states with N and $N - 1$ electrons. The total energies, in turn, may be calculated within the one-particle SCF approximation using a variety of quantum mechanical methods ranging from semiempirical to *ab initio* or by using one of the many-body methods which take into account implicitly electron correlation (*e.g.*, the CI, MCSCF, MP methods).[3] Thus, to calculate the E_i or the electron affinity (E_{ea}) of a molecule one needs to carry out separate calculations for two species: *e.g.*, for the neutral species and for corresponding cation- or anion-radical. The 'direct' methods are aimed at the formulation of straightforward equations which will provide in a single calculation the desired ionization energy. Traditionally, Koopmans' theorem which equates the E_i to the negative value of the orbital energy has been used for this purpose.[2a,b,j,k] However, these results are not quantitatively reliable because Koopmans' theorem does not take into account electron relaxation and correlation. One possible solution to the correlation and relaxation problems in the 'direct' method is to use the Green's function method or the equation of motion approach: coupled either with the *ab initio* method or with semiempirical methods.[4] *Ab initio* quantum mechanical techiques are generally costly and are therefore still not routinely accessible for calculating the E_i values of large molecules. The situation is even less encouraging with the calculations of electron affinities where reliable *ab initio* calculations are still rare,[5] even for small species, not to mention large organic species. It is apparent therefore that at least at present, one must continue to rely on semiempirical techniques. However, to obtain the desired reliability it is important to supplement the semiempirical methods with proper correlation corrections.

Recently two of us have shown in a series of papers[6,7] that the Outer Valence Green's Function (OVGF) method, developed by the Cederbaum group,[8] can be coupled to semiempirical MO methods to form a fast and reliable method for calculating ionization potentials for a variety of closed-shell molecules. It has been shown that the OVGF method when coupled with any of the commonly used semiempirical methods (MNDO, AM1, PM3) gives significantly better agreement with experiment than the semiempirical methods themselves. This method is now incorporated into the MOPAC package of programs[9] and it is available for general use. The major merit of the OVGF method is that it takes proper account of the relaxation and correlation effects inherent in the ionization process,[6–8] and does so in an effective and exact manner.

The OVGF method was used previously to study the ionization processes of closed-shell molecules. However, there is no fundamental reason why the method cannot be applied to a study of the ionization energies of open-shell species.[8] We have therefore decided to extend the application of the OVGF method to the calculation of ionization potentials and electron affinities of radicals, as well as to the electron affinities of close-shell molecules. We find that the OVGF technique coupled with the AM1 or with the PM3 methods provides these quantities with good accuracy for a large variety of molecules, reaching significantly better agreement with experiment than with the AM1 and PM3 calculations by themselves.

In the present paper we restrict the applications to vertical quantities. However, the extension to adiabatic values does not pose a fundamental problem and this will be a topic of future investigations.

Theoretical Methods

The OVGF method is described in detail in ref. 8. The application of this method to the case of semiempirical wave functions was discussed in detail in ref. 6 and 7 and computer programs implementing the method are available for public use.[9,10] Here we repeat in brief some of the main points and the interested reader is referred to refs. 6–8 for more details.

The OVGF technique was used with the self-energy part

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extended to include third-order perturbation corrections.[8] The higher-order contributions were estimated by the renormalization procedure. The actual expression used to calculate the self-energy part, $\Sigma_{pp}(w)$, chosen in the diagonal form, is given in eqn. (1), where $\Sigma_{pp}^{(2)}$ and $\Sigma_{pp}^{(3)}$ are the second- and third-order corrections, and A is the screening factor accounting for all the contributions of higher orders.

$$\Sigma_{pp}(w) = \Sigma_{pp}^{(2)}(w) + (1 + A)^{-1}\Sigma_{pp}^{(3)}(w) \qquad (1)$$

The particular expression which was used for the second-order corrections is given in eqn. (2).

$$\Sigma_{pp}^{(2)}(w) = \sum_{a}\sum_{i,j}\frac{(2V_{paij} - V_{paji})V_{paij}}{w + \varepsilon_a - \varepsilon_i - \varepsilon_j} + \sum_{a,b}\sum_{i}\frac{(2V_{piab} - V_{piba})V_{piab}}{w + \varepsilon_i - \varepsilon_a - \varepsilon_b} \qquad (2)$$

where

$$V_{pqrs} = \iint \varphi_p^*(1)\varphi_q^*(2)(1/r_{12})\,\varphi_r(1)\varphi_s(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

In eqn. (2), i and j denote occupied orbitals, a and b denote virtual orbitals, p denotes orbitals with unspecified occupancy and ε denotes the orbital energy while w is the corrected ionization potential. The equations were solved by an iterative procedure which is given in eqn. (3).

$$w_p^{i+1} = \varepsilon_p + \Sigma_{pp}(w^i) \qquad (3)$$

The SCF energies and the corresponding integrals which were calculated by a semiempirical method (MNDO, AM1 or PM3) were taken as the zeroth approximation and all MOs were included in the active space for the OVGF calculations.

The SCF orbital energies of the open-shell species were calculated by the half-electron (HE) method,[11] using doublet correction for ionization potentials. The expressions used for $\Sigma_{pp}^{(3)}$ and A are given in ref. 8(*b*).

The geometries of all compounds under consideration were fully optimized with the specified semiempirical methods, *e.g.*, AM1,[12] PM3,[13] MNDO,[14] using the MOPAC program.[9] The RHF procedure was used for closed-shell species and the HE method was used for open-shell species.

Results and Discussion

(*a*) *Vertical Ionization Potentials of Radicals.*—In Table 1 are collected vertical ionization potentials of 43 important organic radicals which are also drawn in Fig. 1 in the order of their entry number in Table 1.

As a basis for our radical selection we used the compilation of Higgins, Thomson and Thiel[15] who have calculated the ionization potentials of these radicals *via* the 'indirect' method, using several semiempirical methods with (by using the MNDOC method)[16] and without correlation correction. In the case of the AM1 and MNDO methods both unrestricted Hartree–Fock (UHF) and the half-electron methods were used.[15] Thiel *et al.* found that the half-electron AM1 method gives the best overall results and the mean deviation $\bar{\Delta}$ of the calculated E_i values from experiment was 0.7 eV. The HE–MNDOC and the HE–MNDO methods gave larger deviations from experiment.

In our study we have deleted a few small and uncommon radicals from Thiel's compilation, but have added larger and more common radicals such as the 1- and 2-adamantyl radicals **15** and **16**, and the 1- and 2-norbornyl radicals **41** and **42**. The list includes carbon-centred radicals as well as silicon-, nitrogen- and oxygen-centred radicals.

A comparison of the computed vertical ionization potentials of the radicals $[E_i^v(R^\bullet)]$ in Table 1, using the different semiempirical methods shows that the OVGF method generally gives lower $E_i^v(R^\bullet)$ values by approximately 0.5 eV than the values calculated by using Koopmans' theorem.[17] Furthermore, comparison of the calculated $E_i^v(R^\bullet)$ values with the experimental values, shows that the experimental values are in better agreement with the OVGF values than with Koopmans' theory values. The improved performance of the OVGF method over the semiempirical methods becomes evident by inspection of the mean-deviation values ($\bar{\Delta}$) in Table 2 which includes 38 radicals. For example, we find that while $\bar{\Delta} = 0.62$ eV for SCF(AM1) it is only *ca.* 0.36 eV for the OVGF(AM1) method. Thus, the mean-deviation of the OVGF(AM1) values is half of that of Koopmans' values, and overall it can be stated that addition of the OVGF scheme to the semiempirical calculations improves significantly the calculated $E_i^v(R^\bullet)$ values.

Among the different semiempirical methods, the coupling of the OVGF method with AM1 produces the smallest mean deviation ($\bar{\Delta} = 0.36$ eV); the OVGF(PM3) method with $\bar{\Delta} = 0.52$ eV is less satisfactory, but is still better than the OVGF(MNDO) method (with $\bar{\Delta} = 0.63$ eV). An especially pleasing and important observation is that the chemical trends in Table 1 are generally well reproduced by the OVGF calculations. For example, the well known decrease in the $E_i^v(R^\bullet)$ along the series: $\mathrm{CH}_3^\bullet > \mathrm{C}_2\mathrm{H}_5^\bullet > \mathrm{Pr}^{i\bullet} > \mathrm{Bu}^{t\bullet}$, is well reproduced by all the OVGF methods. Other cases can be seen, for example, in the xylyl series, *i.e.*, the E_i order **12** > **11** > **13**, in the comparison of $\mathrm{Bu}^{t\bullet}$ (**4**) with the adamantyl radicals **15** and **16**, cyclopentadienyl (**30**) *vs.* tropyliumyl (**33**), and so on. In all these cases the OVGF(AM1) method gives the correct trends. E_i values of delocalized radicals such as benzyl (**10**), allyl (**20**), cyclopentadienyl (**30**), tropyliumyl (**33**), *etc.* are very well described including the relative ordering by all the OVGF methods with $\bar{\Delta}$ values usually smaller than 0.2 eV. The OVGF(PM3) method performs less satisfactorily in this sense but the differences are not all that big.

The largest single deviations, of the order of 0.85–1.58 eV, are observed for simple tertiary carbon centred radicals, *i.e.*, the *tert*-butyl radical, the 1-adamantyl and 2-adamantyl radicals and the cyclopropenyl radical, and they are common to all the methods. Yet, even in these cases, the OVGF methods always give significantly better agreement with experiment than the non-augmented semiempirical methods. A closer examination of the series of primary, secondary and tertiary radicals, shows that the OVGF (semiempirical) methods significantly underestimate the lowering of $E_i^v(R^\bullet)$ as a result of methyl substitution. Thus, the deviation Δ increases along the series $\mathrm{C}_2\mathrm{H}_5^\bullet$ (0.26), $\mathrm{Pr}^{i\bullet}$ (0.47), $\mathrm{Bu}^{t\bullet}$ (0.85) using the OVGF(AM1) method. Similar results, even more exaggerated, are observed with OVGF(PM3) and OVGF(MNDO) and with the Koopmans-based methods (Table 2). These deviations appear therefore to originate in the semiempirical methods themselves and not in the OVGF correction. A closer look at these radicals shows that the poor performance for these specific radicals does not originate from their poorly calculated geometries (calculations using optimized *ab initio* geometries do not significantly change the results) and it is probably rooted in the parametrization of the methods. It is interesting to note that *ab initio* calculations at the 6-311G** level using Koopmans' theorem also provide ionization potentials that are significantly higher than the experimental values (*i.e.*, 10.59, 9.59, 8.04 and 7.59 eV for $\mathrm{CH}_3^\bullet$, $\mathrm{C}_2\mathrm{H}_5^\bullet$, $\mathrm{Pr}^{i\bullet}$ and $\mathrm{Bu}^{t\bullet}$, respectively).[18,19] On the other hand, 'indirect' calculations of the E_i value of $\mathrm{Bu}^{t\bullet}$ at the UHF/6-31G*//6-31G* and MP3/6-31G*//6-31G* levels give values of 6.33 and 6.98 eV in good agreement with experiment.[19] Thus, in contrast with the 'direct' Koopmans' level, the 'indirect' methods give reliable results even at the UHF level. This is so because even at the UHF level the 'indirect' method takes into account the effects of electron relaxation and some electronic correlation.

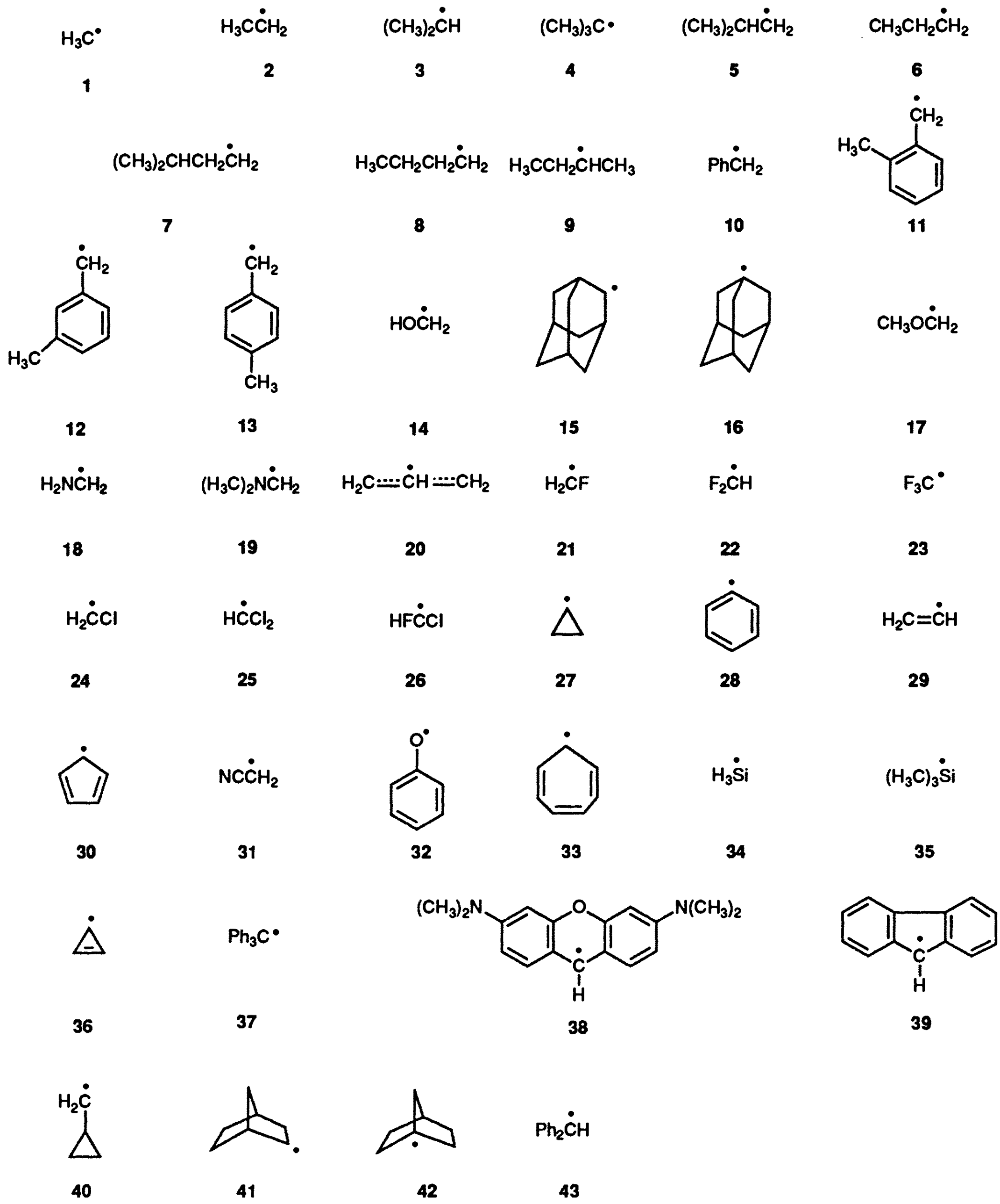

Fig. 1 Structures for Tables 1 and 2

A radical for which we find significant deviation from the literature value is the trityl radical. At the OVGF(AM1) and OVGF(PM3) levels the calculated $E_i^v(R^•)$ values are 6.42 eV and 6.67 eV, respectively, while the normally cited literature value is 7.26 eV.[20] The fact that the $E_i^v(R^•)$ of the benzyl radical is reproduced very well by both methods and based on substituent effects in the series $PhCH_2^•$ (**10**), $Ph_2CH^•$ (**43**) and trityl$^•$ (**37**) we suggest that the reported experimental E_i value of the trityl radical (**37**) is too high and should be reassessed based on our estimation.

Fig. 2 shows a plot of the $E_i^v(R^•)$ values calculated by the OVGF(AM1) method against the experimental values. It is possible to draw an approximately straight line with a correlation coefficient of 0.80 which improves significantly to 0.93 by excluding the strongly deviating species: $Bu^{t•}$ (**4**), the adamantyls (**15** and **16**), cyclopropenyl (**36**) and trityl (**37**), radicals. Note, that without the above-mentioned radicals, the mean deviation $\bar{\Delta}$ for 32 radicals is only 0.26 eV.

The vertical ionization potentials of $R^•$ refer to an ionization process which leaves R^+ at the geometry of the radical. However, we also considered a reversed vertical process shown in eqn. (4) in which an electron is added to the relaxed R^+ cation, the radical being formed in the geometry of the cation.

$$R^+(g) + e^- \longrightarrow (R^•)^*(g); \quad \Delta E = -E_i^v(R^•)^* \qquad (4)$$

Here the product radical has the geometry of the ion, as indicated by the asterisk $(R^•)^*$. The energy of this process is equal to the negative value of the vertical ionization potential of the $(R^•)^*$ species, *i.e.*, a deformed non-stationary radical having the geometry of the cation. These quantities are important in dictating the reactivity of electron transfer (ET) and in polar processes, where vertical electron transfer energy from a donor to an acceptor is a key property.[21] For example, in the ET process between a nucleophile ($Nu^{:•}$) and a carbenium ion (R^+) one requires the $E_i^v(R^•)^*$ quantity,[21b] *i.e.*, the E_i of the corresponding $(R^•)^*$ radical. Table 3 shows calculated $E_i^v(R^•)^*$ values for several representative radicals. Some interesting trends are apparent.

Table 1 Vertical ionization potentials (eV) of radicals calculated by the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO, and OVGF(MNDO) methods and experimental values

Entry	Radical	Symmetry	Exp.	AM1	OVGF-(AM1)	PM3	OVGF-(PM3)	MNDO	OVGF-(MNDO)
1	Methyl	D_{3h}	9.84[a]	9.77	9.63	9.84	9.79	9.60	9.48
2	Ethyl	C_1	8.51[a]	9.03	8.77	9.15	9.00	9.32	9.06
3	Isopropyl	C_1	7.69[a]	8.53	8.17	8.67	8.44	9.12	8.76
4	*tert*-Butyl	C_{3h}	6.92[a]	8.21	7.77	8.37	8.07	9.00	8.53
5	Isobutyl	C_1	8.31[a]	9.06	8.70	9.19	8.95	9.34	8.99
6	*n*-Propyl	C_1	8.43[a]	9.01	8.70	9.10	8.91	9.34	9.02
7	*sec*-Pentyl	C_1	8.25[a]	8.98	8.62	9.09	8.84	9.32	8.96
8	*n*-Butyl	C_1	8.50[a]	9.06	8.69	9.19	8.95	9.33	9.01
9	*sec*-Butyl	C_1	7.59[a]	8.53	8.12	8.66	8.39	9.13	8.71
10	Benzyl	C_{2v}	⩾7.2[b,c]	7.69	7.28	7.83	7.49	7.62	7.21
11	*o*-Xylyl	C_s	⩾7.07[b,c]	7.60	7.17	7.72	7.36	7.60	7.18
12	*m*-Xylyl	C_1	⩾7.12[b,c]	7.67	7.23	7.80	7.44	7.66	7.22
13	*p*-Xylyl	C_1	⩾6.96[b,c]	7.54	7.12	7.66	7.32	7.57	7.15
14	Hydroxymethyl	C_s	8.14[d]	8.57	8.35	8.55	8.44	8.53	8.33
15	2-Adamantyl	C_1	6.99[e]	8.58	7.93	8.79	8.31	9.06	8.41
16	1-Adamantyl	C_1	6.36[e]	8.44	7.76	8.72	8.25	9.04	8.34
17	Methoxymethyl	C_s	⩾6.9,[f] 7.0[g,c]	8.43	8.08	8.47	8.24	8.44	8.11
18	Aminomethyl	C_1	⩾6.2,[f] 6.8[g,c]	7.68	7.46	7.89	7.76	8.22	7.99
19	Dimethylaminomethyl	C_s	⩾5.7[f,c]	7.37	6.93	7.59	7.31	7.69	7.25
20	Allyl	C_{2v}	⩾8.06[h,c]	8.36	8.05	8.46	8.25	8.27	7.97
21	Fluoromethyl	C_{2v}	⩾8.9[h,c]	9.40	9.23	9.68	9.58	9.57	9.43
22	Difluoromethyl	C_{2v}	⩾8.73[h,c]	9.35	9.16	9.68	9.55	9.76	9.61
23	Trifluoromethyl	D_{3h}	⩾9.17[h,c]	9.50	9.27	9.76	9.60	10.16	10.02
24	Chloromethyl	C_{2v}	8.87[i]	9.45	9.23	9.00	8.87	9.87	9.65
25	Dichloromethyl	C_{2v}	8.54[i]	9.34	9.09	8.76	8.57	10.05	9.73
26	Chloro(fluoro)methyl	C_1	9.16[i]	9.43	9.16	9.24	9.07	9.95	9.69
27	Cyclopropyl	C_s	8.05[j]	9.06	8.69	9.21	8.96	9.32	8.94
28	Phenyl	C_{2v}	9.20[j]	9.95	9.20	10.22	9.67	10.02	9.24
29	Ethenyl	C_{2v}	⩾8.59[k,c]	8.86	8.56	9.15	8.97	9.07	8.77
30	Cyclopentadienyl	C_{2v}	8.7[j]	9.06	8.77	9.15	8.94	8.97	8.64
31	Cyanomethyl	C_{2v}	10.0[j]	10.01	9.63	9.97	9.70	9.99	9.60
32	Phenoxyl	C_{2v}	8.8[j]	8.79	8.42	8.80	8.51	8.63	8.26
33	Tropyliumyl	C_1	6.28,[h] 6.6[g,c]	7.0	6.67	7.40	6.88	7.17	6.82
34	Silyl	C_{3v}	8.74[l]	8.98	8.90	8.29	8.32	7.17	7.16
35	Trimethylsilyl	C_1	6.81[m]	7.31	7.14	7.23	7.21	7.17	6.98
36	Cyclopropenyl	C_s	5.80[j]	7.63	7.38	7.65	7.49	7.70	7.45
37	Trityl	C_1	7.26,[n] 6.82[o]	7.21	6.42	7.40	6.67	9.32	7.81
38	Pyroninyl	C_1		6.38	5.81	7.15	6.64	7.01	6.42
39	Fluorenyl	C_1		7.63	7.08	7.73	7.25	7.54	6.99
40	Cyclopropylmethyl	C_1		9.17	8.79	9.29	9.02	9.31	8.93
41	2-Norbornyl	C_1		8.60	8.05	8.74	8.35	9.08	8.54
42	1-Norbornyl	C_1		9.23	8.64	9.43	9.04	9.40	8.78
43	Diphenylmethyl	C_2		7.38	6.76	7.47	6.94	7.42	6.76

[a] From ref. 23. [b] From ref. 26. [c] The tabulated quantities are adiabatic values. [d] From ref. 27. [e] From ref. 28. [f] From ref. 29. [g] From ref. 2(*h*). [h] From ref. 30. [i] From ref. 31. [j] From ref. 32. [k] From ref. 33. [l] From ref. 34. [m] From ref. 35. [n] From ref. 20. [o] Estimated from data in ref. 2(*h*) for benzyl and trityl but using E_i(benzyl) from entry **10** here.

For some radicals, like allyl (**20**), the calculated $E_i^v(R^\bullet)^*$ values are only slightly smaller than the $E_i^v(R^\bullet)$ values of these radicals (compare Table 3 with Table 1). This indicates that the geometries of the radical and the cation are quite similar, as might be expected considering the non-bonding nature of the singly occupied allylic orbital from which the electron is ionized. However, in other radicals, such as in $H_2NCH_2^\bullet$ (**18**), the differences between $E_i^v(R^\bullet)^*$ and $E_i^v(R^\bullet)$ are much larger, *e.g.*, ~0.6 eV in the above case. In this case there is a significant interaction between the singly occupied radical orbital and the lone-pair on nitrogen and therefore the geometries of the $H_2NCH_2^\bullet$ radical and of the corresponding $H_2NCH_2^+$ cation are very different. A very large difference between $E_i^v(R^\bullet)$ and $E_i^v(R^\bullet)^*$ is computed for the $C_2H_5^\bullet$ radical, *i.e.*, 8.77 eV and 7.09 eV, respectively, at the OVGF (AM1) level. This large difference is a result of the dramatic structural differences between $C_2H_5^\bullet$ and $C_2H_5^{\bullet *}$, the latter having the bridged structure of the $C_2H_5^+$ cation.[22] We conclude that large differences in $E_i^v(R^\bullet)^*$ and $E_i^v(R^\bullet)$ are expected whenever the radical $R^\bullet$ and the corresponding cation R^+ differ significantly in their geometries.

In this connection we note that knowledge of the E_i values of radicals $[E_i^v(R^\bullet)]$, of their adiabatic ionization potentials $[E_i^{ad}(R^\bullet)]$, and the corresponding $E_i^v(R^\bullet)^*$ provide us with the reorganization energies (E_r) of the radical [eqn. (5a)] and cation species [eqn. (5b)]. These reorganization energies are of some importance in the consideration of electron transfer in the redox couples, $R^\bullet/R^+$.

$$E_r(R^\bullet) = E_i^v(R^\bullet) - E_i^v(R^\bullet)^* - E_r(R^+) \qquad (5a)$$

$$E_r(R^+) = E_i^v(R^\bullet) - E_i^{ad}(R^\bullet) \qquad (5b)$$

(*b*) *Vertical Electron Affinities of Radicals.*—The adiabatic electron affinity (E_{ea}) is defined by eqn. (6), where R^- and $R^\bullet$ species are at their optimized geometries.

$$R^-(g) \longrightarrow R^\bullet(g) + e^-; \quad E_{ea}(R^\bullet) \equiv E_i^{ad}(R^-) \qquad (6)$$

The corresponding vertical process is defined in eqn. (7), where the asterisk denotes that $(R^\bullet)^*$ has the same geometry as R^-.

Table 2 Deviation of the calculated vertical ionization potentials (eV) of radicals calculated by the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO and OVGF(MNDO) methods from the experimental values

Entry	Radical	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
1	Methyl	0.07	−0.21	0.00	−0.05	−0.24	−0.36
2	Ethyl	0.52	0.26	0.64	0.49	0.81	0.55
3	Isopropyl	0.84	0.47	0.98	0.75	1.43	1.07
4	*tert*-Butyl	1.29	0.85	1.45	1.15	2.08	1.61
5	Isobutyl	0.75	0.39	0.88	0.64	1.03	0.68
6	*n*-Propyl	0.58	0.27	0.67	0.48	0.91	0.59
7	*sec*-Pentyl	0.73	0.37	0.84	0.59	1.07	0.71
8	*n*-Butyl	0.56	0.19	0.69	0.45	0.83	0.51
9	*sec*-Butyl	0.94	0.53	1.07	0.80	1.54	1.12
10	Benzyl	≈0.40[a]	≈0.00[a]	≈0.50[a]	≈0.15[a]	≈0.40[a]	≈ −0.10[a]
11	*o*-Xylyl	≈0.75[a]	≈0.00[a]	≈1.02[a]	≈0.47[a]	≈0.82[a]	≈0.04[a]
12	*m*-Xylyl	≈0.40[a]	≈0.00[a]	≈0.50[a]	≈0.15[a]	≈0.40[a]	≈0.00[a]
13	*p*-Xylyl	≈0.40[a]	≈0.05[a]	≈0.50[a]	≈0.20[a]	≈0.40[a]	≈0.10[a]
14	Hydroxymethyl	0.43	0.20	0.41	0.30	0.39	0.19
15	2-Adamantyl	1.59	0.94	1.80	1.32	2.07	1.42
16	1-Adamantyl	2.08	1.40	2.36	1.89	2.68	1.88
17	Methoxymethyl	≈0.80[a]	≈0.50[a]	≈0.90[a]	≈0.65[a]	≈0.80[a]	≈0.51[a]
18	Aminomethyl	≈0.40[a]	≈0.20[a]	≈0.60[a]	≈0.50[a]	≈1.00[a]	≈0.70[a]
19	Dimethylaminomethyl	≈0.70[a]	≈0.20[a]	≈0.90[a]	≈0.60[a]	≈1.00[a]	≈0.50[a]
20	Allyl	≈0.10[a]	≈0.00[a]	≈0.20[a]	≈0.10[a]	≈0.10[a]	≈ −0.15[a]
21	Fluoromethyl	0.50	0.33	0.78	0.68	0.67	0.53
22	Difluoromethyl	0.62	0.43	0.95	0.82	1.03	0.88
23	Trifluoromethyl	0.33	0.10	0.59	0.43	0.99	0.85
24	Chloromethyl	0.58	0.36	0.13	0.00	1.00	0.78
25	Dichloromethyl	0.80	0.55	0.22	0.03	1.51	1.19
26	Chloro(fluoro)methyl	0.27	0.00	0.08	−0.09	0.79	0.53
27	Cyclopropyl	1.01	0.64	1.00	0.70	1.10	0.70
28	Phenyl	0.75	0.00	1.00	0.47	0.82	0.04
29	Ethenyl	≈0.06[a]	≈ −0.24[a]	≈0.35[a]	≈0.17[a]	≈0.27[a]	≈0.03[a]
30	Cyclopentadienyl	0.40	0.10	0.50	0.30	0.30	0.00
31	Cyanomethyl	0.01	−0.37	0.03	−0.30	0.01	0.04
32	Phenoxy	0.00	−0.38	0.00	−0.29	−0.17	−0.54
33	Tropyliumyl	≈0.60[a]	≈0.25[a]	≈1.0[a]	≈0.45[a]	≈0.80[a]	≈0.40[a]
34	Silyl	0.24	0.16	0.45	0.42	1.57	1.58
35	Trimethylsilyl	0.50	0.33	0.42	0.40	0.36	0.17
36	Cyclopropenyl	1.83	1.58	1.85	1.69	1.90	1.65
	Mean deviation	0.62	0.36	0.73	0.52	0.92	0.63

[a] Only lower limits for E_i are available experimentally and therefore the deviations are approximate.

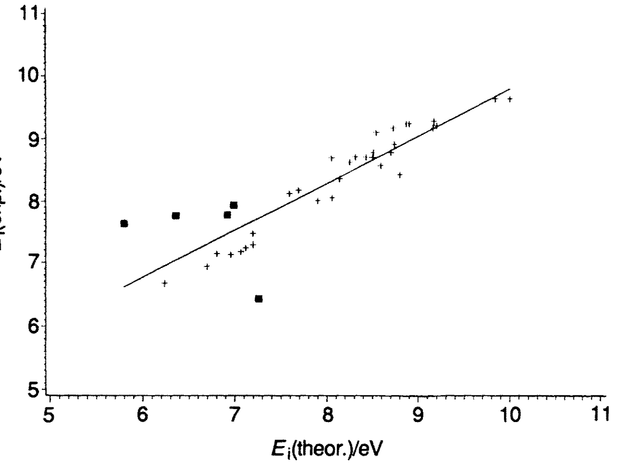

Fig. 2 A plot of calculated OVGF(AM1) (E_i^{theor}), against experimental (E_i^{exp}), ionization potentials for all the species in Table 1. The data points in squares are those with the largest deviations (see the text). The correlation coefficient without the squared data is 0.93.

$$R^-(g) \rightarrow (R^\bullet)^*(g) + e^-; \quad E^v_{ea}(R^\bullet)^* \equiv E^v_i(R^-) \quad (7)$$

These vertical electron affinities of radicals are identical with the vertical ionization potentials of the corresponding anions. These quantities are needed for calculating the vertical electron transfer energies occurring from these anions to electron acceptors in ET processes.

A reliable reproduction of E_{ea} values is an especially demanding computational task, as may be evidenced from the available good quality *ab initio* work,[5] which indicates that even very large basis sets and high correlation levels are not always sufficient to give good results. Thus, it is here in this difficult and demanding area where the present OVGF method can prove to be very useful.

Table 4 is a collection of calculated vertical electron affinities and of the corresponding experimental quantities. The corresponding anions are drawn in Fig. 3 following the entry numbers in Table 4. Table 5 lists the deviations of the calculated values from experiment for all the methods which were used.

Inspection of the data shows again the same trends as found previously for the vertical ionization potentials of the radicals. Thus, the OVGF values are consistently less positive than the corresponding Koopmans' values, and they are in better accord with experiment. This becomes apparent from the mean deviation, $\bar{\Delta}$ data in Table 5. Thus, while $\bar{\Delta}$ is 0.57, 0.66 and 0.62 eV for AM1, PM3 and MNDO, respectively, it is reduced to only 0.33, 0.43 and 0.47 eV when the OVGF procedure is used with the same semiempirical methods. The importance of electron correlation and thus of the OVGF method is especially

Table 3 Calculated vertical ionization potentials (eV) of 'frozen' radicals possessing the geometries of the corresponding cations

Entry[a]	Radicals	Symmetry	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
1	Methyl	D_{3h}	9.73	9.58	9.84	9.78	9.59	9.46
10	Benzyl	C_{2v}	7.59	7.20	7.70	7.40	7.52	7.14
14	Hydroxymethyl	C_s	8.19	7.95	8.13	8.02	8.15	7.94
18	Aminomethyl	C_{2v}	7.07	6.84	6.98	6.85	7.23	7.03
20	Allyl	C_{2v}	8.33	8.02	8.45	8.24	8.26	7.95
33	Cycloheptatrienyl	C_s	6.80	6.50	6.87	6.65	6.95	6.64
36	Cyclopropenyl	D_{3h}	7.29	7.02	7.21	7.05	7.32	7.04
38	Pyronine	C_1	5.96	5.44	6.00	5.53	6.09	5.57
—	C_2H_5 (bridged)	C_{2v}	7.32	7.09	7.48	7.37	7.45	7.24

[a] Numbering of the radicals corresponds to Fig. 1 and Table 1.

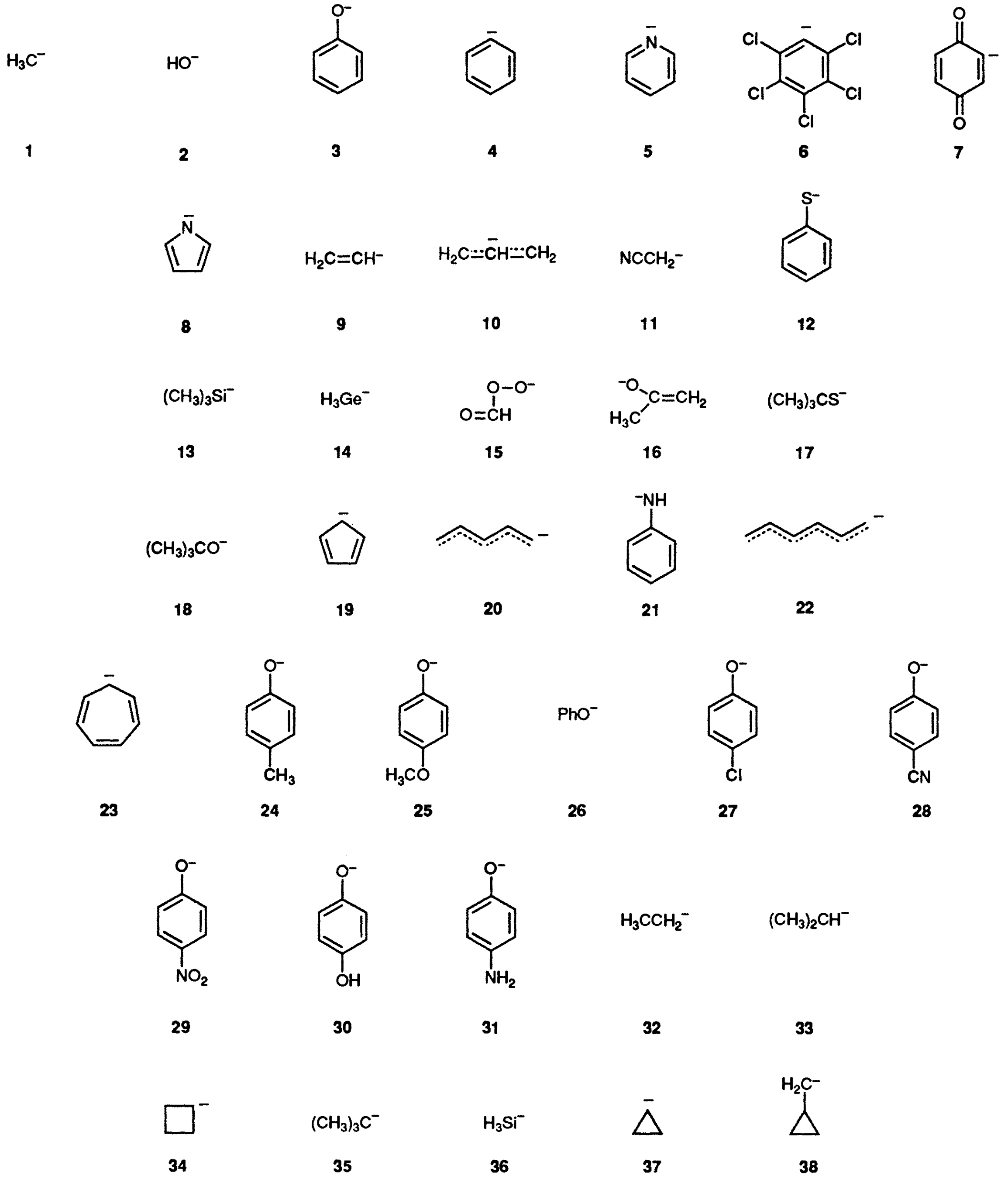

Fig. 3 Structures for Tables 4 and 5

notable, in cases such as the phenyl (**4**), pyridyl (**5**), pentachlorphenyl (**6**), benzoquinolyl (**7**), *tert*-butoxide (**18**), pentadienyl (**20**) and the heptatrienyl (**22**) anions, where the OVGF(AM1) method gives $E_i^v(\mathrm{R}^{\bullet})$ values which are lower than the Koopmans' theorem values by approximately 1.0 eV. Overall, the OVGF(AM1) method shows the best performance ($\bar{\Delta}$

Table 4 Vertical ionization potentials (eV) of anions[a] calculated by the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO and OVGF(MNDO) methods and experimental values

Entry	Anion	Symmetry	exp.	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
1	Methanide	D_{3h}	0.30[b]	−0.99	−1.12	−0.81	−0.85	−1.22	−1.33
2	Hydroxide	$C_{\infty v}$	⩾1.80[c,d]	0.88	0.72	1.01	0.93	0.47	0.33
3	Phenoxide	C_{2v}	⩾2.38[e,d]	2.70	2.31	2.69	2.39	2.53	2.14
4	Benzenide	C_s	1.03[f]	2.04	1.27	2.06	1.47	1.83	1.03
5	Pyridinide	C_s	2.40[g]	2.46	1.72	2.35	1.78	2.22	1.46
6	Pentachlorobenzenide	C_1	2.70[g]	3.87	2.86	3.75	2.93	4.02	2.98
7	Benzoquinone anion	C_s	2.00[g]	3.10	2.34	3.04	2.49	2.79	2.02
8	Pyrrolide	C_s	2.40[g]	2.55	2.34	2.72	2.59	2.40	2.20
9	Ethenide	C_s	⩾0.70[g,d]	0.76	0.40	0.81	0.60	0.47	0.12
10	Allyl anion	C_{2v}	⩾0.4[g,d]	0.71	0.41	0.74	0.52	0.63	0.32
11	Cyanomethanide	C_{2v}	⩾1.3,[g] 1.51[h,d]	1.40	1.06	1.67	1.41	1.23	0.87
12	Phenylsulfide	C_{2v}	⩾2.47[h,d]	2.92	2.51	3.10	2.71	2.63	2.22
13	Trimethylsilanide	C_{3v}	0.97[i]	1.05	0.89	2.09	2.07	0.76[j]	0.56[j]
14	Germanide	D_{3h}	1.74[h]	2.19	2.13	3.28	3.21	0.33[k]	0.32[k]
15	Performate	C_s		2.44	1.74	3.32	2.72	2.33	1.68
16	Acetonate	C_1	1.79[h]	1.97	1.60	1.95	1.69	1.75	1.40
17	*tert*-Butylsulfide	C_{3v}	2.07[h]	2.34	2.11	2.58	2.37	2.00	1.70
18	*tert*-Butoxide	C_{3v}	1.87[h]	2.59	1.86	2.55	1.95	2.63	1.86
19	Cyclopentadienide	D_{5h}	1.84[h]	2.30	2.04	2.33	2.15	2.14	1.87
20	Pentadienide	C_{2v}	0.91[h]	3.29	2.56	3.29	2.74	3.09	2.35
21	Phenylamide	C_s	1.70[h]	2.17	1.76	2.23	1.87	2.19	1.77
22	Heptatrienide	C_{2v}	1.27[h]	3.86	2.99	3.82	3.14	3.66	2.80
23	Cycloheptatrienide	C_s	0.96[l]	1.05	0.70	1.05	0.81	1.16	0.79
24	*p*-Methylphenoxide	C_1	2.24[e]	2.71	2.29	2.69	2.37	2.67	2.23
25	*p*-Methoxyphenoxide	C_1	2.09[e]	2.89	2.46	2.84	2.51	2.75	2.32
26	*p*-Fluorophenoxide	C_{2v}	2.45[e]	2.87	2.48	2.92	2.61	2.79	2.40
27	*p*-Chlorophenoxide	C_{2v}	2.63[e]	3.04	2.60	2.99	2.65	3.03	2.58
28	*p*-Cyanophenoxide	C_{2v}	3.33[e]	3.50	2.99	3.53	3.12	3.35	2.83
29	*p*-Nitrophenoxide	C_{2v}	3.55[e]	4.14	3.61	4.24	3.82	4.04	3.48
30	*p*-Hydroxyphenoxide	C_s	1.98[e]	2.84	2.44	2.60	2.30	2.69	2.28
31	*p*-Aminophenoxide	C_1	1.67[e]	2.57	2.17	2.59	2.27	2.57	2.17
32	Ethanide	C_s	−0.28[m]	−0.27	−0.56	−0.36	−0.54	−0.13	−0.41
33	Isopropanide	C_{2v}	−0.41[m]	0.10	−0.28	−0.03	−0.30	0.49	0.09
34	Cyclobutanide	C_{2v}	−0.33[m]	0.18	−0.25	0.05	−0.27	0.48	0.04
35	2-Methylpropan-2-ide	C_{3v}	−0.26[m]	0.38	−0.07	0.24	−0.09	0.92[j]	0.45[j]
36	Silanide	D_{3h}	1.41[i]	1.35	1.30	2.42[j]	2.42[j]	−0.09[j]	−0.08[j]
37	Cyclopropanide	C_1	0.36[l]	0.52	0.11	0.55	0.31	0.37	−0.03
38	Cyclopropylmethanide	C_s	0.14[m]	0.35	−0.04	0.37	0.08	0.37	−0.05

[a] The calculated values can also be described as the vertical electron affinities of the corresponding radicals. [b] From ref. 36. [c] From ref. 2(*g*). [d] The tabulated quantities are adiabatic values. [e] From ref. 37. [f] From ref. 41. [g] From ref. 32. [h] From ref. 39. [i] From ref. 38. [j] Point group of symmetry C_{3h}. [k] Point group of symmetry C_{3v}. [l] From ref. 40. [m] From ref. 41.

=0.33 eV), OVGF(PM3) comes second ($\bar{\Delta}$ = 0.43 eV) and OVGF(MNDO) is the least satisfactory ($\bar{\Delta}$ = 0.47 eV), though the differences in $\bar{\Delta}$ between the three methods are not large.

The largest specific deviations are found on the one hand for small anions like CH_3^- and HO^- (**1** and **2**), but on the other hand (and surprisingly) also for the pentadienyl (**20**) and heptatrienyl (**22**) anions. The deviations in these cases are largely independent of the semiempirical method, and may reflect therefore deficiencies in the semiempirical methods themselves or, in some of the cases, an error in the experimental values.

The success of the OVGF (semiempirical) calculations in reproducing the electron affinities is encouraging in view of the difficulties encountered in *ab initio* methods in this field. For example, *ab initio* calculations by the 'indirect' method of the electron affinity of OH^- shows that a satisfactory result can be obtained only with many-body perturbation theory (MBPT). Using the 6-311++G(3df/2p) basis-set the electron affinity of OH^- is calculated to be: −0.282, 1.927, 1.374, 1.532 and 1.764 eV for ΔSCF, ΔMBPT(2), ΔMBPT(3), ΔMBPT(4SDQ) and ΔMBPT(4), respectively,[24] compared with the experimental value of 1.825 eV. Using the electron propagator theory (EPT), with the self-energy part extended to include higher (than third) order, perturbation corrections, gives much larger errors than the MBPT results[24] [E_{ea} = 2.65 eV for the EPT (outer valence approach) method]. These results show that, for the OH^- anion, relaxation effects are very important and even *ab initio* outer valence Green's function methods with full expression for the self-energy part do not give satisfactory E_i values for this anion. From the experience gained with OH^- it is clear that, for larger anionic systems, there is at this time no satisfactory substitute for the OVGF methods coupled with semiempirical calculations used in this paper.

(*c*) *Vertical Ionization Potentials of Anion-radicals.*—The vertical ionization potential of an anion-radical $M^{-\bullet}$ is defined in eqn. (8) which also shows the relation of $E_i^v(M^{-\bullet})$ to the corresponding electron affinity of the molecule $E_{ea}(M)$.

$$M^{-\bullet}(g) \rightarrow M^*(g) + e^-; \quad E_i^v(M^{-\bullet}) \geqslant E_{ea}(M) \quad (8)$$

Table 6 collects the calculated $E_i^v(M^{-\bullet})$ values of several anion-radicals for which experimental data are also available and Fig. 4 shows their formulae.

The experimental quantities in Table 6 refer to adiabatic electron affinities determined by gas-phase equilibrium methods and therefore they give only lower limit values of $E_i^v(M^{-\bullet})$ as

Table 5 Deviation of the theoretical from the experimental vertical ionization potentials (eV) of anions calculated by the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO and OVGF(MNDO) methods

Entry	Anion	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
1	Methanide	-1.29	-1.42	-1.11	-1.15	-1.52	-1.63
2	Hydroxide	≈ -0.92[a]	≈ -1.08[a]	≈ -0.79[a]	≈ -0.87[a]	≈ -1.33[a]	≈ -1.47[a]
3	Phenoxide	≈ 0.32[a]	≈ -0.07[a]	≈ 0.31[a]	≈ 0.01[a]	≈ 0.15[a]	≈ -0.24[a]
4	Benzenide	1.01	0.24	1.03	0.44	0.80	0.00
5	Pyridine anion	0.06	-0.68	-0.05	0.62	-0.18	-0.94
6	Pentachlorobenzenide	1.17	0.16	1.05	0.23	1.32	0.28
7	Benzoquinone anion	1.10	0.34	1.04	0.49	0.79	0.02
8	Pyrrolide	0.15	-0.06	0.32	0.19	0.00	-0.20
9	Ethenide	≈ 0.06[a]	≈ -0.30[a]	≈ 0.11[a]	≈ -0.10[a]	≈ -0.23[a]	≈ -0.58[a]
10	Allyl anion	≈ 0.31[a]	≈ 0.01[a]	≈ 0.34[a]	≈ 0.12[a]	≈ 0.23[a]	≈ -0.08[a]
11	Cyanomethanide	≈ 0.10[a]	≈ -0.24[a]	≈ 0.37[a]	≈ 0.11[a]	≈ -0.07[a]	≈ -0.43[a]
12	Benzenethiolate	≈ 0.52[a]	≈ 0.04[a]	≈ 0.63[a]	≈ 0.24[a]	≈ 0.16[a]	≈ -0.25[a]
13	Trimethylsilanide	0.08	-0.08	1.12	1.10	-0.21	-0.41
14	Germanide	0.45	0.39	1.54	1.47	1.41	1.42
16	Acetonate	0.18	-0.19	0.16	-0.10	-0.04	-0.39
17	*tert*-Butylsulfide	0.27	0.03	0.51	0.30	-0.07	-0.37
18	*tert*-Butoxide	0.72	-0.01	0.68	0.08	0.76	-0.01
19	Cyclopentadienide	0.46	0.20	0.49	0.31	0.30	0.03
20	Pentadienide	2.38	1.65	2.38	1.83	2.18	1.44
21	Phenylamide	0.47	0.06	0.53	0.17	0.49	0.07
22	Heptatrienide	2.59	1.72	2.55	1.87	2.39	1.53
23	Cycloheptatrienide	0.09	-0.26	0.09	-0.15	0.20	0.17
24	*p*-Methylphenoxide	0.47	0.05	0.45	0.13	0.43	-0.01
25	*p*-Methoxyphenoxide	0.80	0.37	0.73	0.42	0.66	0.23
26	*p*-Fluorophenoxide	0.42	0.03	0.47	0.16	0.34	-0.05
27	*p*-Chlorophenoxide	0.41	-0.03	0.36	0.02	0.40	-0.05
28	*p*-Cyanophenoxide	0.17	-0.34	0.20	-0.21	0.02	-0.50
29	*p*-Nitrophenoxide	0.59	0.06	0.69	0.27	0.49	-0.07
30	*p*-Hydroxyphenoxide	0.86	0.46	0.62	0.32	0.61	0.30
31	*p*-Aminophenoxide	0.09	0.50	0.92	0.06	0.90	0.50
32	Ethanide	0.01	-0.28	-0.08	-0.16	-0.15	0.13
33	Isopropanide	0.51	0.13	0.38	0.11	0.90	0.50
34	Cyclobutanide	0.51	0.08	0.38	0.06	0.81	0.37
35	2-Methylpropanide	0.64	0.19	0.50	0.17	1.18	0.71
36	Silanide	-0.06	-0.11	1.01	1.01	1.50	1.49
37	Cyclopropanide	0.16	-0.25	0.19	0.05	0.01	-0.39
38	Cyclopropylmethanide	0.21	-0.18	0.23	0.06	0.23	-0.19
	Mean deviation	0.57	0.33	0.66	0.43	0.62	0.47

[a] See note *a* in Table 2.

Table 6 Vertical ionization potentials (eV) of anion-radicals as calculated with the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO and OVGF(MNDO) methods[a] and experimental values

Entry	Anion-radical	Symmetry	Exp.	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
1	Benzoquinone	D_{2h}	$\geqslant 1.89$[b]	2.49	2.23	2.44	2.25	2.26	2.04
2	Tetracyanoquinodimethane	C_{2v}	$\geqslant 2.8$[b]	4.09	3.50	4.24	3.72	4.06	3.45
3	Chloranil	C_{2v}	$\geqslant 2.76$[b]	3.45	3.04	3.24	2.92	3.59	3.22
4	Tetracyanoethylene	C_{2h}	$\geqslant 2.8$[b]	3.55	2.87	3.71	3.16	3.62	2.87
5	Nitrobenzene	C_s	$\geqslant 1.18$[c]	1.93	1.62	1.97	1.74	2.05	1.72
6	Anthracene	C_s	$\geqslant 0.75$[c]	1.58	1.27	1.60	1.34	1.61	1.29
7	Naphthalene	C_{2h}	$\geqslant 0.15$[d]	0.98	0.72	0.99	0.80	1.08	0.81
8	Azulene	C_1	$\geqslant 0.69$[d]	1.88	1.42	1.91	1.55	1.99	1.52

[a] The calculated values can also be described as the adiabatic electron affinities of the corresponding molecules. The experimental values are adiabatic quantities. [b] From ref. 39. [c] From ref. 42. [d] From ref. 43.

defined by eqn. (8). The molecules in Table 6 include species ranging from very strong electron acceptors like tetracyanoethylene to relatively weak acceptors like naphthalene. As in the previous cases, the OVGF values are consistently lower than the Koopmans' values and are in better agreement with experimental values. Also in this case the OVGF(AM1) method exhibits the best performance.

(*d*) *Vertical Electron Affinity of Molecules.*—The vertical electron affinity of a molecule is defined in eqn. (9), where the anion-radical has the geometry of the neutral molecule. The energy of this process is equal to the vertical ionization potential of $(M^{-\bullet})^*$ which can be computed using the OVGF method. Experimentally these quantities can be related to the negative electron affinities of unbound anions which are determined by electron transmission techniques.[25]

$$M + e^- \longrightarrow (M^{-\bullet})^*; \quad E^{v}_{ea}(M) = E^{v}_{i}(M^{-\bullet})^* \qquad (9)$$

Table 7 collects the calculated as well as the experimental vertical E_{ea} values of a number of molecules which are also illustrated in Fig. 4. Inspection of the data in Table 7 shows that

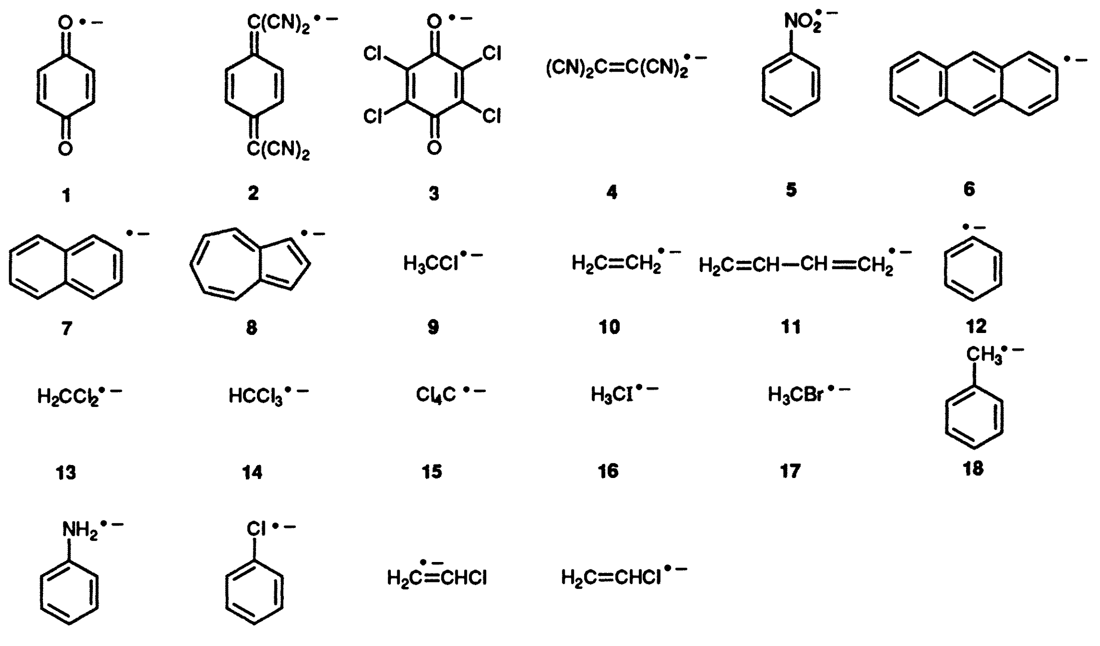

Fig. 4 Structures for Tables 6 and 7

Table 7 Vertical ionization potentials (eV) of anion-radicals as calculated with the AM1, OVGF(AM1), PM3, OVGF(PM3), MNDO and OVGF(MNDO) methods[a] and experimental values

Entry	Anion-radical	Symmetry	Exp.	AM1	OVGF(AM1)	PM3	OVGF(PM3)	MNDO	OVGF(MNDO)
9	CH_3Cl	C_{3v}	−3.7,[b] −3.45[c]	−1.08	−1.25	−0.89	−0.91	−0.57	−0.74
10	$H_2C{=}CH_2$	D_{2h}	−1.78[d]	−1.00	−1.16	−1.12	−1.17	−0.91	−1.06
11	Buta-1,3-diene	C_{2h}	−0.62[d]	0.08	−0.12	0.04	−0.09	0.14	−0.06
12	Benzene	C_{3h}	−1.15[d]	−0.03	−0.30	−0.12	−0.28	0.13	−0.15
13	CH_2Cl_2	C_{2v}	−1.23[c]	0.095	0.007	−0.53	−0.60	0.19	0.06
14	$CHCl_3$	C_1	−0.35[c]	1.16	1.07	1.19	1.16	1.56	1.44
15	CCl_4	T_D	>0[c]	2.12	2.07	1.95	1.84	2.39	2.33
16	CH_3I	C_{3v}	⩽0	−0.02	−0.19	0.94	0.89	−0.06	−0.25
17	CH_3Br	C_{3v}	—	−0.40	−0.57	0.47	0.43	−0.24	−0.41
18	Toluene	C_s	−1.11[d]	0.10	−0.21	−0.001	−0.20	0.36	0.04
19	Aniline	C_s	−1.13[d]	−0.01	−0.34	−0.035	−0.25	0.24	−0.08
20	Chlorobenzene	C_{2v}	−0.75[d]	0.48	0.17	0.38	0.18	0.77	0.44
21	$H_2C{=}CHCl$ (π^*)	C_s	−1.28[e]	−0.22	−0.46	−0.32	−0.44	0.05	−0.19
22	$H_2C{=}CHCl$ (σ^*)	C_s	−2.48[e]	2.23	1.85	2.16	1.93	2.50	2.19

[a] The corresponding radical anions have the geometry of the neutral molecules. These values can also be described as the vertical electron affinities of corresponding molecules. [b] From ref. 44. [c] From ref. 25. [d] From ref. 45. [e] From ref. 46.

the OVGF values are more *negative* (or less positive) than the corresponding Koopmans' values. As in the previous cases the OVGF quantities are in better agreement with experiment and the OVGF(AM1) method shows the best performance. However, now the agreement with experiment is fairly good only for π-systems, whereas for the σ systems (*e.g.*, entry **9**) the absolute deviations are very large. Part of the problem seems again to originate in the semiempirical method itself. It should be noted, however, that calculations of negative electron affinities [5e–g] are generally very difficult and the results for most methods are in poor accord with experiment.

Conclusions

We have used the Outer Valence Green Function (OVGF) method coupled with semiempirical MO approximations to calculate the ionization potentials and electron affinities of a variety of organic species. The calculations cover a wide variety of radical centres (*e.g.*, carbon, nitrogen, oxygen) and molecules and a substantial range of energies spanning more than 11 eV. *It is found that in general the OVGF calculations give significantly better agreement with the experimental data than the results from semiempirical calculations using the Koopmans' values.* Of the three semiempirical methods used (AM1, PM3, MNDO) the OVGF(AM1) method gives the best agreement with experiment (*e.g.*, mean deviation of 0.36 eV for the vertical ionization potential of 38 radicals) and it is therefore the most useful method currently available for calculating the ionization potentials and electron affinities of a wide variety of molecules.

Acknowledgements

David Danovich acknowledges a scholarship from the Center of Absorption in Science, Israel Ministry of Immigrant Absorption, the State of Israel. The research by Yitzhak Apeloig and by Sason Shaik was partially supported by the Basic Science Foundation Administered by the Israeli Academy of

Sciences and Humanities. Yitzhak Apeloig also acknowledges support from the Technion's V.P.R. Fund–B. G. Greenberg Research Fund (Ottawa).

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Paper 2/05727A
Received 27*th October* 1992
Accepted 16*th November* 1992