Chem. Rev. **2002,** *102,* 231–282

Atomic and Molecular Electron Affinities: Photoelectron Experiments and Theoretical Computations

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Received June 13, 2001

Contents

I. Introduction and Scope

The energy difference between an uncharged species and its negative ion, referred to as an electron affinity (EA), is an important property of atoms and molecules. Negative ions, or anions, result from neutral molecules (often radicals) binding an additional electron. The importance and utility of EAs extend well beyond the regime of gas-phase ion chemistry.[1] Indeed, there are many areas of pure chemistry,[2−6] materials science, and environmental chemistry[7] where the properties of negative ions and radicals are important. A survey of recent examples illustrates the diversity of areas in which electron affinities play a role: silicon[8] and quantum dot (nanocrystal) semiconductor chemistry,[9−12] Schottky diodes,[13] molecular clusters,[14,15] fullerene chemistry,[16−18] interstellar chemistry,[19,20] polymer photoluminescence,[21−23] microelectronics,[24] flat panel displays,[25] and even hypotheses regarding the shuttle glow phenomenon.[26]

Furthermore, the stabilities of free radicals and anions are of great importance in the determination of biochemical pathways for electron transfer, photosynthesis, oxidative phosphorylation, and oxidative stress.[27] Recent examples here include the binding of type 1 human immunodeficiency virus (HIV-1) to nucleic acids,[28] toxin chemistry,[29] photosynthesis,[30−32] electron transfer in biological systems,[33−35] and electron attachment to nucleic acid bases.[36,37]

Such examples demonstrate the importance of electron affinities in chemistry. Clearly, the magnitudes of the electron binding energies are of great

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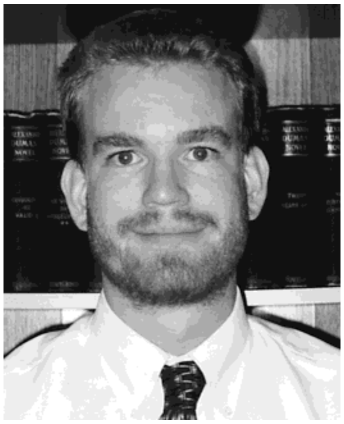

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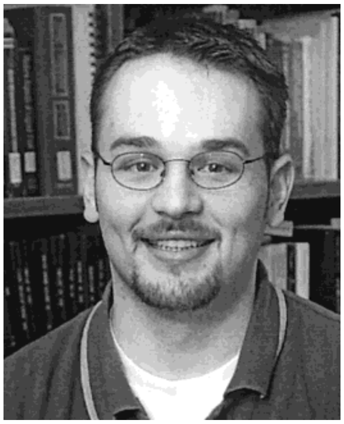

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interest. The experimental measurement and/or theoretical determination of these energetic quantities is an important task. In this review, the experimental determination of electron affinities is examined. Also examined is the ability of computational chemistry methods to predict electron affinities. A major portion of this work is a review (through January 2000) of 1101 experimentally determined electron affinities via photoelectron techniques, found in Table 10. Also included are reports of theoretical values (Tables 8 and 9) for electron affinities of 163 atoms or molecules, as predicted by density functional theory (DFT) from results by the Schaefer group.

Unfortunately, a complete survey of all experimental techniques and theoretical methods currently used for the determination of EAs is not possible, even in a review, hence the limitation in scope of Tables 8−10. On the other hand, photoelectric techniques are currently the most accurate and reliable experimental methods for measuring electron affinities, and DFT is perhaps the only widely applicable and easily employed theoretical method in use today which achieves satisfactory accuracy (within 0.2 eV) in the prediction of EAs for large molecules (with no elements of point group symmetry), by which we mean molecules with more than 50 first-row atoms C, N, and O. An entire review of all theoretical EA predictions is both impossible and impractical. Thus, our statistical analysis is restricted to a careful evaluation of the DFT results in Table 8. Nonetheless, discussion is not limited to DFT, and comparisons to the coupled-cluster (CC), Gaussian-X (G2, G3), complete basis set (CBS-M, CBS-Q), and Weizmann-X (W1, W2) theoretical methods are made. Additionally, DFT EA predictions for 53 atoms or molecules with unmeasured or uncertain experimental EAs are presented in Table 9.

This assessment of electron affinities presents a source for those seeking accurate experimental electron affinities of atoms or molecules or for those desiring an introduction to EA determination via photoelectric techniques. For experimentalists or theoreticians desiring to learn the definitions, conventions, concepts, and difficulties encountered in the study of electron affinities, this review should answer most questions. For theoreticians wishing to compare and contrast computational methods, the summary and discussion of various theoretical methods alongside the results presented in Table 8 will serve as a valuable resource. This work should facilitate further collaborations between the complementary fields of experimental and theoretical chemistry.

In this review we state definitions and conventions used in determining atomic and molecular electron affinities from both experimental and theoretical points of view. After a brief historical introduction and discussion of the photoeffect, experimental methods which exploit the photoeffect are described. A detailed examination of experimental photoelectron electron affinities is presented in Table 10, and some thermochemical uses of electron affinities are examined. The development and present status of computational chemistry techniques for the prediction of atomic and molecular EAs is also reviewed in a historical context. Specific discussion of DFT follows with a particular emphasis on the applicability of DFT to anionic species. Through comparisons to experimental EAs and results from other theoretical methods, analysis of DFT EAs is given (see Tables 6−9). In the context of other theoretical methods, the successes and failures of DFT EA predictions are detailed. The review is concluded with a brief examination of some specific EAs which are of experimental and theoretical interest.

A. Definitions of Atomic Electron Affinities

Atoms represent the simplest chemical systems from which a discussion of electron affinities can begin. Early reviews on atomic electron affinities by Hotop and Lineberger[38,39] provide a clear definition of atomic electron affinities, "The **electron affinity**, EA, of an atom A is the difference between the total energies (E_{tot}) of the ground states of A and its negative ion A^-":

$$EA(A) = E_{tot}(A) - E_{tot}(A^-) \quad (1)$$

Note that the electron affinity is positive for systems in which the neutral atom lies energetically above the anion. Time scales must be considered when the stability of the negative ion is discussed. In general, anions of atoms with positive EAs exist sufficiently long enough to play a role in chemical reactions and allow for straightforward, direct experimental investigations. Anions of atoms with negative electron affinities do not exist for any chemically significant time period (typically only a few picoseconds) and thus are usually of less interest to chemists. Only positive atomic electron affinities are discussed in this review.

The interpretation of an atomic electron affinity depends on a chemist's perspective. For example, an experimentalist may view the quantity as the energy required to remove the excess electron from the negative ion,[40] while it may be more convenient for a theoretician to consider the energy gain upon addition of the electron.[41] Both definitions are correct but imply important differences which must be delineated in any comparison of experimental and theoretical electron affinities. Specifically for atoms, an experimentally determined EA automatically includes *all* electronic effects, such as relativistic and spin−orbit effects, and is limited only by the accuracy and precision of a particular technique. Conventional quantum theoretical approaches do not typically include such "difficult" electronic effects; although theoretical evaluation of all electronic terms is possible via construction of an appropriate Hamiltonian. For practical reasons, many terms are often not included and consequently ignored or added later as energy corrections. Thus, the theoretical determination of an EA is limited by the completeness of the selected method, that is, the approximations made within the method to the full electronic Hamiltonian.

B. Definitions of Molecular Electron Affinities

The **electron affinity** of a neutral molecule is the binding energy of an electron to the molecule. From an experimental viewpoint, it is useful to think of this in analogy to a spectroscopic transition, as depicted in Figure 1. Consider a negative ion, R^-, that is stable with respect to the corresponding neutral, R, and a free electron. The electron affinity of R is the transition energy:

$$EA(R) = \Delta E(R \leftarrow R^-) \quad (2)$$

Familiar examples of R^- might be the hydroxide, methide, and vinyl anions [OH^-, CH_3^-, and $CH_2{=}CH^-$]; all are bound with respect to the corresponding neutral and a free electron, e^-. More specifically, Figure 1 indicates that the electron affinity of R is the transition energy from the ground vibrational/rotational state of the anion to the ground vibrational/rotational state of the neutral:

$$EA(R) = E\,|R, v' = 0, J' = 0\rangle \leftarrow E\,|R^-, v'' = 0, J'' = 0\rangle \quad (3)$$

The electron affinity associated with the (0, 0) band in Figure 1 is often referred to as the "adiabatic EA". It is common for spectroscopists to refer to the ground electronic state of a polyatomic species as $\tilde{X}$ and any excited electronic states of the same multiplicity as $\tilde{A}$, $\tilde{B}$, etc. Occasionally, the spectroscopic threshold corresponding to the (0, 0) band cannot be identified by experimental methods, and thus, the adiabatic EA is not available. In these cases the transition corre-

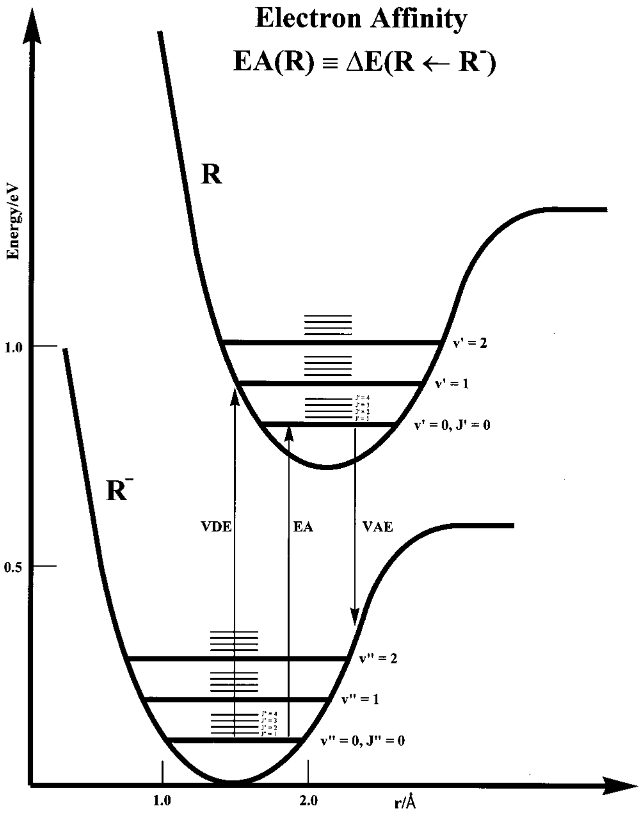


Figure 1. A qualitative diagram of potential energy surfaces for an anionic molecule, R^-, and a neutral molecule, R. The surfaces are meant to represent all diatomic and polyatomic molecules, though all anions are not necessarily lower in energy than the neutrals (cf. the text). Transitions shown represent the vertical detachment energy (VDE), adiabatic electron affinity (EA), and the vertical attachment energy (VAE). In the case of a nonlinear polyatomic with n atoms, there are $3n - 6$ modes, and this figure shows a cut through the active mode(s).

sponding to the most intense Franck–Condon features of the detachment spectrum is sometimes reported as the "vertical detachment energy", VDE.

From a theoretical perspective, the progression from atoms to molecules necessarily complicates matters. A change in nuclear configuration accompanies the transition between the neutral molecule and its anion. In electronic structure theory this introduces two Born–Oppenheimer potential energy surfaces requiring the specification of the geometries of both the neutral and anion, thereby giving rise to a myriad of possible energy differences. Only three separations are particularly useful. Figure 1 represents these cases graphically. The vertical attachment energy (VAE) and VDE are conceptually the simplest. A physical interpretation of a VAE is the energy released from the near-instantaneous addition of an electron to a neutral molecule. During such a process there is no time for geometry relaxation; both the anion and neutral species are thus at the optimized equilibrium nuclear configuration (r_e) of the neutral molecule. The VDE is conceptually equivalent, but is instead the energy required for the near-instantaneous removal of an electron from an anion. Here both anion and neutral species are at the optimized equilibrium nuclear configuration (r_e) of the anion. Note that the VDE is sometimes referred to as the first vertical ionization potential of the anion.[41] The theoretical "adiabatic" electron affinity, AEA or simply EA, represents the difference between the total energies of the neutral and anion at their respective equilibrium (r_e) nuclear configurations. A conceptual model of the corresponding physical process is a bit more difficult to imagine. An infinitely slow removal/addition of an electron which changes the anion/neutral nuclear configuration by infinitesimal increments would require/liberate an energy equal to the EA. In summary, theoretical definitions of VAE, VDE, and EA in terms of optimized, r_e, geometries are

$$\text{VAE} = E(\text{optimized neut.}) - E(\text{anion at optimized neut. geometry}) \quad (4)$$

$$\text{VDE} = E(\text{neut. at optimized anion geometry}) - E(\text{optimized anion}) \quad (5)$$

$$\text{EA} = E(\text{optimized neut.}) - E(\text{optimized anion}) \quad (6)$$

Experimental measurements, which do not directly correspond to r_e geometries, in principle, differ from all of these theoretical energy separations. That is, experimental molecular adiabatic electron affinities (eq 3) should be viewed as an EA_0 (explicitly shown in Figure 1), whereas the theoretical molecular electron affinities should be viewed as EA_e. In general, however, both values are referred to simply as "EA", and the experimental EA is usually well approximated by the theoretical adiabatic value.

The vertical quantities offer limiting values for most molecules. In situations where the nuclear configuration of the negative ion does not drastically differ from that of the uncharged parent species (as in Figure 1), the VAE and VDE provide lower and upper bounds, respectively, for the EA. These inequalities logically follow from the definition of an equilibrium geometry as the geometry at the energy minimum on the potential energy surface. Changing the geometry relative to the equilibrium structure must increase the energy. When the change occurs on the potential energy surface of the anion, the neutral–anion energy separation decreases (VAE), while the opposite is true for changes on the potential energy surface of the neutral molecule (VDE). This relationship can break down in pathological cases in which the nuclear configuration dramatically changes upon the addition or removal of an electron. ClF_7 provides an example of this behavior.[42] For this molecule, the theoretical EA near 9 eV lies approximately 2 eV above the VDE. The instability with respect to dissociation of this molecule provides a reasonable explanation of this phenomenon. The equilibrium nuclear configuration of the anion corresponds to some point along the pathway to dissociation of neutral ClF_7 into ClF_6 and F (or even ClF_5 and F_2).

In addition to the difficult electronic effects noted in atoms, another complicating factor introduced at the molecular level arises from vibrations. Harmonic zero-point vibrational energies (ZPVEs)

$$\mathrm{ZPVE} = (1/2) \sum^{3n-6} h\omega_e \tag{7}$$

where h is Plank's constant and ω_e the $3n - 6$ set (n = number of atoms) of harmonic frequencies, provide a reasonable approximation of zero-point energy contributions from the fundamental, ν, vibrations. Addition of ZPVE corrections to electron affinities allows one to approximate a theoretical EA_e as an EA_0, though the r_e optimized geometry is still used:

$$\mathrm{ZPVE\ EA} = [E(\text{optimized neut.}) + \mathrm{ZPVE}_{\text{neut.}}] - [E(\text{optimized anion}) + \mathrm{ZPVE}_{\text{anion}}] \tag{8}$$

In this review, the theoretical molecular electron affinities are presented both with and without the inclusion of ZPVE corrections. In many instances the effect is negligible, as the ZPVEs of the neutral and anionic species are usually quite similar (cf. Figure 1) and consequently the $\mathrm{ZPVE}_{\text{neut.}}$ and $\mathrm{ZPVE}_{\text{anion}}$ nearly cancel in eq 8. However, in certain molecules, such as polycyclic aromatic hydrocarbons, ZPVE corrections can account for a large percentage of the total electron affinity[43] (see Section IV.3).

To minimize confusion,[44,45] it is important to specify the electronic states of all species for the EA results presented here. Whenever possible, the electronic states for both the neutral and anionic species examined in this review are specifically stated.

It should also be noted that an electron affinity is typically only a fraction of the size of the ionization energy (IE) or, equivalently, the ionization potential (IP). **Photoionization** of a neutral species (R) induces charge separation and produces a free electron–positive ion pair, $R + h\nu \rightarrow R^+ + e^-$. As a consequence of Coulomb's law, charge separation requires a considerable amount of energy. In contrast to photoionization, **photodetachment** of an anion (R^-) produces a free electron and a neutral atom or molecule, $R^- + h\nu \rightarrow R + e^-$. For example, consider the simplest atom, hydrogen, and recall[46] that IP(H) is 13.6 eV while[47] EA(H) is only 0.75 eV. For most molecules, ionization energies are about 10 eV, and the electron affinities of most species are roughly 1 eV; IP(R) $\approx$ 10 eV, but EA(R) $\approx$ 1 eV.

While every atom and molecule has an IP, they need not have an EA. There is a large class of anions which are not bound species. Many common molecules such as N_2, H_2O, and C_6H_6 do not form stable anions. In the gas phase H_2O^- decays to H_2O plus a free electron and $C_6H_6^-$ is not stable with respect to benzene and e^-. The carbon dioxide anion is metastable for roughly 100 μs before it disintegrates: $CO_2^- \rightarrow CO_2 + e^-$. Generally, radicals, such as OH, CH_3, or $CH_2{=}CH$, bind an electron into their "half-filled molecular orbital" and form stable anions. In contrast, many closed-shell species, such as N_2, H_2O, or C_6H_6, have filled valences and do not bind an electron.

In the gas phase "temporary" negative ions, such as N_2^-, H_2O^-, and $C_6H_6^-$, can be studied by resonant electron scattering.[48,49] Several of these temporary negative ions are of great practical importance; an electrical discharge generates the N_2^- ion, which drives CO_2 lasers. The scattering resonances are "negative" electron affinities because the potential curves of the ion and neutral in Figure 1 are inverted. The anion curve is *above* that of the neutral species. Useful reviews of the spectroscopy of temporary negative ions have been written.[50,51] Jordan and Burrow's review has a complete report of electron transmission spectroscopic resonances for all molecules through 1986. It is possible to obtain theoretical predictions of negative electron affinities. At a first approximation, a negative VAE often corresponds to the resonant electron scattering energy.

Although they have no formal, positive electron affinity, water and benzene will bind an electron in clusters[52−54] or in solution.[55] The naphthalene anion is stabilized by a single water molecule.[56] However, for simplicity in this review we focus on the EA of single molecules. Other molecules without an EA may be stabilized by other means; for example, $C_6H_6^-$ has a beautiful EPR spectrum in cryogenic matrices.[57] In condensed phases, solvent molecules help stabilize binding of the electron to the host molecule by a wonderful set of dipole and multipole couplings.[58] Such stabilizations are also not discussed here.

Finally, recent research has focused on multiply charged anions (molecules binding more than one extra electron).[18,59−67] Because the number of known, well-characterized, multiply charged anions is few, only singly charged anions are analyzed in this review.

II. Experimental Photoelectron Electron Affinities

A. Historical Background

Historically, the experimental determination of electron affinities has proven difficult. Prior to 1970, experimental measurements of this chemical property were typically indirect and unreliable.[68,69] Early methods of anion photodetachment using conventional light sources were implemented by Branscomb and co-workers for the direct determination of EAs, but often there were large uncertainties associated with the results.[38,70−76] This experimental situation quickly improved with the advent of tunable laser light sources. Advancements in the production of atomic and molecular negative ions have also led to significant improvement in this field.[38] A survey of atomic electron affinities beautifully illustrates the profound impact of these recent technological advancements. In 1970, Lineberger and Woodward reported the first application of dye lasers to the measurement of an electron affinity, specifically that of the sulfur atom determined via threshold photodetachment spectroscopy.[77] By 1975, laser threshold photodetachment techniques had successfully measured the electron affinities of 19 atoms.[38] A decade later, the number of atomic systems conquered had more than doubled to 40.[39] Today, in Table 10 of this review, 1101 atomic and molecular EAs determined through photoelectron experiments are reviewed.

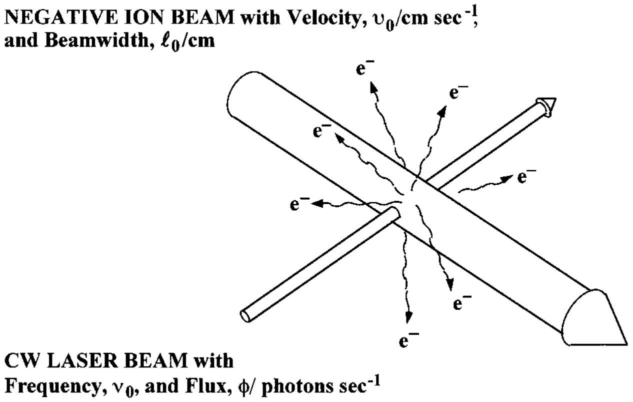


Figure 2. Negative ion photodetachment occurs at the intersection of a beam of negative ions with a laser beam.

B. The Photoeffect

Several methods have been employed to measure the electron affinities of isolated molecules. Charge-transfer reactions in a mass spectrometer, collisional ionization with fast alkali-metal beams, plasma and optogalvanic spectroscopies, and collisional ionization have been used to deduce molecular electron affinities.[1] However, the most effective methods to measure electron affinities, for either atoms or molecules, use the photoelectric effect.[78] These measurements routinely produce EA values of “chemical accuracy” with uncertainties of less than ±1 kJ mol^{-1} (±0.24 kcal mol^{-1}, ±0.01 eV).

The essential experiment is to bombard a target ion, R$^-$, with a light beam of frequency ν and to monitor either the photodestruction of R$^-$ or the appearance of the scattered electrons, e$^-$:

$$\mathrm{R}^- + h\nu \rightarrow \mathrm{R} + \mathrm{e}^- \tag{9}$$

How does the photoeffect in eq 9 work?[79,80] Consider in Figure 2 a light beam that strikes an ion beam. Suppose the frequency of the light beam is fixed at ν_0, and the photon flux, measured as photons per second, is ϕ. The target anions, called R$^-$ in eq 9, are formed into a beam of velocity v_0 (cm s^{-1}) and beam width l_0 (cm). By simple conservation of energy, if $h\nu_0 <$ EA(R), then no photodetachment can occur and no scattered electrons will be produced. If $h\nu_0$ equals or exceeds this photodetachment threshold, then photoproduction of electrons is possible. Typically one uses Beers’ law to describe photodetachment.

In Figure 2, the incident flux of photons that strike the ion beam is ϕ and the intensity of the transmitted light is $\phi e^{-\rho\sigma_D l_0}$. Consequently the current of scattered photoelectrons, j_{elect} (electrons s^{-1}), in Figure 2 is related to the incident photon flux ϕ through the photodetachment cross section, σ_D (cm^2), the ion density, ρ (cm^{-3}), and the optical path length, l_0 (cm):

$$j_{\mathrm{elect}} = \phi[1 - e^{-\rho\sigma_D l_0}] \tag{10}$$

The photoelectrons in Figure 2 are not scattered randomly or isotropically. Instead, the angular distribution of the scattered electrons can be described by a simple expression[81] that is based on dipole selection rules and angular momentum conservation. For linearly polarized light producing photoelectrons of kinetic energy E, the angular distribution has the general form

$$\sigma_D(E) = \frac{\overline{\sigma_D}}{4\pi}[1 + \beta(E)\, P_2(\cos\theta)] \tag{11}$$

where $P_2(\cos\theta) = (1/2)(3\cos^2\theta - 1)$, $\overline{\sigma_D}$ represents the total photodetachment cross section, θ measures the angle between the direction of the ejected electron and the polarization of the incident light, and $\beta(E)$ is an asymmetry parameter. Commonly, experimentalists fix the angle θ to be 54.7°, so $P_2(\cos 54.7°)$ is zero; consequently, eq 11 ensures that the angular distribution of the detached photoelectrons will be isotropic at this “magic angle”.

Time-dependent optical perturbation theory, with dipole selection rules, yields a simple expression[82,83] for the photodetachment cross section, $\overline{\sigma_D}$:

$$\overline{\sigma_D}(\nu) = \frac{16\pi^3 m^2 (-e)^2 v\nu}{3\hbar c^2} |\langle \Psi''(q)\, \mu(q)\, \Psi'(q)\rangle|^2 \tag{12}$$

In eq 12, m and e^- are the electron mass and charge while v is the asymptotic electron velocity and ν is the photon frequency. If the dipole transition moment operator is written as $\mu(q)$ (where q is the nuclear coordinate), then the transition moment integral is $\langle\Psi''(q)\, \mu(q)\, \Psi'(q)\rangle$, with $\Psi''(q)$ being the state of the initial anion and $\Psi'(q)$ the state of the final neutral. It is common to assume that the rotational/vibrational and electronic degrees of freedom are separable in both the anion, $\Psi''(q)$, and the final neutral, $\Psi'(q)$. If $\mu(q)$ is slowly varying or a constant, then $\mu(q) \approx \mu_0$ and the Condon approximation yields

$$\langle\Psi''(q)\, \mu(q)\, \Psi'(q)\rangle \approx \langle\psi''_{\mathrm{elect}}\, \mu_0 \psi'_{\mathrm{elect}}\rangle\langle\varphi''(Q'')\varphi'(Q')\rangle \tag{13}$$

The rovibrational wave functions, $\varphi''(Q'')$, are functions of the normal coordinates, Q''; the vibrational overlaps give rise to the familiar Franck−Condon factors.

Can an estimate of how many photoelectrons, j_{elect}, which will be produced when a laser crosses a stream of anions, j_{anions} (ions s^{-1}), be made? The expression for Beers’ law in eq 10 is not very convenient. Typically, experimentalists manipulate properties of the negative ion beam (the current, the beam width, and velocity) and try to generate the most laser light possible. By doing some elementary sums, the Beers’ law expression in eq 10 can be manipulated into a different form which relates the scattered photoelectrons to the current of negative ions (or anions), j_{anions}. It has been shown[84] that eq 10 can be recast so that the current of scattered photoelectrons, j_{elect}, is

$$j_{\mathrm{elect}} = j_{\mathrm{anions}}[1 - e^{-\sigma_D\phi/v_0 l_0}] \tag{14}$$

In eq 14, the current of scattered photoelectrons, j_{elect}, can never exceed the flux of anions, j_{anions}. If the detachment cross section (σ_D) becomes huge or if the photon flux (ϕ) is gigantic, then $e^{-\sigma_D\phi/v_0 l_0} \rightarrow 0$ and $j_{\mathrm{elect}} \approx j_{\mathrm{anions}}$. On the other hand, if the ion beam velocity

(v_0) is very large, then $e^{-\sigma_D\phi/v_0 l_0} \approx 1$ with the consequence that $j_{elect} \approx 0$.

What are some common experimental values? Typically j_{anions} is approximately 0.1 nA or 10^9 ions s^{-1}. Ar III laser radiation at 351 nm has a frequency (ν) of 8.5×10^{14} Hz or a wavenumber of 28490 cm^{-1}. If the laser beam in Figure 2 is thought of as a stream of photons, then ϕ is $nh\nu$, where h is Planck's constant, 6.6×10^{-34} J s. Consequently, a 50 W Ar III laser generates roughly 9×10^{19} photons s^{-1}. Suppose the photodetachment[82,85] cross section, σ_D, is 6×10^{-18} cm^2 and that the ions are focused down to a small beam diameter, typically $l_0 \approx 0.1$ mm. The ion beam energy is roughly 40 V, so the ions have a velocity, v_0, of 2.2×10^6 cm s^{-1}. Inserting parameters, one estimates $\sigma_D\phi/v_0 l_0$ to be 0.02. This small number ensures that eq 14 can be linearized and used to compute the flux of scattered photoelectrons:

$$j_{elect} \approx j_{anions}\left[\frac{\sigma_D\phi}{v_0 l_0}\right] \qquad (15)$$

Inserting numbers into eq 15, it can be conjectured that the rate of photodetachment will be 2×10^7 electrons s^{-1}. This estimate of the photodetached electrons supposes that they are scattered into all space (4π steradians), but the experimental apparatus generally has a hemispheric analyzer to count the electrons. This detector only collects the small fraction of the photoelectrons that are scattered into a 5° acceptance angle, so $d\Omega \approx 4\pi/2000$. This implies that the electrostatic analyzer will experience count rates of $(4\pi/2000)(2 \times 10^7$ electrons $s^{-1})$ or roughly 2×10^5 electrons s^{-1}. This is the approximate electron count rate that is observed from most atoms. The rates for molecules are commonly much smaller because of molecular Franck−Condon factors and lower ion beam currents.

C. Experimental Methods

One of the most powerful methods to study the photoelectric effect in eq 9 is to scan the frequency of the laser, ν, and monitor[86−88] either the appearance of the scattered electrons, e^-, or the photodestruction of the ions, R^-. This can be a very precise method to find the **threshold** for photodetachment ($h\nu_{thresh}$) because it is straightforward to control the laser frequency to a few megahertz; thus, ν is measured to be $\sim\pm 3 \times 10^{-4}$ cm^{-1} or $\pm 4 \times 10^{-8}$ eV! In Table 10 threshold EA values are denoted "ThD". Thus, the electron affinity of the H atom has been measured by observation of the photodestruction threshold[47] for H^- at 6082.99 ± 0.15 cm^{-1}, corresponding[89] to EA(H) = 0.754195 ± 0.000019 eV. The deuterium atom, D, has a slightly different electron binding energy. The photodetachment threshold for D^- was found to be 6086.2 ± 0.6 cm^{-1}, implying that EA(D) = 0.754593 ± 0.000074 eV. When threshold measurements can be carried out on a polyatomic molecule, very precise electron affinities can be determined. As an example,[90−92] the threshold for the detachment $CH_2CHO^- \rightarrow CH_2CHO$ is measured to be $\nu_{thresh} = 14718^{+2}_{-5}$ cm^{-1} or EA(CH_2CHO) = 1.8248 ± 0.0004 eV. The selection rules for atomic and molecular threshold processes have been reviewed.[93]

As the target ions become larger and more complex, it becomes very difficult to identify the true threshold for electron detachment. So instead of scanning the frequency of the radiation ν in eq 9, a fixed-frequency, ν_0, laser can be used to detach the electron provided that $h\nu_0$ is greater than $h\nu_{thresh}$.

$$R^- + h\nu_0 \rightarrow R + e^-(KE) \qquad (16)$$

In eq 16 a neutral, R, is produced along with detached electrons that have a distribution of kinetic energies (KEs). To study the **photoelectron spectroscopy** (PES) of R^-, the scattered electrons must be collected and their kinetic energies measured. The electron affinity is simply the difference (Figure 1) between the incident photon, $h\nu_0$, and the KE of the electrons arising from the (0,0) band: $EA(R) = h\nu_0 - KE(0,0)$. In Table 10 photoelectron EA values are denoted "PES". In addition to the electron affinity, the photoelectron spectrum of a negative ion provides the experimentalist with a set of different electronic bands each with their attendant Franck−Condon factors (vide infra).

The classical negative ion photoelectron experiment is carried out with continuous laser irradiation followed by electron analysis with a hemispherical analyzer.[94,95]

Figure 3 is a sketch of a continuous wave (CW) negative ion photoelectron spectrometer. The ions in eq 16 are produced in a variety of high-pressure sources. An effective method for generating anions is to use ion−molecule chemistry in a flowing afterglow device[94] to generate target anions. A flowing afterglow ion source is chemically versatile and has the virtue of producing collisionally relaxed target ions which suffer roughly 10^4 collisions with the buffer gas.[96−100] For example, one can easily produce[101] ion beams of the *o*-benzyne anion from the oxide anion and benzene: $O^- + C_6H_6 \rightarrow H_2O + C_6H_4^-$. In Figure 3, ions are extracted from the ion source at pressures of 10^{-4} mbar, formed into a beam in a separate chamber (10^{-5} mbar), and accelerated to approximately 700 V. A Wien filter velocity-selects the anions; since the ions are delivered at a constant potential (so $(1/2)mv^2$ is fixed), this is tantamount to mass selection. The mass-selected negative ions then enter a chamber outfitted with a laser/electrostatic analyzer.

The negative ion beam enters the scattering chamber at an energy of roughly 700 eV, and beam currents are typically about 0.1 nA. The ions are decelerated to a beam energy of about 40 eV and are carefully focused onto a laser/ion interaction region (Figure 4) where they are subjected to irradiation by a CW laser.

Generally, the continuous light source is an argon ion laser operating on one of the 488.0 nm (2.540 eV), 364.0 nm (3.406 eV), or 351.1 nm (3.531 eV) lines; laser powers of 50−75 W can be achieved. The resolution for these hemispherical electrostatic analyzers is approximately ±0.005 eV.

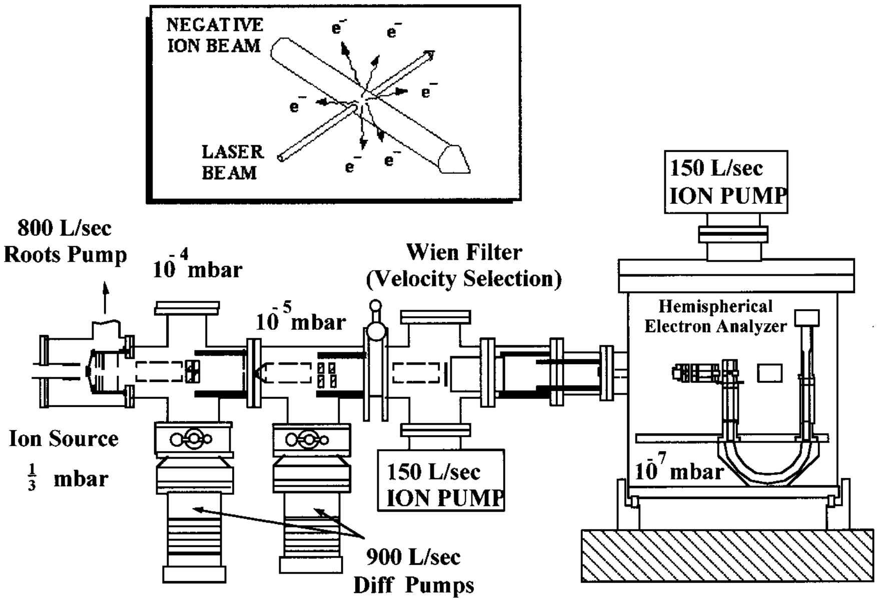


Figure 3. An overview of a negative ion photodetachment spectrometer. Negative ions are produced by microwave bombardment of an appropriate gas mixture, extracted into an ion beam, selected by a Wien filter, and delivered to a laser interaction/hemispherical analyzer chamber.

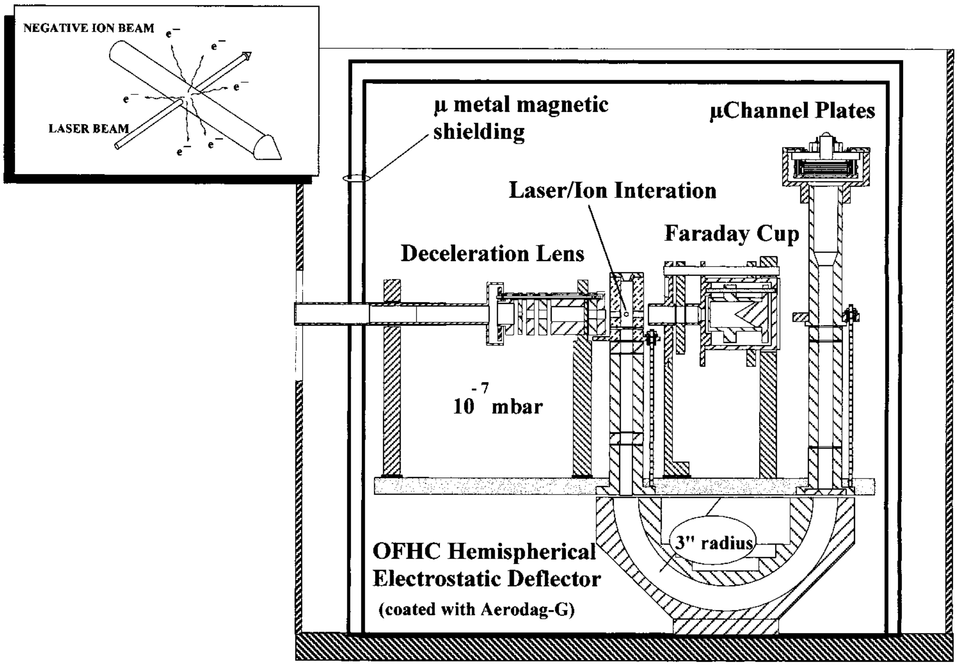


Figure 4. A schematic view of the electrostatic hemispherical analyzer used for analysis of the scattered photoelectrons. The laser beam is directed out of the plane of the figure and focused at the spot marked "Laser/Ion Interaction".

A typical negative ion photoelectron spectrum,[102] namely, that for the hydroperoxide anion, HO_2^-, is shown in Figure 5. This figure shows the origin for $HO_2^- + h\nu_{351\,nm} \rightarrow HO_2 + e^-(KE)$ is observed at a center-of-mass (CM) kinetic energy of 2.448 ± 0.006 eV. To correct for voltage drifts in the electrostatic analyzer due to contact potentials, etc., the photoelectron spectra must be internally calibrated with a "known" atomic ion. In Figure 5 the photoelectron spectrum is calibrated[103] with respect to O^- and transformed to the CM frame by a standard[104] expression where E is the CM kinetic energy (eV) of an electron detached from an ion of mass M (Da) which is passed by the energy analyzer when the slit voltage is V. The beam energy is W, m_e is the mass of an electron, and γ is a dimensionless scale compression factor (typically 1.000 ± 0.006): $E = E_{cal} + \gamma(V - V_{cal}) + m_eW\,(1/M_{cal} - 1/M)$. The "raw" electron affinity of HO_2^- is extracted from the (0, 0) band at 2.448 eV (see Figure 1) and yields an initial value for EA(HO_2) of 1.083 eV (3.531 − 2.448 eV).

One must include a final, small correction. Photoelectron spectroscopy may be considered a low-resolution technique since the resolution of the electron analyzer is roughly ±0.005 eV (or 40 cm^{-1}). This means that a photoelectron spectrometer can resolve most electronic and vibrational bands but is inadequate to separate rotational transitions. Con-

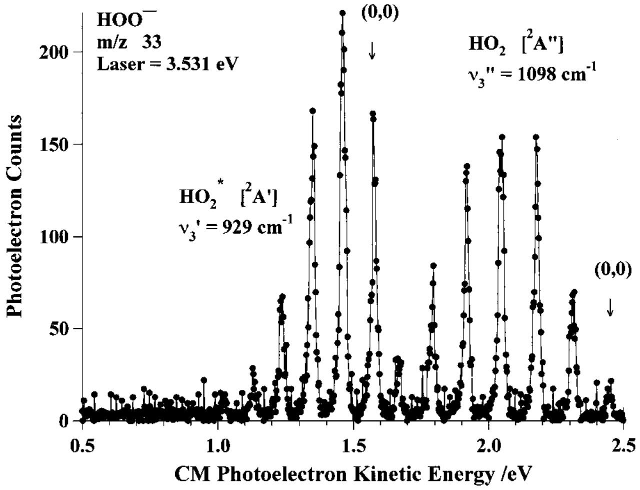


Figure 5. Negative ion photoelectron spectrum of HO_2^- as a function of the center-of-mass electron kinetic energy (eV). No scattered electrons will have energies exceeding that of the laser, 351.1 nm or 3.531 eV. The origin of the spectrum at 2.448 ± 0.006 eV marks the HO_2 ($v' = 0$) ← HO_2^- ($v'' = 0$) transition and is labeled (0, 0). When suitably corrected (see the text), this feature yields the electron affinity of ground-state $\tilde{X}\ ^2A''$ of HO_2; EA(HO_2) = 1.078 ± 0.006 eV. The origin for detachment of HO_2^- to the excited state of HO_2 is indicated by (0, 0) at 1.576 eV. The splitting between the two origins yields the term value for the HO_2 radical, $\Delta E(\tilde{A}\ ^2A'-\tilde{X}\ ^2A'')$, of 0.872 ± 0.007 eV.

sequently, the EA (see Figure 1) is rotationally uncertain. Suppose that the target anions in eq 9 have a mean rotational energy, $\epsilon''_{\mathrm{rot}}$, where $\epsilon''_{\mathrm{rot}}$ is the Maxwell–Boltzmann average of the ion distribution, $\epsilon''_{\mathrm{rot}} = \langle E''_{\mathrm{rot}}\rangle$. Consequently, the measured, raw EA is simply

$$\text{raw EA} = \text{EA} - \epsilon''_{\mathrm{rot}} + \epsilon'_{\mathrm{rot}} = \text{EA} + \Delta_{\mathrm{rot}} \quad (17)$$

Engelking[105] has derived useful, approximate expressions for the rotational correction, $\Delta_{\mathrm{rot}} \equiv \epsilon'_{\mathrm{rot}} - \epsilon''_{\mathrm{rot}}$. In his expressions, k_B is the Boltzmann constant, T is the "effective" temperature of the ion beam, and A_e, B_e, and C_e are the rotational constants of the ion (double prime state) and final neutral (single prime state):

$$\Delta_{\mathrm{rot}} \approx k_B T\left[\frac{A'}{2A''} + \frac{B'}{2B''} + \frac{C'}{2C''} - \frac{3}{2}\right] + \left(\frac{B'' - B'}{3}\right) \quad (18)$$

Use of the rotational correction (using calculated and/or known rotational constants) improves the raw EA(HO_2) and results in the final adiabatic electron affinity. The 200 K rotational correction, Δ_{rot} in eq 18, is found to be 0.005 eV, which yields the final value for EA(HO_2) as 1.078 ± 0.006 eV.

At an electron kinetic energy of 1.576 ± 0.010 eV, the (0, 0) band or origin for detachment to the first excited state of HO_2 is observed. After rotational correction (eq 18) to determine the (0, 0) feature for the $\tilde{A}$ state, these data fix the separation ΔE(ground state − excited state)[HO_2] as 0.872 ± 0.007 eV. The vibrational fine structure in the photoelectron spectrum of HO_2^- is controlled by the Franck–Condon factors via eqs 12 and 13. Both spectral bands in Figure 5 show extensive activity in the HO–O stretching vibration of the *neutral radical*, HO_2. The vibrational frequencies for the hydroperoxyl radicals that are extracted from Figure 5 are found to be 1098 cm^{-1} for the HO_2 ground-state stretch (ν''_3), while the excited HO_2* state stretch is 929 cm^{-1} (ν'_3).

As mentioned earlier, the yields of photodetached electrons are angle dependent. The anisotropy factor $\beta(E)$ in eq 11 can vary from −1 to +2 ($-1 \le \beta \le +2$). The photoelectron spectra shown in Figure 5 are collected under conditions where θ is set to the magic angle of 54.7° so that $I(\theta) = \bar{\sigma}/4\pi$ and is independent of $\beta(E)$. If spectra are collected at $\theta = 0°$ ($\mathbf{E}_{\mathrm{laser}}$ and collection direction parallel) and $\theta = 90°$ ($\mathbf{E}_{\mathrm{laser}}$ and collection direction perpendicular), one can extract a value for the anisotropy factor:

$$\beta = \frac{I_{0°} - I_{90°}}{(1/2)I_{0°} + I_{90°}} \quad (19)$$

The value of β provides important information as to the nature of the photodetached electron. In atoms, detachment of an s-electron leads to an outgoing p-wave ($l = 1$) and $\beta = +2$, independent of the electron kinetic energy. Detachment of a p-electron results in a mixture of interfering s- and d-waves and leads to an energy-dependent value for $\beta(E)$. At the photodetachment threshold, s-wave ($l = 0$) detachment dominates, giving $\beta = 0$ and yielding an isotropic photoelectron angular distribution. At photoelectron kinetic energies roughly 1 eV above the threshold, d-wave detachment becomes important and $\beta \to -1$. Electron detachment from molecular ions is more complicated than the atomic case, but β is generally found to be positive for detachment from σ (s-like) orbitals and negative for detachment from π (p-like) orbitals.

For the HO_2^- spectrum in Figure 5, $\beta = -0.80 \pm 0.15$ for the $\tilde{X}$ state and -0.59 ± 0.15 for the $\tilde{A}$ state. These different values of β indicate detachment from two different orbitals of the negative ion; they are both negative, indicating detachment from π-type orbitals, as predicted[102] from general valence bond (GVB) diagrams.

D. Time-of-Flight Negative Ion Photoelectron Spectroscopy

A major advance in photoelectron spectroscopy was the use of pulsed lasers to photodetach negative ion beams.[106] These devices offer the use of photons in eq 16 that are more energetic than the 488 and 351 nm lines of a continuous wave argon ion laser. The pulsed negative ion beams are intersected with the output of a pulsed yttrium aluminum garnet (YAG) solid-state laser and the resultant detached electrons detected by time-of-flight (TOF) spectrometry.[107,108] Use of a pulsed laser (20 Hz) provides the third (354.6 nm/3.496 eV), fourth (266.0 nm/4.661 eV), and fifth (212.8 nm/5.826 eV) harmonics of the YAG.

The first negative ion photoelectron spectrometers were based on continuous (both laser and ion) beam methods.[104] While these instruments were capable of exquisite resolution, they were limited to species with low electron affinities (<3.5 eV) due to their reliance

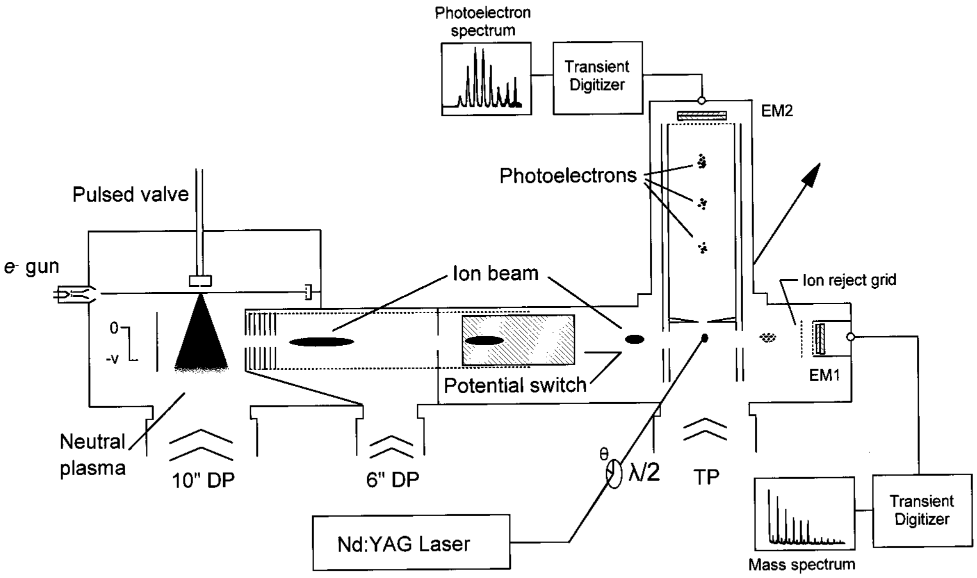


Figure 6. Schematic diagram of a time-of-flight negative ion photoelectron spectrometer. EM1 and EM2 are microchannel plate electron multipliers, DP = diffusion pump, TP = turbomolecular pump, and $\lambda/2$ = half-wave retardation plate. The "potential switch" drops from 2.5 kV to ground while the ions are inside to allow both the ion source and the electron analyzer to be maintained at ground potential during operation.

on argon ion lasers to carry out photodetachment. Pulsed lasers (e.g., Nd:YAG), on the other hand, have no such limitation since their energy coverage can be readily extended using nonlinear optical schemes to generate high harmonics of the powerful fundamental beam. The ion community was slow to adopt pulsed laser sources, however, due to the dramatic difference in duty cycles between the continuous ion beam spectrometers and the rather low repetition rates (10–30 Hz) at which Nd:YAG lasers can operate.

The duty cycle problem was overcome in 1986 when Posey and Johnson[106] developed a new type of photoelectron spectrometer (shown schematically in Figure 6) based entirely on time-of-flight concepts for *both* mass selection and electron energy analysis. In their method, the ions were generated using an electron-beam-ionized, pulsed supersonic expansion to create an overall electrically neutral plasma containing a high density of thermally equilibrated electrons.[109] Negative ions were formed by attachment of these electrons in the dense region near the nozzle, and the plasma was allowed to dissipate until its Debye length increased to the point that molecular ions could be extracted into a time-of-flight mass spectrometer by simply pulsing the voltage across two grids. To achieve mass selection, they used a so-called "Wiley–McLaren" two-field acceleration configuration[110] to spatially focus the ions along the drift axis. In its usual implementation, a particle detector is placed at this transient focus so that the resulting TOF mass spectra display optimal resolution. In the Posey–Johnson scheme, however, the photodetachment laser is timed to intersect the focused ion packet just at it arrives at the sampling orifice of a photoelectron drift tube. This strategy, in essence, bunches the ion beam for efficient overlap with the infrequent pulses from the laser.[109]

The performance of the TOF instrument is illustrated in Figure 7, displaying the spectrum from

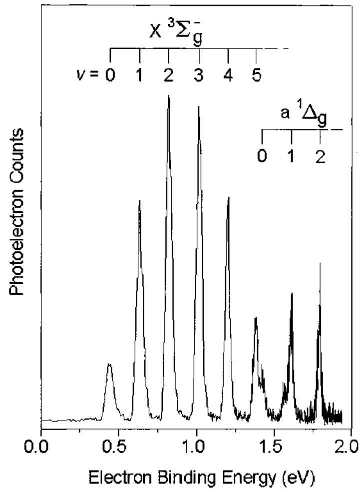


Figure 7. Photoelectron spectrum of O_2^- taken using a TOF apparatus (cf. Figure 6) at $h\nu = 2.33$ eV. Notice that the singlet/triplet splitting, $\Delta E(^3\Sigma_g^-, {}^1\Delta_g)$, of the "diradical" O_2 can be directly read from the spectrum.

O_2^- photodetached with 2.33 eV photons (second harmonic from a Nd:YAG laser). Each mass-selected ion packet contains on the order of 10^5 ions, 90% of which can be photodetached with readily achieved output or fluences from commercial lasers (~100 mJ/pulse). The Yale instrument used a field-free electron velocity analyzer, shielded from stray magnetic fields by two concentric μ-metal cylinders. Like the CW instruments, this arrangement has a rather poor electron collection efficiency (~10^{-3}), resulting in typical count rates of a few photoelectrons per laser pulse. Data are therefore acquired for 10^5 laser shots or so to obtain spectra with signal-to-noise ratios comparable to those of the spectra generated using the CW spectrometers. The resolution of the TOF instrument depends on the electron kinetic energy, and is about 10 meV in the 1 eV kinetic energy range. This is comparable to that obtained using CW

Table 1. Hydrocarbon Energetics

A. Hydrocarbon Electron Affinities (cf. Table 10)

R	EA(R)/ kcal mol^{-1}	R	EA(R)/ kcal mol^{-1}
CH_3	1.8 ± 0.7	CH_6H_5	25.3 ± 0.1
$CH_2{=}CH$	15.4 ± 0.6	$HC{\equiv}C$	68.5 ± 0.1

B. Bond Energies and Hydrocarbon Acidities (Related by Eq 20)

bond energy	DH_{298}(R−H)/ kcal mol^{-1}	acidity	$\Delta_{acid}H_{298}$(R−H)/ kcal mol^{-1}
$CH_4 \rightarrow CH_3 + H$	104.9 ± 0.1	$CH_4 \rightarrow CH_3^- + H^+$	416.7 ± 0.7
$CH_2{=}CH_2 \rightarrow CH_2CH + H$	109.7 ± 0.8	$CH_2{=}CH_2 \rightarrow CH_2CH^- + H^+$	409.4 ± 0.6
$C_6H_6 \rightarrow C_6H_5 + H$	113.5 ± 0.5	$C_6H_6 \rightarrow C_6H_5^- + H^+$	401.7 ± 0.5
$HC{\equiv}CH \rightarrow HCC + H$	131.3 ± 0.7	$HC{\equiv}CH \rightarrow HCC^- + H^+$	378.0 ± 0.6

techniques (<5 meV),[95,111] but note that the CW instruments maintain this resolution over the entire scan. On the other hand, the TOF approach expands the range of PES to essentially all species, independent of electron binding energy, and it has become the method of choice for most workers presently active in the field. Many of these newer TOF instruments exploit "magnetic bottle" technology[112,113] to capture almost 100% of the photoelectrons at a modest cost in resolution (20−30 meV), usually arising from the velocity of the ion beam.

E. Some Thermochemical Uses of Electron Affinities

As discussed in section I, there are a number of chemical uses for molecular electron affinities. Here their role in the measurement of several molecular thermochemical properties is highlighted. The experimental electron affinities are presented in Table 10.

There are a number of regularities in the electron affinities reviewed in Table 10 that will be familiar to any structural chemist. Indeed, one could write several additional articles relating the EAs of families of atoms or molecules to each other. For example, one expects that, as the "hybridization" of carbon changes from sp^3 to sp, the electron affinity will increase because the s-character of the binding orbital increases. Table 1 gives the appropriate values, and one sees that [sp^3] EA(CH_3) < [sp^2] EA($CH_2{=}CH$) < [sp^2] EA(C_6H_5) < [sp] EA($HC{\equiv}C$). It is notable to see how fragile the methide anion [CH_3^-] is. From Table 10, notice that EA(C) = 1.26 eV and EA(CH) = 1.23 eV but EA(CH_2) = 0.65 eV and EA(CH_3) = 0.08 eV. Since the kinetic energy of a gas−kinetic collision is 3/2 k_BT [for $T = 298$ K this is roughly 0.04 eV], CH_3^- will easily suffer collisional detachment and, hence, will be difficult to prepare. This is why it is hard to prepare negative ion beams of CH_3^- or to study it in a flow tube.

In conjunction with gas-phase acidities,[114−116] $\Delta_{acid}G_{298}$(RH), and enthalpies of deprotonation, $\Delta_{acid}H_{298}$(RH), the radical electron affinity, EA(R), can be combined in a thermochemical cycle[117] to provide a measurement of the molecular bond energy, D_0(RH), and the bond enthalpy, DH_{298}(RH):

$$\Delta_{acid}H_{298}(RH) = DH_{298}(RH) + IP(H) - EA(R) - \text{thermal correction} \quad (20)$$

The correction is simply the difference in heat capacities, thermal correction = $\int dT\{C_p(R) - C_p(R^-) + C_p(H) - C_p(H^+)\}$, and is small (≤1.3 kJ mol^{-1}). To a very good approximation one can write $\Delta_{acid}H_{298}(RH) \approx DH_{298}(RH) + IP(H) - EA(R)$. If the heat of formation, Δ_fH_{298}(RH), of the neutral precursor is available, the EA/acidity cycle will provide absolute heats of formation of the corresponding radicals, Δ_fH_{298}(R), since $\Delta_fH_{298}(R) = DH_{298}(RH) + \Delta_fH_{298}(RH) - \Delta_fH_{298}(H)$. For example,[118] measurements of the electron affinities of $HC{\equiv}C$, $H_2C{=}CH$, and $H_2C{=}C$ [EA(HCC) = 2.969 eV, EA(CH_2CH) = 0.667 eV, EA(CH_2C) = 0.490 eV] and the corresponding hydrocarbon enthalpies of deprotonation, $\Delta_{acid}H_{298}$(HCC−H), $\Delta_{acid}H_{298}$(H_2CCH−H), and $\Delta_{acid}H_{298}$(H_2CC−H), were used to establish the bond energies of acetylene and ethylene. Likewise, the gas-phase acidity of benzene[119] has been reported as well as the electron affinity of the phenide anion.[120] Use of the negative ion cycle in eq 20 was used to find the bond enthalpies (DH_{298} − bond energies at 298 K) of some of the most fundamental bonds in organic chemistry;[117] these values are collected in Table 1.

There is a small detail that must be considered in the thermodynamics of ions; this has to do with the heat capacity of a free electron.[121] This question is extensively discussed in Ervin's recent review.[116] Instead of a transition energy in eq 2, many chemists like to consider the electron affinity as the enthalpy of reaction, eq 21, where EA(R) ≡ Δ_rH_T (eq 21) =

$$R^- \rightarrow R + e^- \quad (21)$$

Δ_fH_T (R) + Δ_fH_T (e^-) − Δ_fH_T (R^-). Of course, at 0 K, the enthalpy is the energy: EA(R) ≡ Δ_rH_0(eq 21). How about other temperatures, T, such as 298 K? A convention that must be agreed on is how to deal with Δ_fH_T (e^-). We, and many others,[122] adopt the "electron convention", which deals with electrons as if they were elements. In this case, $\Delta_fH_T (e^-) \equiv 0$ for all temperatures. The other major convention, the "ion convention", assigns the integrated heat capacity of the electron to the electron's standard enthalpy of formation at each temperature, i.e., $\Delta_fH_T (e^-) = \int dT\, C_p(e^-)$ or 6.197 kJ mol^{-1} at 298 K in the ideal gas approximation. For example, let us consider the methyl radical and the methide anion (CH_3 and CH_3^-), the simplest organic radical/carbanion pair. Table 10 lists EA(CH_3) = 0.080 ± 0.030 eV, while the heat of formation of the CH_3 radical is well-known.[117,122] If we adopt the electron convention and use Ervin's "corrected" expression (29), $\Delta_f H_T(CH_3^-) = \Delta_f H_T(CH_3) - (0.080 \pm 0.030\ \mathrm{eV})$ or $\Delta_f H_0(CH_3^-) = 142.0 \pm 2.9\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H_{298}(CH_3^-) = 138.6 \pm 2.9\ \mathrm{kJ\ mol^{-1}}$.

In addition to bond energies, the proper determination of electron affinities is an important goal in the field of gas-phase ion thermochemistry[123] and complements the determination of other thermochemical properties, such as ionization potentials and gas-phase acidities. Furthermore, as discussed in section I, electron affinities play a role in many chemical processes. Because the emphasis in this review is on the determination of EAs, discussion of other uses of electron affinities is not included here.

F. Layout of Table 10: Experimental Photoelectron Electron Affinities

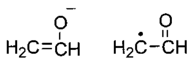
The most effective method to determine atomic and molecular electron affinities is the photoelectric effect, and this technique has been used to measure most of the experimental values found in the literature.[116] To limit the scope of this review, the table of experimental electron affinities, Table 10, only includes values determined by photoelectron spectroscopy or threshold detachment spectroscopy, and EA values determined from charge-transfer reactions,[124] plasma and optogalvanic spectroscopies, collisional ionization processes,[125] electron capture,[126,127] electron attachment negative ion mass spectrometry,[128] or other methods are not included. A short overview of many of these methods has been presented by Lias and Bartmess,[123] and the reader interested in methods other than photoelectron techniques should consult their work.

In all photoelectron experiments, the target anion is identified by measurement of the mass-to-charge ratio (m/z) of the negative ion beam. The use of sharply tuned lasers and modern electrostatic or TOF analyzers generally provides molecular electron affinities with uncertainties of roughly ±0.005−0.020 eV, ±0.1−0.5 kcal mol^{-1}, or ±0.4−2.0 kJ mol^{-1} or better. Because several atoms do not form bound ions, these are not included in Table 10; atoms without a positive electron affinity are He, Be, N, Ne, Mg, Ar, Mn, Zn, Kr, Cd, Xe, Hg, and Rn. The binding energies of all atoms has been reviewed elsewhere.[39,129] There have been several earlier atomic and molecular electron affinity tables.[1,38,39,115,129−134] Perhaps the most useful source to date is available on the Internet as part of the NIST Chemistry Webbook,[134] which also provides other thermochemical data such as ionization energies, appearance energies, and gas-phase acidities. The present review in Table 10 includes newer EA data that have been recently reported and is intended to provide the most accurate source of photoelectron-determined EAs, thus complementing the online NIST Chemistry Webbook.

Table 10 reviews 1101 experimental electron affinities for atoms and molecules that is inclusive up to January 2000. There are many ways to organize a review such as this, and the chosen format is convenient for ion chemists. This table displays the atoms and molecules in order of their m/z ratio (Da). For convenience, the nominal atomic masses to compute m/z have been used. For example, Cl is 35 Da under this convention. Because there are a number of specifically deuterated ions, the ^{2}H isotope of hydrogen has been included and is listed as D. Each EA is labeled as "ThD" if it results from a threshold measurement, eq 9, or "PES" if a photoelectron experiment was reported, eq 16. All electron affinities are reported in units of electronvolts.[89] Often it is convenient to know the optical assignments for the anions and neutrals. Consequently, if the spectroscopic assignments have been made for either the neutral (M) or the ion (M$^-$), Table 10 presents them as M ← M$^-$. For example, cyanide anion (CN$^-$, $^1\Sigma^+$) is detached to produce the cyano radical (CN, $^2\Sigma^+$), so this transition is listed in Table 10 as $^2\Sigma^+ \leftarrow {}^1\Sigma^+$. In the case of atoms, it is useful to include the dominant configurations of the species as well. For example, for carbon, C (2p^2) $^3P_0 \leftarrow$ C$^-$ (2p^3) $^4S_{3/2}$.

Several of the molecular ions have complex structures and specialized names, for example, the benzyne anions, o-$C_6H_4^-$ and p-$C_6H_4^-$. To help keep track of these compounds, a number of these species have their structures drawn in an accompanying list of structures in Chart 2. Many times there are differences between the structures of the anion and the neutral. For example, the vinyl oxide anion, CH_2CHO^- at m/z 43 Da, is best represented as the enolate structure, while the neutral, CH_2CHO, is depicted as the formylmethyl radical where the dot marks the radical site as depicted in Chart 1.

Chart 1



$H_2C{=}\overset{O^-}{\overset{|}{C}}H \qquad H_2\dot{C}{-}\overset{O}{\overset{\|}{C}}H$

In a review of this complexity, it is easy to confuse negative ions (−) and radicals (•). In most cases the radical site is obvious; for example, the hydroxyl or vinyl radicals are written as OH (not •OH) and CH_2-CH (not CH_2CH•). Table 10 is the set of electron affinities presented in a manner suitable to mass spectroscopists and ion−molecule chemists. But many biochemists, atmospheric scientists, engineers, etc. might prefer a different, simpler list in which all EAs are arranged from lowest to highest. This has been done in Table 11, which is submitted as Supporting Information.

III. Theoretical Determination of Electron Affinities

A. Historical Background

1. Theoretical Predictions of Atomic Electron Affinities

The simplest EA to examine from a theoretical perspective is EA(H). The early work of Pekeris,[135,136] which included a Hylleras treatment of H$^-$ followed by various corrections (e.g., relativistic, spin−orbit, and Lamb shift), yielded a theoretical electron affinity for the hydrogen atom, the precision of which was not challenged experimentally until 1991.[47] Even more precise experiments are required to resolve the

0.04 cm^{-1} variance between Pekeris' electron affinity and that obtained by Aashamar using Hylleras−Scherr−Knight variational perturbation wavefunctions through 20th order.[137]

However, theoretical determination of other atomic electron affinities has been plagued by difficulties and is best understood by examining the methods used to make theoretical predictions of atomic EAs. As pointed out by Blondel,[40] the existence of negative ions depends significantly upon the instantaneous correlation of the motions of electrons. In retrospect, it is not surprising that Hartree−Fock theory, an ab initio quantum chemical method which only correlates the motions of electrons with parallel spin, essentially fails when employed to compute electron affinities. For example, of the first-row atoms (H, Li, ..., F) only carbon and fluorine have positive electron affinities at the Hartree−Fock level of theory.[138−140] Early attempts to include electron correlation[141−146] in ab initio computations of EAs immediately led to qualitatively correct descriptions of the first-row negative atomic ion stabilities. Yet, as demonstrated by the work of Sasaki and Yoshimine in 1974,[146] obtaining quantitative agreement with experiment, even for atomic systems, poses a far greater challenge. Their extensive configuration interaction (CI) computations recovered more than 95% of the basis set correlation energy for several neutral and anionic atomic systems by including all single and double excitations as well as selected triple and quadruple excitations. Yet, with an average error of 0.2 eV for B, C, O, and F, this thorough ab initio treatment could not even reproduce the first digit past the decimal of electron affinities obtained via laser photoelectron spectroscopy.

More than a decade after the configuration interaction study of Sasaki and Yoshimine, the situation had improved only marginally.[147] In the context of ab initio quantum chemistry, accurate electron affinities of atoms were defined as those lying within 0.1 eV of the experimental values.[148,149] The systematic analysis of atomic systems by Feller and Davidson[148] beautifully illustrates the difficulties associated with calculating a small difference between two large quantities, specifically the large total energies of a neutral species with N electrons and its negative ion with $N + 1$ electrons. Even for atomic oxygen, convergence to the full CI limit for a given basis set is slow as well as unbalanced (in the sense that the correlation energy is not recovered at an equal rate for the neutral species and the negative ion as one moves toward this limit). Matters are further complicated since extremely high angular momentum basis functions are required to approach the complete basis set limit.

Today electronic structure theory has become one of the most important tools in the chemical laboratory—frequently a major influence in experimental analysis—primarily due to advances in methodology and technology. New methodologies now allow for extremely accurate predictions of chemical properties for atoms and molecules of small to moderate size (e.g., coupled-cluster (CC) theory) or for extensions of correlated methods to the treatment of large molecular systems (e.g., density functional theory). New technological advances in computational resources, which have increased in CPU power by several orders of magnitude while simultaneously drastically decreasing in price, now allow for sophisticated computations to be routinely performed.

These advancements provide the means for accurate theoretical determination of atomic electron affinities. For instance, the accuracy of CI ab initio predictions has improved by more than an order of magnitude for small atomic systems.[150,151] Average absolute errors of only a few thousandths of an electronvolt are achievable when CC or explicitly correlated R_{12} methods using large basis sets and incorporating spin−orbit and relativistic corrections are employed.[152−155]

2. Theoretical Predictions of Molecular Electron Affinities

Historically, the development of theoretical predictions of EAs of molecular systems parallels that for atomic systems. Early discussions of molecular electron affinities depended on qualitative discussions of molecular orbital (MO) theory[69,156] or semiempirical computations.[157] Initially, only Hartree−Fock and simple CI ab initio methods could be applied in the computation of molecular EAs.[158] Good reviews of theoretical progress up to 1987 are given by Gutsev and Boldyrev[41] and Baker, Nobes, and Radom,[159] who report errors greater than 0.2 eV compared to experiment, and by Simons and Jordan.[160] By the mid 1980s, Møller−Plesset methods (MP*n*) were most commonly employed for studies of molecular EAs.[161,162] A decade later, much as the case with atoms, sophisticated methods, such as coupled-cluster theory, could be used on small molecules, usually less than six heavy atoms.[152,163−165] (See also reviews of small anions by Kalcher and Sax.[166,167]) While the accuracy achieved with CC methods can be impressive (often within a few hundrendths of an electronvolt), the extra complications encountered when molecules are treated, such as zero-point vibrational energy corrections, ensure that the accuracy in EA predictions for molecules remains less than what can be achieved with atoms—in much the same manner that experimental values for atoms are often more accurate than those for molecules. Nonetheless, the theoretical accuracy achieved by methods such as CC theory is often sufficient to be used to identify incorrect or interpret unresolved assignments of experimental EAs.[168−172]

B. Present Status of Theoretical Electron Affinity Predictions

The preceeding historical survey illustrates the use of the self-consistent field (SCF), CI, MP*n*, and CC methods for the computation of atomic and molecular EAs, all of which are commonly used, conventional, ab initio methods. Despite the accuracy achieved for atoms and small molecules, the prediction of electron affinities is not a solved problem in theoretical chemistry. For all but the smallest molecules, the definition of accurate theoretical electron affinities has not changed from the 0.1−0.2 eV range for small atoms of one or two decades ago. Despite all the advances mentioned, theory still lags far behind the best experiments, barely reproducing the first few digits of the experimentally determined values.[40] To this end, theoretical predictions of EAs remain a heavily researched area, with the number of computational studies of molecular EAs over the past decade being vast and covering a broad range of methods and approaches.

One of these approaches, and a major advance in the accurate computation of EAs for small- to medium-sized molecular systems, occurred with the development of Gaussian-X (G2, G3) theory. Commonly referred to as a "model chemistry" method, Gaussian-X theory is a composite technique which utilizes a sequence of ab initio methods and some empirical corrections to arrive at a total molecular energy which is intended to approximate a high-level, large basis set method.[173−178] Because the empirical corrections in Gaussian-X methods are derived from experimental data which include electron affinities, the methods are able to achieve electron affinities often within 0.1 eV or less of experimental values for many small- to medium-sized organic molecules. In addition to Gaussian-X methods, other model chemistry methods have been developed and used for electron affinity predictions. For example, the complete basis set (CBS) methods developed by Petersson and co-workers,[179] such as CBS-4 and CBS-Q, employ extrapolations to estimate total energies near the complete basis set limit and can achieve average errors for EAs below 0.09 eV.[180] Perhaps the most sophisticated and computationally demanding of the model chemistry methods are the Weizmann techniques (W1 and W2) recently developed by Martin and co-workers.[181] These computationally intensive methods incorporate high-level ab initio coupled-cluster computations with relativistic and spin−orbit corrections and can achieve average errors for electron affinities of less than 0.02 eV.[182] Despite their accuracy, model chemistry methods such as the Gaussian-X, CBS, and Weizmann methods are in most instances too computationally demanding for electron affinity predictions of large molecules—those containing more than six heavy atoms—though future applications to larger molecules are foreseeable. These methods are preferable for electron affinity predictions of certain small molecules, and the results of these theories are analyzed further in section IV.A.

By far the method most commonly employed in the theoretical determination of electron affinities is DFT. A rather new method, DFT can be applied to a greater range of atoms and molecules than almost any ab initio or model chemistry method currently in use. DFT methods can be used to treat species as simple as atoms to those as complex as molecules consisting of several hundred atoms. Electron affinities obtained with DFT methods are fairly accurate (within 0.2 eV or less) in most cases. Because of its wide applicability, reliability, and ease of use, DFT is a popular method among both theoreticians and experimentalists. Recent studies of various DFT functionals for EA predictions of atoms[154,183] and/or small (three or fewer heavy atom) molecules[174,178,184,185] have shown that functionals such as B3LYP can achieve average errors between 0.1 and 0.2 eV compared to experiment. However, a complete assessment of DFT methods which includes large molecules and many inorganic molecules, is lacking. In sections III.D and IV.A we closely examine and review DFT computations of electron affinities for a large number of atoms and molecules. Comparisons to model chemistry theories and coupled-cluster theories are made. The discussion of DFT in this review is intended to guide the user in the proper application and analysis of DFT for EA predictions, when appropriate, or the use of other theoretical methods when DFT may prove insufficient.

In addition to the conventional ab initio methods, model chemistry methods, and DFT methods just discussed, other theoretical methods for predicting electron affinities should be noted, although they are not examined in detail in this review. Specifically, electron affinities for very large molecules, which are often not accessible experimentally or by sophisticated computational methods, can be estimated on the basis of structure−activity relationships,[186] computed via advanced semiempirical methods,[187] or calculated from known, experimental half-wave reduction potentials.[188] Other, less common, but useful ab initio methods are sometimes employed, such as Green's function methods,[189] or those based on the extended Koopmans theorem[190] or electron propogator approximations.[191]

Finally, as discussed in section II.E, the computational prediction of electron affinities, be it by any of the above theoretical methods, is an important component in the field of computational thermochemistry. The reader interested in this area should consult the recent review by Irikura and Frurip.[192]

C. Basis Sets and Theoretical Electron Affinities

Every DFT or conventional ab initio method employs a basis set—one which is usually comprised of atom-centered Gaussian functions. The choice of a proper basis set can greatly influence the EA value obtained with a particular method. It is common knowledge that a proper description of the electronic structure of atomic and molecular anions requires basis sets with diffuse functions. These functions have small orbital exponents and extend radially farther from the nucleus than typical basis functions. Such additional basis functions can greatly increase the CPU time for performing a computation. Furthermore, an accurate EA can only be obtained by using the same basis set for both neutral and anion species. The basis sets typically need to be of at least double-ζ quality and augmented with appropriate diffuse functions and polarization functions.

There are a great variety of basis sets which include diffuse functions. In standard Pople-type basis sets, those with diffuse functions are commonly indicated with a "+", such as 6-31+G.[193] The DZP++ basis set employed in the DFT results examined in this study is described in detail in section III.F. The most accurate, generally available basis sets with diffuse functions in use today are the augmented correlation-consistent (aug-cc-pVXZ, X = 2−6) basis sets of Dunning and co-workers.[194] These basis sets include one set of diffuse functions for each value of the angular momentum, *l*. The greatest drawback in using the aug-cc-pVXZ basis sets is their large size, and hence high computational expense, which limits their applicability to small molecules.

D. Density Functional Theory (DFT) and Electron Affinities

Although DFT is a simple, widely applicable, and computationally efficient means for estimating electron affinities to within a few tenths of an electronvolt, a thorough analysis of its use for EA determinations is lacking. In this section we discuss the use of density functional methods for predicting EAs, with further statistical analysis given in section IV.A.

Before doing so, a brief overview of density functional theory is provided for those less familiar with this computational method. For those wishing a more complete review of DFT, the work of Kohn, Becke, and Parr[195] is recommended. Within the Born–Oppenheimer approximation, the nonrelativistic electronic Hamiltonian, $\hat{H}_e$, for an atom or molecule is uniquely determined by the number of electrons, N, and the potential created by the nuclei, V_n. Consequently, one can determine for a particular system (N, V_n) an energy, E, and a corresponding many-electron wave function, Ψ. The direct computation of Ψ—in terms of the $3N$ electron coordinates and expressed in MOs composed of linear combinations of atomic orbitals (AOs, given through a basis set)—and its associated energy (E) is the goal of conventional ab initio methods, such as Hartree–Fock theory (HF or SCF), MPn ($n \geq 2$) theory, CI, or CC theory. The latter two methods extend HF theory in a systematic, convergent manner to correlate electrons of opposite spin, thereby achieving energies as close as possible to the true energy, E, depending on the sophistication (and thus computational demand) of the method.

Density functional theory builds on the Hohenberg–Kohn theorem[196,197] which states that V_n is a unique functional of the (ground-state) electron density, ρ, which is dependent on $|\Psi^2|$. In principle, given the exact functional, $F[\rho]$, for a given system, one may determine the ground-state wave function, Ψ, and the exact, correlated energy, E. Note that computation of E from $F[\rho]$ depends only on the 3 coordinates of ρ instead of the $3N$ coordinates of the electrons. However, the exact functional is not known, and thus a variety of inexact functionals have been developed. Furthermore, there is no known systematic method of improving inexact functionals. Thus, while even simple functionals include electron correlation, which is so painstakingly computed with conventional ab initio methods, their inexact, rough nature often leads to only moderate accuracy with little understanding of successes or failures.

In 1965, Kohn and Sham[198,199] defined a procedure for obtaining E from $F[\rho]$ by use of self-consistent equations using molecular orbitals built from linear combinations of atomic basis orbitals, in much the same manner as SCF theory. In conjunction with an inexact functional, correlated energies (and virtually any energy-dependent property, such as geometry, frequencies, etc.) of atoms and molecules could be computed at speeds comparable to those of HF theory. Although inexact and not systematic, even simple functionals represented an improvement over Hartree–Fock theory due to inclusion of electron correlation. The Kohn–Sham approach also gives rise to MOs similar to those obtained with conventional ab initio methods.[200] Indeed, for the unknown, exact functional, Koopmans' theorem rigorously applies: the energy of the highest occupied molecular orbital (HOMO) gives the first ionization potential of an atomic or molecular system.[201]

Among the earliest functionals, the X_α and local spin density approximations (LSDA or SVWN) treat the electron density locally as a uniform electron gas. More advanced functionals, known as generalized gradient approximations (GGAs), correct the uniform approximation by including the gradient of the electron density. Nearly all functionals are divided into linear combinations of smaller functionals approximating either electron exchange or electron correlation energies. Furthermore, because the exact exchange energy is given in HF theory, certain exchange functionals include varying amounts of the exact electron exchange via inclusion of HF terms, giving rise to "hybrid" functionals, whereas those without HF exchange are denoted as "pure" functionals. Thus, a particular DFT method is most easily defined by its functional approximation, which is often a combination of one exchange or hybrid exchange functional and one correlation functional. In this review we focus primarily on six common exchange–correlation functionals: B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA (see section III.F for the exact specification of each functional). Finally, note that some of these exchange or correlation functionals include adjustable parameters which are determined through fits to experimental data but, in contrast to semiempirical methods, are not adjusted for particular atoms and are held fixed during the Kohn–Sham procedure.

In 1982, Cole and Perdew[202] studied the ability of the LSDA to reproduce known electron affinities of atoms and found errors ranging from 0.3 to 1.0 eV or more. The ability of the primitive, non-gradient-corrected density functional, X_α, was used by Gutsev and Boldyrev in 1985 to compute EAs for several small oxides and fluorides.[41] They report errors in the range of 0.5–1.0 eV, which were deemed "acceptable". Later studies in 1992 by Ziegler and Gutsev[203] (LSDA with Becke's 1988 nonlocal correction method, two atoms, five di- or triatomics) and Gill, Johnson, Pople, and Frisch[204] (BLYP, three atoms, nine di- or triatomics) gave average errors of about 0.2 eV. In 1996, a study by Miller, Allen, and Schaefer[205] indicated that the BLYP and B3LYP functionals in conjunction with a modest-sized atomic orbital basis set (DZP++; see section III.F) appeared to provide reasonable electron affinity predictions for CF_3. For example, when compared to high-level CCSD(T) computations, the density functional EA(CF_3) results agreed to within 0.15 eV (cf. section IV.D).

Despite the lack of a reliable experimental value for EA(CF_3) at that time, and the initial successes reported between 1982 and 1992, to many theoreticians it was surprising that DFT performed well at all for EA predictions. An interesting discussion was reopened by the 1996 work of the Schaefer group:

Namely, is DFT, in terms of the functional approximations being used—particularly GGA functionals—applicable to negative ions and consequently electron affinities? Early studies by Schwarz[206,207] and Shore and co-workers[208] indicated that anion HOMO energies computed by various density functionals would be positive; thus, by consequence of Koopmans' theorem, anions would be unstable toward electron detachment.

Why is the HOMO energy positive? Studies by Perdew and co-workers[202,209,210] indicated that due to the inexact nature of the exchange−correlation functionals the functionals fail to fully cancel electron−electron self-repulsion terms and thus suffer from electron "self-interaction" error (SIE). This incomplete cancelation (which does not occur in conventional ab initio methods) causes the potential for an N-electron ion to asymptotically approach $(N - Z)/r$ rather than the physically correct limit of $(N - 1 - Z)/r$, where r indicates a large distance of the electron from the nuclear center. Thus, even for a system as simple as the one-electron H atom, electron self-interaction error exists. While corrections for the SIE in inexact functionals are easily made in the case of H, for many-electron systems a complete correction for any functional has not been developed. Electron self-interaction error often elevates the atomic or molecular orbital energies obtained through the Kohn−Sham formalism of DFT. For anions, which contain an extra electron, the SIE can be particularly severe, and often raises the HOMO energy to the extent that it becomes positive. Interpretation of this positive energy as instability toward electron detachment via Koopmans' theorem led many to conclude that inexact density functionals are not applicable for treatment of anions. Indeed, in the fitting of parameters to experimental data for his famous "B3" exchange functional in 1993, Becke[211] explicitly omitted electron affinities from the set of experimental numbers because of the assumed failure of DFT methods to bind an extra electron.

Yet what explains the early successes of inexact functionals for the prediction of electron affinities? Those results seemed to indicate that DFT could be applied to anions and conclusions of unbound anions were perhaps premature. Conclusions of unboundedness were based on applications of Koopmans' theorem—valid for the unknown, *exact* functional—to anions with positive HOMO energies, a consequence of electron SIE in *inexact* functionals. This begs the question of whether Koopmans' theorem holds for inexact functionals. Motivated by the apparently contradictory successes of DFT in predicting EAs in their early studies,[205] Galbraith and Schaefer[212] tested the hypothesis that the additional electron of a negative ion would become unbound by examining anions near the complete basis set limit with several inexact functionals. Their results for F^- indicated that the extra electron remained bound even though the energy of the highest occupied Kohn−Sham orbital was positive. It appeared that application of Koopmans' theorem to inexact functionals should not be a strict criterion for determination of a functional's applicability to anions—precisely because the functional is inexact. That is, there is no evidence that the extra electron is trying to remove itself from the anion.

In response to Galbraith and Schaefer's work, Rösch and Trickey[213] argued that a positive-eigenvalue DFT orbital is energetically unfavorable for occupancy, even for inexact functionals. However, in a later study, Jaręcki and Davidson[214] obtained negative orbital energies for the HOMO of F^- by using very large, diffuse basis sets with the LSDA and BLYP functionals. Consequently, the positive HOMO energies obtained with inexact DFT functionals appear to be a manifestation of the fact that the exact functional is not known and that approximate basis sets are employed in most practical computations. Furthermore, results of positive HOMO energies for anions do not occur in every computation but are instead highly dependent on the particular anionic species being examined and the particular inexact functional employed. For example, it is well-known that hybrid functionals alleviate some SIE through their partial incorporation of HF exchange, and often produce negative HOMO energies for even anions.[215]

Additionally, because EAs are computed as differences between the total energies of the anion and neutral (cf. eq 6), and not through direct interpretation of the anion HOMO energy, empirical evidence from previous studies of EAs with DFT[41,202−205] suggests that density functional theory can be successfully applied to predict EAs for atoms and molecules even with inexact functionals and finite basis sets. This result is related to the fact that the total energy is not the sum of the orbital energies. Indeed, Baerends, Gritsenko, and co-workers[216,217] have shown that the total energies obtained by inexact GGA functionals do not exhibit the large errors associated with individual orbital energies. Furthermore, despite their objections to the presence of positive HOMO energies in DFT examinations of anions, Rösch and Trickey concede that DFT can provide reasonable estimates of molecular EAs.[213] Thus, by the late 1990s it became clear that DFT, in the form of inexact functionals, *is* applicable to anionic species.

Emboldened by the DFT results for CF_3, and the success of a number of inexact functionals for F and F_2, Schaefer and co-workers[42,218−226] embarked on a series of DFT studies examining EAs of fluorine compounds: BrF_n, C_2F_n, ClF_n, SiF_n, Si_2F_n, SF_n, PF_n, SeF_n, GeF_n, Ge_2F_n, and $BrClF_n$, where n ranged from 1 to 5, 6, or 7 depending on the central atom(s). However, few reliable experimental electron affinities are available for these molecules; thus, a critical characterization of the performance of the employed density functionals was not possible. To resolve this discrepancy, the Schaefer group began a series of systematic investigations comparing the EAs obtained from density functional methods to known electronic affinities[43,215,227−231] as well as those of a number of oxide systems:[232−236] CF_3O, ClO_4, BrO_n ($n = 1-4$), TiO_n ($n = 1-3$), ScO, and ScO_2.

The cumulative result of these studies is a compilation of 163 atomic and molecular electron affinities predicted by each of the B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA functionals. These results reside in Tables 8 and 9.

E. Layout of Tables 8 and 9: Theoretical DFT Electron Affinities

Table 8 presents computed, adiabatic EAs for atoms and molecules which have reliable experimental EA values available. Results with each of six functionals, B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA, for every species are reported. The DZP++ basis set, described next, was employed in every instance. Complete geometry optimizations were carried out for each molecular species with each of the six functionals (cf. eq 6). Thus, in the present review we incorporate more than 1750 distinct structural optimizations and frequency determinations and more than 2000 distinct atomic and molecular energy computations. For molecules, harmonic ZPVE-corrected results are given in parentheses below the "classical", uncorrected value. For each species, a theoretical reference for the DFT results is provided and an experimental reference for the known EA is also given. In certain instances, "notes"—listed as footnotes in Tables 8 and 9—have been added to entries, providing additional information and references. The species are ordered by molecular weight with the point group and electronic state for the anion and neutral of each species also presented. The results complement the experimental results presented in Table 10, though some experimental results determined by methods other than photoelectron techniques are allowed in Table 8. Table 9, organized as Table 8, reviews computed, adiabatic EAs for atoms and molecules for which no reliable experimental EA value is available.

It should be noted that the DFT papers from which these results have been tabulated often discuss and evaluate results from other theoretical methods and include molecular properties besides EAs: molecular geometries, harmonic frequencies, and/or dissociation energies. Full discussion of these properties is beyond the scope of this review, and those investigating EAs are encouraged to consult original references in instances where details beyond the EA value are needed. Note also that in some references one or two of the six functionals included in Tables 8 or 9 were missing. Additionally, a small number of results for particular atoms or molecules have not been previously published. In both these cases, the missing EAs were computed for this review to complete the present data set.[237−241]

In certain instances, theoretically challenging molecular phenomena are encountered when EAs are computed, such as Jahn−Teller splitting (cf. C_5H_5)[215] and Renner−Teller splitting (cf. C_3O and AlO_2).[172,228,229] In a few instances uniform agreement on a particular geometry or molecular state is not found among the six functionals examined here (cf. C_6H),[228] which can usually be traced to differences between hybrid and pure functionals. Occasionally electronic symmetry breaking (cf. BO_2, AlO_2, and Si_2H_2)[227,229,230] in the DFT orbitals was found. In instances where the above problems lead to significant effects on the EA interpretation, brief comments on the particular problem in the footnotes of Tables 8 and 9 are provided.

Finally, besides harmonic ZPVE corrections, no other energy corrections such as relativistic effects or spin−orbit coupling have been applied. In general, such effects are known to be small for most molecules examined in this study. Indeed, the effects of relativistic corrections on electron affinities have been investigated and found to be typically (i.e., for small systems) less than 0.02 eV.[242] Furthermore, such corrections, when applied to the anion, are often similar to those applied to the neutral species, therefore nearly cancel upon subtraction of energies, and hence change the theoretical EA values only slightly.

F. Details of Density Functional Methods Employed in Tables 8 and 9

The electron affinities comprising the theoretical results of Tables 8 and 9 were computed in the following manner: total energies, equilibrium geometries, and harmonic vibrational frequencies were determined for each species (neutral, anion) included in Tables 8 and 9 with six different exchange−correlation density functionals. The functionals used in this study have been denoted B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA. The first five are GGAs and employ either the correlation functional of Lee, Yang, and Parr (LYP)[243] or that of Perdew (P86)[244,245] in conjunction with one of Becke's exchange functionals: the three-parameter HF/DFT hybrid exchange functional (B3),[211] a modification (as implemented by GAUSSIAN 94) of the half-and-half HF/DFT hybrid method (BH),[246] or the 1988 pure DFT exchange functional (B).[247] The sixth density functional scheme used in the study is LSDA, which employs the 1980 correlation functional of Vosko, Wilk, and Nusair[248] along with the Slater exchange functional.[196,249,250]

The quantum chemical computations of this study were conducted with the GAUSSIAN 94[251] system of DFT programs. Spin-unrestricted Kohn−Sham orbitals were used for all computations, as recommended by Pople, Gill, and Handy.[252] It should be noted that one must be careful that spin-unrestricted results for closed-shell species obtained with GAUSSIAN 94 are truly unrestricted (α spin orbitals $\neq \beta$ spin orbitals). Both the neutral and anion geometries were fully optimized via analytic gradients with each of the six density functionals. Residual Cartesian gradients were less than 2×10^{-6} hartree/bohr. Elements of the density matrices were converged to six decimal places, while the root mean square of these elements was converged to eight decimal places. This resulted in total energies that were numerically converged to at least 1×10^{-7} hartree (2.7×10^{-6} eV). Numerical integration of the functionals was carried out using the default integration grid consisting of 75 radial shells with 302 angular points per shell. The harmonic vibrational frequencies and corresponding ZPVE corrections were determined analytically for all DFT methods.

Throughout all computations, a basis set of contracted double-ζ Gaussian functions augmented with a set of polarization (p or d) and diffuse (s or s and p) functions, denoted DZP++, was employed. The double-ζ basis employed was the Huzinage−Dunning[253,254] set for each H, Li, Be, B, C, N, O, and F atom, the Huzinage−Dunning−Hay[253,255,256] set for each Al, Si, P, S, and Cl atom, or the Schäfer−Horn−Ahlrichs[257] set for each Ge, Se, and Br atom. Each

Table 2. Number of Basis Functions, Polarization Exponents, and Diffuse Exponents for Each Atom in the "DZP++" Basis Sets Used for EA Computations in Tables 8 and 9

atom	total no. of basis functions	polarization exponent	diffuse exponent(s)
H	6	p, 0.75	s, 0.04415
Li	14	p, 0.0205	s, 0.00717523 p, 0.00713759
Be	14	p, 0.050195	s, 0.01702094 p, 0.01703562
B	19	d, 0.7	s, 0.02879 p, 0.02246
C	19	d, 0.75	s, 0.04302 p, 0.03629
N	19	d, 0.8	s, 0.06029 p, 0.05148
O	19	d, 0.85	s, 0.08227 p, 0.06508
F	19	d, 1.0	s, 0.1049 p, 0.0826
Al	27	d, 0.4	s, 0.02148 p, 0.01891
Si	27	d, 0.5	s, 0.02729 p, 0.025
P	27	d, 0.6	s, 0.03448 p, 0.03346
S	27	d, 0.7	s, 0.04267 p, 0.04096
Cl	27	d, 0.75	s, 0.05048 p, 0.05087
Ge	45	d, 0.246	s, 0.024434 p, 0.023059
Se	45	d, 0.338	s, 0.03888 p, 0.03819
Br	45	d, 0.389	s, 0.0469096 p, 0.0465342

double-ζ basis was augmented with a set of p or d polarization functions and completed by adding one even-tempered s diffuse function to each H atom and a set of even-tempered s and p diffuse functions to all other atoms. These even-tempered orbital exponents were determined according to the guidelines of Lee and Schaefer.[258] That is, the s- or p-type diffuse function exponent, α_{diffuse}, for a given atom was determined by

$$\alpha_{\text{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1 \tag{22}$$

where α_1 is the smallest, α_2 the second smallest, and α_3 the third smallest Gaussian orbital exponent of the s- or p-type primitive functions of that atom. All polarization and diffuse orbital exponents were unscaled, and are summarized in Table 2. Finally, note that the number of radial shells included in the numerical integration techniques places restrictions on the size of the Gaussian exponents used.[214] Specifically, for the 75 radial shells used in this study, s- and p-orbital exponents should be between 1.0×10^5 and 1.0×10^{-4}.

IV. Discussion and Observations

A. Statistical Analysis of DFT Results Through Comparisons to Experiment and Other Theoretical Methods

Table 3 presents a statistical analysis of the 110 DFT/DZP++ EA results found in Table 8 compared to experimental values for each of six functionals: B3LYP, B3P86, BHLYP, BLYP, BP86, and LSDA. Without zero-point corrections, the B3LYP and BLYP functionals each have an average absolute error of 0.19 eV. The BP86 and BHLYP functionals have errors of 0.23 and 0.25 eV, respectively, while the LSDA and B3P86 yield unacceptable average absolute errors greater than 0.6 eV. The addition of harmonic ZPVE corrections causes a slight increase in the average error of about 0.01 eV. ZPVE effects thus serve little to improve agreement between theory and experiment, though it can be assumed that improvements in the ZPVE correction itself, through inclusion of anharmonic effects, might increase agreement with experiment. Another solution, scaling ZPVE energies, has been investigated by Curtiss and co-workers[176,178] and found to have a small effect on the average absolute error for electron affinities: less than 0.001 eV. Note, however, that ZPVE corrections are not given for 5 of the 96 molecules in Table 8. Nonetheless, in all further discussions, unless otherwise noted, the EA statistics discussed here refer to unscaled ZPVE-corrected EAs.

Table 3. Average Absolute Error, Percentage of EAs Overestimated, Absolute Maximum Error, and Standard Deviations as Compared to Experimental EAs, for Each Functional Studied, for the 110 Species Listed in Table 8[a]

	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA
av abs error	0.19 (0.20)	0.62 (0.63)	0.25 (0.26)	0.19 (0.20)	0.23 (0.23)	0.69 (0.69)
% overestimated	74.5 (70.3)	98.2 (97.8)	30.9 (34.1)	51.8 (49.5)	86.4 (84.6)	99.1 (98.9)
abs max error	1.59	1.76	1.03	2.15	1.93	1.78
std dev	0.24	0.22	0.19	0.28	0.24	0.21

[a] The harmonic ZPVE-corrected statistics are listed in parentheses.

For all but the BHLYP functional, DFT EA results tend to overestimate experimental values. The LSDA functional, which does not include gradient corrections to the electron density in its formulation, is expected to perform poorly. Indeed, LSDA overestimates the EA of nearly all 110 species. It is unclear why the B3P86 functional also performs poorly, especially when considering that the B3 exchange functional performs well in the B3LYP functional and the P86 correlation functional performs well in the BP86 functional. LSDA and B3P86 aside, it is clear that the remaining four functionals provide excellent estimations of EAs, with average absolute errors of less than 0.26 eV, standard deviations of about 0.22 eV, and maximum errors of about 1.7 eV. In Table 8, the greatest errors in theoretical EAs occur for SF_6 and SeF_6, both of which are discussed further in section IV.E.2. Excluding SF_6 and SeF_6, average absolute errors drop by about 0.01 eV while maximum errors are significantly reduced to about 1.0 eV.

Can agreement be improved even further? Perhaps inaccuracies in the experimental values provide some of the errors. To investigate this, the 110 species were narrowed to the 91 species with experimental uncertainties of less than 0.09 eV, which in general only allows experimental results obtained by photoelectron techniques. To avoid skewing of the data, SF_6 is also excluded from this smaller set (SeF_6 being

Table 4. Average Absolute Error, Percentage of EAs Overestimated, Absolute Maximum Error, and Standard Deviations as Compared to Experimental EAs, for Each Functional Studied, for 91 Species Listed in Table 8 with Experimental Uncertainities Less than 0.09 eV and Excluding SF_6[a]

	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA
av abs error	0.14	0.59	0.24	0.14	0.18	0.68
	(0.16)	(0.60)	(0.25)	(0.15)	(0.19)	(0.67)
% overestimated	71.4	98.9	25.3	46.2	86.8	100.0
	(68.4)	(98.7)	(28.9)	(44.7)	(85.5)	(100.0)
abs max error	0.71	1.04	0.87	0.67	0.62	1.23
	(0.76)	(1.14)	(0.87)	(0.71)	(0.66)	(1.01)
std dev	0.14	0.16	0.17	0.13	0.13	0.16
	(0.17)	(0.18)	(0.18)	(0.14)	(0.15)	(0.14)

[a] The harmonic ZPVE-corrected statistics are listed in parentheses.

excluded by virtue of its experimental EA uncertainty). Table 4 presents results for each functional as compared to experimental EAs in this revised set. Significant improvement is now seen, with average absolute errors for B3LYP, BLYP, and BP86 now just 0.16, 0.15, and 0.19 eV. Maximum errors are also reduced to 0.76 eV or less for these three functionals. The BHLYP average error remains somewhat higher at 0.25 eV, with LSDA and B3P86 average absolute errors still unacceptably large. For all species, the standard deviations in the error are between 0.14 and 0.18 eV. This smaller set indicates that the B3LYP, BLYP, and BP86 functionals produce excellent electron affinities, which are within 0.16 eV of experiment for most molecules.

The smaller set of 91 electron affinities can be divided into subgroups which provide for further analysis of the performance of DFT on electron affinities. Average absolute errors and standard deviations for each of the six functionals with various subgroups are presented in Table 5. Note that all results, except those for atoms, include ZPVE corrections.

In 1997, Rösch and Trickey[213] stated that “for low-charge, relatively large molecular anions, the spurious self-repulsion [SIE] can be spread out over a large-enough volume that reasonable estimates of *EAs* ... can be obtained”. The implication here is that for species of small size, such as atoms, the SIE would be significant and lead to large errors in EAs by DFT. As the size of the species increases from diatomics and triatomics to larger polyatomic molecules, EA predictions would become more reasonable. To investigate this hypothesis, results for subgroups of atoms, diatomics, triatomics, and molecules with four or more atoms are presented in Table 5. The trends in average absolute error for the three best functionals are (eV) 0.13 → 0.17 → 0.20 → 0.11 (B3LYP), 0.12 → 0.13 → 0.18 → 0.15 (BLYP), and 0.27 → 0.18 → 0.21 → 0.17 (BP86). For no functional does the increase in species size directly translate into a reduction of EA error. Indeed, with the B3LYP functional, results for atoms are nearly as good as those for species containing four or more atoms. (For more DFT results on atoms see the work of de Oliveira and co-workers.[154]) For the BLYP functional, results for atomic and diatomic species are better than those for species with four or more atoms! It is indeed true, as evidenced by these results, that DFT can achieve accurate EA predictions for large molecules, but it is equally true that DFT can achieve accurate EA predictions for smaller species such as atoms and diatomic molecules. These results are inconsistent with the hypothesis of Rösch and Trickey.[213]

In 1998, Curtiss, Redfern, Raghavachari, and Pople[174] noted that DFT EA predictions have large deviations from experiment for 10 EAs in which the

Table 5. Average Absolute Error (eV) for ZPVE-Corrected DFT EAs Compared to Various Subgroups of the 91 Experimental EAs Specified in Table 4[a]

group (no. of species in subgroup)	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA
exptl error ≤0.09 eV (91)	0.16	0.60	0.25	0.15	0.19	0.67
	(0.17)	(0.18)	(0.18)	(0.14)	(0.15)	(0.14)
atoms (14)	0.13	0.64	0.16	0.12	0.27	0.78
	(0.07)	(0.10)	(0.12)	(0.09)	(0.11)	(0.24)
diatomics (28)	0.17	0.61	0.21	0.13	0.18	0.66
	(0.18)	(0.17)	(0.20)	(0.15)	(0.15)	(0.16)
triatomics (21)	0.20	0.64	0.26	0.18	0.21	0.65
	(0.21)	(0.22)	(0.22)	(0.15)	(0.16)	(0.16)
four or more atoms (28)	0.11	0.57	0.27	0.15	0.17	0.70
	(0.10)	(0.15)	(0.12)	(0.11)	(0.13)	(0.12)
closed-shell anion to open-shell neut (43)	0.09	0.49	0.29	0.12	0.10	0.65
	(0.11)	(0.10)	(0.17)	(0.10)	(0.08)	(0.14)
open-shell anion to open-shell neut (28)	0.14	0.59	0.17	0.15	0.19	0.65
	(0.10)	(0.14)	(0.14)	(0.14)	(0.12)	(0.13)
open-shell anion to closed-shell neut (20)	0.30	0.81	0.23	0.22	0.34	0.75
	(0.21)	(0.16)	(0.22)	(0.17)	(0.15)	(0.15)
organics[b] (38)	0.13	0.59	0.25	0.15	0.18	0.71
	(0.11)	(0.15)	(0.12)	(0.11)	(0.13)	(0.12)
inorganics[c] (53)	0.18	0.61	0.24	0.15	0.19	0.64
	(0.21)	(0.21)	(0.23)	(0.16)	(0.16)	(0.16)
halogens[d] (15)	0.24	0.70	0.21	0.18	0.24	0.67
	(0.22)	(0.19)	(0.17)	(0.21)	(0.21)	(0.10)
non-halogens[e] (78)	0.14	0.58	0.25	0.15	0.18	0.68
	(0.15)	(0.18)	(0.18)	(0.12)	(0.13)	(0.15)

[a] Also listed are standard deviations of the error in parentheses. [b] Species which contain a C atom. [c] Species which do not contain a C atom. [d] Species which contain at least one atom of F, Cl, and/or Br. [e] Species which do not contain any atoms of F, Cl, or Br.

electron affinity corresponded to the addition of an electron to a closed-shell molecule. In particular, there are three categories of EAs in terms of electronic shell configuration: (1) detachment from a closed-shell anion to an open-shell neutral, (2) detachment from an open-shell anion to an open-shell neutral, and (3) detachment from an open-shell anion to a closed-shell neutral. DFT results for these three EA types are presented in Table 5. In case 1, agreement between DFT EAs and experiment is truly excellent, being, on average, 0.12 eV or better with the B3LYP, BLYP, and BP86 functionals. Standard deviations are also small, less than 0.11 eV. In case 2, agreement is nearly as good, with average absolute errors below 0.19 eV and standard deviations 0.14 eV or smaller. In direct contrast, results for case 3 are quite poor; average absolute errors are large, 0.30 eV (B3LYP), 0.22 eV (BLYP), and 0.34 eV (BP86), with standard deviations greater than 0.15 eV. Furthermore, in this case, EAs are typically overestimated [100% (B3LYP), 85% (BLYP), 90% (BP86)] in contrast to those of case 2 [79% (B3LYP), 42% (BLYP), 84% (BP86)] and case 3 [45% (B3LYP), 24% (BLYP), 84% (BP86)]. These results confirm the observation of Curtiss et al. The poor performance of DFT for EA predictions when the neutral species is closed shell indicates that the computed DFT electronic energies of open-shell anions are too negative and/or the energies of closed-shell species are perhaps not negative enough (cf. eq 6). Note that in cases 1 and 2 the neutral and anion HOMOs are always occupied by at least one electron and thus well-described in the Kohn−Sham procedure. In case 3, the HOMO on the anion species is unoccupied in the neutral species, and thus poorly described. The results of case 3 deliver a note of caution to those using DFT to predict EAs in which the neutral species is a closed shell. In such instances, results should not be expected to be as accurate as other DFT EA predictions.

The remaining subgroups in Table 5 show that there is only a small difference between DFT EA results for carbon-containing (organic-like) species and species without any carbon atom (inorganic-like). The greatest difference is for B3LYP, which has an average absolute error 0.05 eV better with organic-like species. Additionally, for species which contain at least one halogen atom, the B3LYP, BLYP, and BP86 functionals all have average absolute errors 0.03−0.10 eV worse than those for species without any halogen atom.

There are two commonly used sets of experimental electron affinities to which the EA predictions of many theoretical methods have been compared. These sets are the G2-1 and G2-2 test sets and were developed to aid in fitting Gaussian-X high-level parameters. The G2-1 test set contains 25 EAs. A comparison of the average absolute errors from various computational methods' EA predictions to the G2-1 test set is given in Table 6. With the DZP++ basis set, the B3LYP, BLYP, and BP86 functionals yield average absolute errors of 0.18, 0.13, and 0.23 eV compared to the G2-1 test set. Of the model chemistry methods, the Gaussian-X and CBS methods have average absolute errors below 0.1 eV. The most accurate methods are the W-1 and W-2 methods, which yield average absolute errors of 0.02 and 0.01 eV, respectively. As seen in Table 7, results are similar for the G2-2 test set, which contains 58 EAs. Note, in particular, the G3//B3LYP results in Table 7, which show that B3LYP energies can be successfully employed within the G3 method.[176]

Table 6. Average Absolute Errors (eV) from Experiment for the 25 Electron Affinities of the G2-1 Test Set[a] with Various Density Functional and Model Chemistry Methods

method/basis	av abs error	ref
G2	0.06	174, 204
G2(MP2)	0.09	174
G3	0.05	175, 180, 182
G3(MP2)	0.06	180
W1	0.02	182
W2	0.01	182
CBS-4M	0.11	180
CBS-QB3	0.05	180
B3LYP/DZP++	0.18	this work
B3LYP/aug-cc-pVDZ	0.15	184
B3LYP/aug-cc-pVTZ	0.12	184
B3LYP/6-311+G(3df,2p)[b]	0.11	174
B3P86/DZP++	0.60	this work
B3P86/6-311+G(3df,2p)[b]	0.59	174
BHLYP/DZP++	0.31	this work
BLYP/DZP++	0.13	this work
BLYP/aug-cc-pVDZ	0.15	184
BLYP/aug-cc-pVTZ	0.13	184
BLYP/6-311+G(3df,2p)[b,c]	0.11	174
BP86/DZP++	0.23	this work
BP86/aug-cc-pVDZ	0.26	184
BP86/aug-cc-pVTZ	0.24	184
BP86/6-311+G(3df,2p)[b]	0.21	174
LSDA/DZP++	0.74	this work
LSDA/aug-cc-pVDZ	0.78	184
LSDA/aug-cc-pVTZ	0.79	184
LSDA/6-311+G(3df,2p)[b]	0.74	174
B3PW91/aug-cc-pVDZ	0.11	184
B3PW91/aug-cc-pVTZ	0.10	184
B3PW91/6-311+G(3df,2p)[b]	0.11	174
BPW91/6-311+G(3df,2p)[b]	0.10	174

[a] The G2-1 test set includes electron affinities of the following species: C, O, F, Si, P, S, Cl, CH, CH_2, CH_3, NH, NH_2, OH, SiH, SiH_2, SiH_3, PH, PH_2, SH, O_2, NO, CN, PO, S_2, Cl_2. [b] Computed at MP2(full)/6-31G(d) geometries using scaled HF/6-31G(d) frequencies for ZPVE corrections. [c] See also ref 204.

The G2-1 set includes only two species (Cl_2 and SiH_2) which represent detachment from an open-shell anion to a closed-shell neutral (case 3) and does not contain EAs from species with more than two heavy atoms. The G2-1 set is thus a poor set by which to evaluate DFT EA results. The G2-2 set is more balanced, containing 12 species out of 58 which belong to case 3, and has several larger molecules. Thus, examining Table 7 further, any of the model chemistry methods listed, except the CBS-4M method, outperform DFT, regardless of the functional or basis set. Thus, model chemistry methods should serve well for EA predictions of small molecules. Nonetheless, the DFT results are encouraging and show that DFT is a viable alternative to model chemistry methods and indeed likely preferable when issues of computational cost and/or molecular size are of importance.

It is interesting to compare the DZP++ results for the six functionals examined in this review in Table 8 to results with other basis sets or other functionals. As seen in Tables 6 and 7 the effects of increasing basis set size are minimal, giving reductions in average absolute error of about 0.02−0.03 eV for most

Table 7. Average Absolute Errors (eV) from Experiment for the 58 Electron Affinities in the G2-2 Test Set[a] for Various Density Functional and Model Chemistry Computational Methods

method/basis	av abs error	ref
G2	0.06	174
G2(MP2)	0.08	174
G3	0.04	175, 178
G3(MP2)	0.06	178, 180
G3(MP3)	0.05	178, 180
G3(CCSD)	0.04	177
G3//B3LYP	0.04	176
W1	0.02	182
CBS-4M	0.13	180
CBS-QB3	0.05	180
B3LYP/DZP++[b]	0.19	this work
B3LYP/6-31+G(2d)[c]	0.16	174
B3LYP/6-311+G(2df,p)[c]	0.13	174
B3LYP/6-311+G(3df,2p)[c,d]	0.13	174
B3P86/DZP++[b]	0.62	this work
B3P86/6-311+G(3df,2p)[c]	0.60	174
BHLYP/DZP++[b]	0.29	this work
BLYP/DZP++[b]	0.14	this work
BLYP/6-311+G(3df,2p)[c,d]	0.11	174
BP86/DZP++[b]	0.22	this work
BP86/6-311+G(3df,2p)[c]	0.19	174
LSDA/DZP++[b]	0.72	this work
LSDA/6-311+G(3df,2p)[c,d]	0.70	174
B3PW91/6-311+G(3df,2p)[c]	0.15	174
BPW91/6-311+G(3df,2p)[c]	0.12	174

[a] The G2-2 test set includes the G2-1 set and electron affinities of the following species: Li, B, Na, Al, C_2, C_2O, CF_2, NCO, NO_2, O_3, OF, SO_2, S_2O, C_2H, C_2H_3, $H_2C{=}C{=}C$, $H_2C{=}C{=}CH$, CH_2CHCH_2, HCO, HCF, CH_3O, CH_3S, CH_2S, CH_2CN, CH_2NC, CHCO, CH_2CHO, CH_3CO, CH_3CH_2O, CH_3CH_2S, LiH, HNO, HO_2. [b] Includes 46 of the 58 EAs in the G2-2 test set. [c] Computed at MP2(full)/6-31G(d) geometries using scaled HF/6-31G(d) frequencies for ZPVE corrections. [d] See also ref 178.

functionals, with the greatest dependence seen in the B3LYP functional. Certainly, a simple basis set of DZP++ quality is sufficient for most DFT EA predictions, making reliable DFT EA predictions accessible for large molecules. Of course, improving the basis set will, in general, improve results, and may be necessary for certain molecules, such as SF_6 (cf. section IV.E.2). The results of Tables 6 and 7 clearly show that the B3LYP, BLYP, and BP86 functionals are excellent choices for EA predictions. Tables 6 and 7 also indicate that functionals employing the PW91 correlation functional, B3PW91 and BPW91, are also excellent choices and are likely to outperform the B3LYP, BLYP, and BP86 functionals for EA predictions.

B. Theoretical EAs for Species with Unknown Experimental EAs

Table 9 provides EA predictions for molecules which have no experimental EA or an unreliable experimental EA. The above analysis shows that the B3LYP, BLYP, and BP86 functionals will provide EA predictions within 0.2 eV or better for most molecules listed in Table 9. Results using any of the B3LYP, BLYP, or BP86 functionals can serve as a guide for experimental determinations of unknown electron affinities. Furthermore, the analysis in section IV.A can aid in judging the accuracy of other DFT EA predictions found in the chemical literature which use functionals and basis sets not found in Table 9. In particular, a number of simple molecules in Table 9 have no known experimental EA: C_2F, SiO, PF, PF_2, SF_2, etc. While a complete tabulation of all theoretical DFT EA predictions in the chemical literature for molecules with unknown experimental EAs is impossible, a few recent examples should be highlighted. In particular, EAs for the BC and AlC diatomic molecules are not known; however, a review of theoretical work suggests values of 1.08 and 2.0 eV, respectively.[259] A whole host of transition-metal molecules and clusters exist for which accurate experimental values are not known; for example, for 11 vanadium oxide clusters, only 5 experimental EAs are known.[260] As just reviewed, theoretical predictions of EAs, whether by DFT, model chemistry methods, or CC theory are now at a level of accuracy that predictions of EAs for species with no known experimental value can be made with confidence.

C. Applicability of DFT to Anions and the Future of DFT EA Predictions

The discussion in section IV.A demonstrates that DFT is indeed applicable to anions and provides EA predictions within 0.2 eV or better of experiment. In particular, the B3LYP, BLYP, BP86, B3PW91, and BPW91 functionals are excellent choices for EA predictions. There is no evidence that DFT will perform poorly on atoms or diatomic species. Furthermore, the basis set dependence of DFT functionals is small, and a DZP++ quality basis set is sufficient for most molecules. For one type of neutral/anion pair DFT does perform poorly for EA predictions: those species in which an electron affinity is between an open-shell anion and a closed-shell neutral.

What does the future hold for the computation of EAs via DFT? Variations on existing functionals can be made to obtain improved EAs.[261] Recently, a new class of density functionals known as “meta-GGAs” have received much attention.[262−264] Although only limited assessments of these newer exchange−correlation functionals have been made,[265] it can be expected that future improvements in functionals will result in improved EA predictions by DFT methods. Indeed, in those newer functionals which are calibrated to experimental data, electron affinities are now being included in the calibration data sets. Furthermore, the development of linear scaling techniques for DFT has greatly reduced the CPU time required for performing DFT computations and has made DFT computations on molecules containing more than 1000 atoms possible.[266] For DFT, the future is very bright: accurate EA predictions and EA computations on very large molecules are just around the corner. This rosy picture is not meant to discredit other theoretical methods. Indeed, as just discussed, model chemistry methods (G2, G3, CBS-M, CBS-Q, W1, W2) and coupled-clustered methods (CCSD, CCSD(T)) are certainly superior for EA computations of small molecules.

D. Specific Theoretical Successes

Examination of the theoretical DFT results in Table 8 have led to identification of errors in the reported experimental values. For example, the electron affinity of BO was experimentally uncertain prior to 1997, with many estimates of EA(BO) > 3 eV.[168] However, the DFT results for BO are significantly below 3 eV. As DFT tends to overestimate EAs (cf. Table 3), it appeared likely that EA(BO) $\leq$ 3 eV. In 1997, Rienstra and Schaefer computed EA(BO) = 2.52 eV at the CCSD(T)/aug-cc-pVQZ level. Later that year, Wenthold, Kim, Jonas, and Lineberger reported a photoelectron spectroscopy EA(BO) = 2.508 ± 0.008 eV.[169] Similarly, in 1996, EA(CF_3) was predicted to be 1.78 ± 0.10 eV by Miller, Allen, and Schaefer[205] on the basis of B3LYP/DZP++ and CCSD(T) computations. Five years later this prediction was confirmed by Deyerl, Alconcel, and Continetti[267] via photoelectron spectroscopy, which gave an experimental value of 1.82 ± 0.05 eV.

Like BO and CF_3, sophisticated theoretical predictions have been made for several other small molecules with uncertain experimental electron affinities: EAs of 0.40, 0.73, and 0.74 eV for CF, PF, and PF_2, respectively, each at the CCSD(T)/aug-cc-pVQZ level,[268,269] and an EA of −0.15 eV for N_2O at the QCISD(T)/aug-cc-pVTZ level in contrast to experimental estimates of a positive EA for N_2O.[270] Note that DFT results for each of CF, PF, PF_2, and N_2O are presented in Table 9. For the first three, DFT results are in reasonable agreement with the high-level theoretical results, although somewhat larger in magnitude. DFT results for N_2O, however, suggest a positive EA. It is also ironic that DFT predicts excellent EAs for CF and CF_3, yet overestimates the EA of CF_2 (cf. Table 8). In any case, these theoretical results dictate that additional experimental investigations for each of these small molecules may be needed (cf. BeH, Table 8).

The above examples demonstrate that DFT results should not be easily dismissed if found to disagree with experiment. If it had not been for systematic study and analysis of the six functionals in Table 8, the discrepancies between theory and experiment for molecules such as BO might have been dismissed as the result of poor theoretical methods rather than originating from incorrect experimental values. Therefore, the systematic study and statistical analysis of the DFT EA results presented in section IV.A can serve as a guide for the proper interpretation of future DFT EA results, thereby avoiding premature dismissal of theoretical results when conflicts with experiment arise. Indeed, such conflicts should be investigated further with more sophisticated methods, if possible. Certainly, as discussed, the CCSD(T) method with a large basis set can result in EA values which are within experimental error. Such large computations should be performed whenever possible, but when not feasible, the average absolute errors reported in Table 3 provide limits to the accuracy of EAs obtained by DFT. For example, the accuracy of the B3LYP method of about ±0.2 eV or better has been used to clarify discrepancies between conflicting experimental EA values for the DNA and RNA bases: uracil, thymine, cytosine, gaunine, and adenine.[231]

E. Interesting Problems

A complete understanding of the EA of an atom or molecule cannot be obtained solely from its EA value. Indeed, answers to questions such as why a particular species binds an electron and why the EA for a particular species is so large (or small) can only be given after careful experimental and theoretical study. Despite theoretical successes, such as those discussed above, in some cases the answers to such questions are not fully understood by either theoreticians or experimentalists.

Rather than a qualitative overview of EA trends in atoms and molecules, in this review we briefly discuss some interesting molecules for which a proper EA determination provides challenges for the experimentalist, theoretician, or both. Specifically for the theoretician, the below discussions of C_2, SF_6 and SeF_6, and polycyclic aromatic hydrocarbons illustrate difficulties encountered with multireference problems, basis set inadequacies, and ZPVE corrections, respectively. For the experimentalist, the discussion of C_4O illustrates the challenges in assigning features seen in photoelectron spectra.

1. C_2

The C_2 molecule is one of the most interesting of the diatomic molecules and plays a varied role in chemistry.[271] In 1991, Ervin and Lineberger determined EA(C_2) to be 3.269 eV.[272] Experimentally, C_2 has a $^3\Pi_u$ excited state which lies just 0.09 eV above the X $^1\Sigma_g^+$ ground state. This near degeneracy can cause great inaccuracies in single-reference-based theoretical methods, such as DFT. Studies of C_2 with density functionals predict the triplet state to be more stable by about 0.8 eV.[174,273,274] While the $^1\Sigma_g^+ \leftarrow {}^2\Sigma_g^+$ EA values obtained by the six density functionals in Table 8 are tolerable for all but the B3P86 and LSDA functionals, it is somewhat disconcerting that DFT suggests a larger $^3\Pi_u \leftarrow {}^2\Sigma_g^+$ EA exists. Until either accurate multiple-reference-based density functional methods or much improved approximate functionals are developed, C_2 will remain a challenge for DFT, as it is for numerous other methods.

2. SF_6 and SeF_6

Perhaps the best experimental value for EA(SF_6) is 1.07 ± 0.07 eV, as determined by Chen, Wiley, Batten, and Wentworth in 1994 using thermal electron attachment negative ion mass spectrometry.[128] The DFT results in Table 8 severely overestimate this value by about 1.8 eV on average. Careful study has shown that DFT EA results for SF_6 can be reduced by as much as 0.7 eV or more by using basis sets which include f-type polarization functions.[275] In a 1998 study, Gutsev and Bartlett[276] obtained EA(SF_6) = 0.92 eV, at the CCSD(T)/6-311+G(3df) level, a result in fair agreement with the experimental value. As with SF_6, similarly poor DFT results are obtained for the third-row congener, SeF_6.[223] Clearly, the DZP++ basis set examined in this review, which contains no f-functions, is insufficient for EA computations of SF_6 and SeF_6. Fortunately, as seen in Table 8 such basis set inadequacies are not often encountered, but SF_6 and SeF_6 do serve as a reminder of the importance of a proper basis set.

3. Polycyclic Aromatic Hydrocarbons

The statistical analysis in section IV.A demonstrated that ZPVE corrections applied to theoretical results generally have little effect on the predicted EAs. This is not always the case. In studies of polycyclic aromatic hydrocarbon (PAH) EAs,[43,277] ZPVE corrections were found to be several tenths of an electronvolt in size and to account for a significant portion (as much as 40%) of computed EAs. In such large molecules, the usually insignificant errors in the computed harmonic ZPVEs become significant and may limit the accuracy of most theoretical methods. The ability to predict EAs of large molecules, such as PAHs, is becoming increasingly possible with accurate computational methods, such as DFT. For such molecules, the computation of accurate ZPVE corrections will be a challenge for theoreticians, and a necessary obstacle to overcome in the path to achieving high-accuracy theoretical EAs.

4. C_4O

In 1999, Brown, Rienstra-Kiracofe, and Schaefer[228] studied the EA of C_4O (see Table 9). Their DFT results suggested an EA(C_4O) of nearly 3.0 eV, which is about 1 eV greater than the experimental PES EA of 2.05 eV.[278] Although, as discussed in section IV.A, DFT often overestimates EAs, overestimations of nearly 1.0 eV are very large and prompted Rienstra-Kiracofe, Ellison, Hoffman, and Schaefer[172] to further investigate EA(C_4O) at levels of theory as sophisticated as CCSD(T)/aug-cc-pVTZ. Their best result, EA(C_4O) = 2.99 eV, validated the prior DFT values.

Yet the 1986 spectrum of C_4O^- contained a feature corresponding to an electron binding energy of 2.05 eV.[278] The later theoretical results just described clearly show that this feature could not be assigned to the EA of C_4O. The origin of this mysterious feature might then be explained by either detachment from an excited electronic state of C_4O^- or by detachment from some less-stable structural isomer of C_4O^-. Both the former and latter explanations are possible complications sometimes encountered in photoelectron experiments, and such effects need to be examined carefully when significant disagreements between experimental spectra and theoretical results are seen. Unfortunately, in the instance of C_4O, neither possibility provided an acceptable explanation for the origin of the 2.05 eV feature.[172] A proper EA for C_4O will certainly require more experimental and theoretical investigations. The apparent discrepancies between theory and experiment for C_4O illustrate the difficulties occasionally encountered in analysis of photoelectron spectra.

V. Conclusions

The future prospects for experimental ion spectroscopy are bright. As photoelectron spectrometers are developed with the capabilities to resolve target ions with higher and higher masses, more complex species can be studied. Hypercomplex ions are certain to be important for the study of reactive intermediates in atmospheric chemistry, materials science, or biophysical chemistry. With the improvement of mass spectrometers and new ion sources, there will always be important new work to be done.

The theoretical study of electron affinities is challenging and complex. Comparisons of theoretical results to experimental values continues to be a measuring stick by which the accuracy of new theoretical methods is assessed. A number of theoretical methods have been employed for the study of atomic and molecular electron affinities: conventional ab initio methods such as SCF, MP*n*, CI, and CC theories, model chemistry methods such as Gaussian-X, CBS, and Weizmann theories, and DFT in the form of approximate functionals. While not the most accurate theoretical technique, DFT can already be applied to large molecules (for example, stacks of DNA base paris), and in conjunction with a modest double-ζ plus polarization and diffuse function basis set can provide EA predictions with an average error of 0.2 eV or less. Future improvements in inexact functionals ensure that DFT will remain a useful and popular method for the theoretical determination of EAs. Theoretical studies (DFT or otherwise) of electron affinities can aid in the interpretation of experimental photoelectron spectra and often will provide accurate predictions of electron affinities for molecules which have not been studied experimentally.

VI. Acknowledgments

The work at the University of Georgia was supported by grants from the United States Department of Energy (DE-FG07-97ER14748) and the National Science Foundation (CHE-9815397). We give thanks to all our coauthors in refs 42, 43, 215, 218−241, and 279−281, whose studies of EAs with DFT provide the basis for much of this review. Special thanks are due to the following members of the Schaefer group for countless hours spent computing electron affinities: Nicole Brinkmann, Shawn Brown, Nancy Richardson, and Yaoming Xie. G.S.T., H.F.S., and J.C.R.-K. thank the following people for helpful discussions and suggestions: Axel Becke, Delano Chong, Ken Jordan, Josef Michl, Jack Simons, and Paul Wenthold. J.C.R.-K. thanks Christine Rienstra-Kiracofe for research assistance. The work at the University of Colorado was supported by a grant from the Chemical Physics Program, U.S. Department of Energy (DE-FG02-87ER13695). G.B.E. is a Fellow of the Guggenheim Foundation. G.B.E. and S.N. thank our experimental colleagues and friends for many discussions and suggestions: Kit Bowen, John Brauman, Charles DePuy, Mark Johnson, Dan Neumark, Kent Ervin, L. S. Wang, Josef Michl, and Pam Arnold. Particular thanks are due to Carl Lineberger for being such good company over the years and to Radoslawa Radziszewska and Ralph Avanzini for help in compiling the initial experimental EA review.

In September 1998 our friend Professor Robert R. Squires succumbed to cancer. In the field of ion chemistry and mass spectroscopy, Squires was simply the flower of his generation. So Bob, these ions are for you.

VII. Compilations of Experimental and Theoretical Electron Affinities

A. Report of Theoretical DFT Electron Affinities, Tables 8 and 9

Table 8. Theoretical Adiabatic Electron Affinities (eV) for 14 Atoms and 96 Molecules. The Harmonic ZPVE-Corrected Electron Affinities Are Listed in Parentheses[a]

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
hydrogen atom [H]	1		^2S	0.84	1.31	0.62	0.75	0.93	1.23	0.75419 ± 2E−05
			^1S	theoretical reference: 227			experimental reference: 47			
lithium atom [Li]	7		^2S	0.56	0.98	0.43	0.45	0.63	0.93	0.618 ± 0.0005
			^1S	theoretical reference: 227			experimental reference: 282			
lithium hydride [LiH]	8	$C_{\infty v}$	$^1\Sigma^+$	0.44	0.87	0.33	0.35	0.51	0.79	0.342 ± 0.012
		$C_{\infty v}$	$^2\Sigma^+$	(0.46)	(0.89)	(0.34)	(0.36)	(0.52)	(0.80)	
				theoretical reference: 227			experimental reference: 283			
beryllium hydride [BeH]	10	$C_{\infty v}$	$^2\Sigma^+$	−0.12	0.40	−0.33	−0.19	0.07	0.44	0.70 ± 0.10
		$C_{\infty v}$	$^1\Sigma^+$	(−0.11)	(0.41)	(−0.32)	(−0.18)	(0.07)	(0.45)	
				theoretical reference: 227			experimental reference: 284			
boron atom [B]	11		^2P	0.46	1.00	0.17	0.43	0.68	1.12	0.279723 ± 2.5E−05
			^3P	theoretical reference: 227			experimental reference: 285			
carbon atom [C]	12		^3P	1.38	1.98	1.04	1.35	1.64	2.22	1.262119 ± 20E−05
			^4S	theoretical reference: 227			experimental reference: 286			
methylidyne [CH]	13	$C_{\infty v}$	$^2\Pi$	1.35	1.93	1.04	1.31	1.57	2.11	1.238 ± 0.008
		$C_{\infty v}$	$^3\Sigma^-$	(1.36)	(1.94)	(1.06)	(1.33)	(1.59)	(2.13)	
				theoretical reference: 227			experimental reference: 287			
methylene [CH_2]	14	C_{2v}	$^3B_1$	0.66	1.08	0.30	0.70	0.79	1.29	0.652 ± 0.006
		C_{2v}	$^2B_1$	(0.72)	(1.13)	(0.35)	(0.75)	(0.84)	(1.33)	
				theoretical reference: 227			experimental reference: 94			
BH_3 [BH_3]	14	D_{3h}	$^1A_1'$	0.11	0.64	−0.17	0.08	0.32	0.76	0.038 ± 0.015
		D_{3h}	$^2A_2''$	(0.17)	(0.71)	(−0.10)	(0.14)	(0.39)	(0.82)	
				theoretical reference: 279			experimental reference: 288			
imidogen [NH]	15	$C_{\infty v}$	$^3\Sigma^-$	0.44	0.88	−0.03	0.52	0.63	1.21	0.370 ± 0.004
		$C_{\infty v}$	$^2\Pi$	(0.45)	(0.89)	(−0.02)	(0.53)	(0.63)	(1.21)	
				theoretical reference: 227			experimental reference: 103			
methyl radical [CH_3]	15	D_{3h}	$^2A_2''$	0.03	0.49	−0.35	0.05	0.19	0.80	0.080 ± 0.030
		C_{3v}	$^1A_1'$	(0.06)	(0.52)	(−0.32)	(0.08)	(0.22)	(0.83)	
				theoretical reference: 279			experimental reference: 290			
amino radical [NH_2]	16	C_{2v}	$^2B_1$	0.70	1.17	0.25	0.76	0.89	1.59	0.771 ± 0.005
		C_{2v}	$^1A_1$	(0.71)	(1.19)	(0.26)	(0.77)	(0.91)	(1.60)	
				theoretical reference: 227			experimental reference: 291			
oxygen atom [O]	16		^3P	1.66	2.11	1.11	1.79	1.88	2.54	1.4611100 ± 7E−07
			^2P	theoretical reference: 227			experimental reference: 40			
hydroxyl radical [OH]	17	$C_{\infty v}$	$^2\Pi$	1.82	2.29	1.28	1.92	2.04	2.80	1.827653 ± 4E−06
		$C_{\infty v}$	$^1\Sigma^+$	(1.81)	(2.29)	(1.28)	(1.92)	(2.04)	(2.80)	
				theoretical reference: 227			experimental reference: 553			
fluorine atom [F]	19		^2P	3.54	4.01	2.94	3.68	3.76	4.63	3.401290 ± 3E−06
			^1S	theoretical reference: 227			experimental reference: 40			
C_2 [C_2]	24	$D_{\infty h}$	$^1\Sigma_g^+$	3.47	4.01	3.10	3.36	3.55	4.29	3.269 ± 0.006
		$D_{\infty h}$	$^2\Sigma_g^+$	(3.45)	(3.99)	(3.08)	(3.35)	(3.54)	(4.28)	
				theoretical reference: 227			experimental reference: 272			note: 1
ethynyl radical [C_2H]	25	$C_{\infty v}$	$^2\Sigma^+$	3.15	3.60	2.91	3.06	3.19	3.73	2.969 ± 0.006
		$C_{\infty v}$	$^1\Sigma^+$	(3.10)	(3.58)	(2.92)	(3.02)	(3.15)	(3.68)	
				theoretical reference: 241			experimental reference: 272			
cyano radical [CN]	26	$C_{\infty v}$	$^2\Sigma^+$	4.04	4.52	4.03	3.75	3.88	4.46	3.862 ± 0.004
		$C_{\infty v}$	$^1\Sigma^+$	(4.04)	(4.52)	(4.04)	(3.75)	(3.88)	(4.47)	
				theoretical reference: 227			experimental reference: 293			
vinylidene [C_2H_2]	26	C_{2v}	$^1A_1$	0.70	1.23	0.49	0.61	0.82	1.20	0.490 ± 0.006
		C_{2v}	$^2B_2$	(0.71)	(1.25)	(0.51)	(0.63)	(0.84)	(1.21)	
				theoretical reference: 279			experimental reference: 379			
aluminum atom [Al]	27		^2P	0.45	1.02	0.27	0.35	0.64	1.01	0.43283 ± 5E−05
			^3P	theoretical reference: 229			experimental reference: 294			
vinyl radical [C_2H_3]	27	C_s	$^2A'$	0.68	1.14	0.39	0.63	0.77	1.29	0.667 ± 0.024
		C_s	$^1A'$	(0.780)	(1.17)	(0.42)	(0.66)	(0.80)	(1.31)	
				theoretical reference: 279			experimental reference: 118			
boron monoxide [BO]	27	$C_{\infty v}$	$^2\Sigma^+$	2.61	3.04	2.47	2.47	2.57	3.09	2.508 ± 0.008
		$C_{\infty v}$	$^1\Sigma^-$	(2.62)	(3.05)	(2.48)	(2.48)	(2.58)	(3.10)	
				theoretical reference: 227			experimental reference: 169			
silicon atom [Si]	28		^3P	1.36	1.99	1.18	1.24	1.57	2.01	1.389521 ± 20E−05
			^4S	theoretical reference: 229			experimental reference: 286			
methylene-amidogen [NCH_2]	28	C_{2v}	$^2B_1$	0.52	1.00	0.13	0.53	0.68	1.27	0.511 ± 0.008
		C_{2v}	$^1A_1$	(0.58)	(1.07)	(0.18)	(0.60)	(0.75)	(1.33)	
				theoretical reference: 279			experimental reference: 295			
formyl radical [HCO]	29	C_s	$^2A'$	0.39	0.85	0.13	0.35	0.48	0.92	0.313 ± 0.005
		C_s	$^1A'$	(0.47)	(0.93)	(0.20)	(0.43)	(0.55)	(0.99)	
				theoretical reference: 227			experimental reference: 296			note: 2
silylidyne [SiH]	29	$C_{\infty v}$	$^2\Pi$	1.28	1.89	1.11	1.16	1.48	1.89	1.277 ± 0.009
		$C_{\infty v}$	$^3\Sigma^-$	(1.30)	(1.90)	(1.12)	(1.17)	(1.49)	(1.90)	
				theoretical reference: 230			experimental reference: 380			

Table 8 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
silylene [SiH$_2$]	30	C_{2v}	$^1A_1$	1.17	1.76	1.00	1.05	1.34	1.74	1.124 ± 0.020
		C_{2v}	$^2B_1$	(1.20)	(1.79)	(1.03)	(1.08)	(1.37)	(1.76)	
				theoretical reference: 230			experimental reference: 380			
nitric oxide [NO]	30	$C_{\infty v}$	$^2\Pi$	0.49	0.94	0.33	0.40	0.48	0.93	0.026 ± 0.005
		$C_{\infty v}$	$^3\Sigma^-$	(0.53)	(0.97)	(0.36)	(0.43)	(0.52)	(0.96)	
				theoretical reference: 227			experimental reference: 111			
phosphorus atom [P]	31		^4S	0.93	1.40	0.68	0.87	1.04	1.47	0.7464 ± 0.0004
			^3P	theoretical reference: 229			experimental reference: 297			
silyl radical [SiH$_3$]	31	C_{3v}	$^2A_1$	1.40	1.89	1.17	1.31	1.49	2.02	1.406 ± 0.014
		C_{3v}	$^1A_1$	(1.45)	(1.94)	(1.22)	(1.37)	(1.55)	(2.06)	
				theoretical reference: 230			experimental reference: 332			
methoxy radical [CH$_3$O]	31	C_s	$^2A'$	1.46	1.97	1.01	1.49	1.65	2.28	1.572 ± 0.004
		C_{3v}	$^1A_1$	(1.50)	(2.01)	(1.05)	(1.53)	(1.69)	(2.29)	
				theoretical reference: 279			experimental reference: 299			
nitrosyl hydride [HNO]	31	C_s	$^1A'$	0.73	1.18	0.56	0.65	0.73	1.13	0.338 ± 0.015
		C_s	$^2A''$	(0.78)	(1.23)	(0.61)	(0.70)	(0.78)	(1.18)	
				theoretical reference: 227			experimental reference: 300			
oxygen molecule [O$_2$]	32	$D_{\infty h}$	$^3\Sigma_g^-$	0.62	1.03	0.33	0.59	0.63	1.05	0.451 ± 0.007
		$D_{\infty h}$	$^2\Pi_g$	(0.65)	(1.06)	(0.36)	(0.62)	(0.65)	(1.08)	
				theoretical reference: 227			experimental reference: 111			
sulfur atom [S]	32		^3P	2.22	2.74	1.97	2.14	2.33	2.89	2.077104 ± 3E−06
			^2P	theoretical reference: 229			experimental reference: 40			
hydrogen phosphide [PH]	32	$C_{\infty v}$	$^3\Sigma^-$	1.09	1.58	0.85	1.02	1.20	1.72	1.028 ± 0.010
		$C_{\infty v}$	$^2\Pi$	(1.10)	(1.59)	(0.86)	(1.02)	(1.20)	(1.72)	
				theoretical reference: 240			experimental reference: 301			
fluoromethylene [HCF]	32	C_s	$^1A'$	0.80	1.29	0.57	0.75	0.89	1.24	0.542 ± 0.005
		C_s	$^2A''$	(0.85)	(1.34)	(0.63)	(0.80)	(0.94)	(1.28)	
				theoretical reference: 227			experimental reference: 302			
hydroperoxy radical [HO$_2$]	33	C_s	$^2A''$	1.01	1.42	0.69	0.99	1.02	1.49	1.078 ± 0.006
		C_s	$^1A'$	(1.04)	(1.45)	(0.72)	(1.02)	(1.05)	(1.52)	
				theoretical reference: 227			experimental reference: 102			
fluoromethyl radical [FCH$_2$]	33	C_s	$^2A'$	0.21	0.63	−0.13	0.22	0.30	0.75	0.2 ± 0.19
		C_s	$^1A'$	(0.26)	(0.67)	(−0.08)	(0.27)	(0.35)	(0.78)	
				theoretical reference: 279			experimental reference: 303			
dihydrogen phosphide [PH$_2$]	33	C_{2v}	$^2B_1$	1.26	1.78	1.03	1.17	1.37	1.94	1.271 ± 0.010
		C_{2v}	$^1A_1$	(1.28)	(1.79)	(1.05)	(1.18)	(1.39)	(1.95)	
				theoretical reference: 240			experimental reference: 301			
hydrogen sulfide [SH]	33	$C_{\infty v}$	$^2\Pi$	2.37	2.90	2.13	2.28	2.48	3.08	2.317 ± 0.002
		$C_{\infty v}$	$^1\Sigma^+$	(2.38)	(2.91)	(2.13)	(2.28)	(2.49)	(3.08)	
				theoretical reference: 241			experimental reference: 304			
chlorine atom [Cl]	35		^2P	3.74	4.29	3.50	3.63	3.84	4.47	3.612724 ± 3E−05
			^1S	theoretical reference: 229			experimental reference: 305			
oxygen monofluoride [FO]	35	$C_{\infty v}$	$^2\Pi$	2.34	2.74	2.02	2.28	2.31	2.85	2.272 ± 0.006
		$C_{\infty v}$	$^1\Sigma^+$	(2.36)	(2.76)	(2.04)	(2.30)	(2.33)	(2.87)	
				theoretical reference: 227			experimental reference: 306			
C$_3$ [C$_3$]	36	$D_{\infty h}$	$^1\Sigma_g^+$	2.24	2.80	2.21	2.02	2.24	2.74	1.995 ± 0.025
		$D_{\infty h}$	$^2\Pi_g$	(2.24)	(2.80)	(2.22)	(2.02)	(2.24)	(2.73)	
				theoretical reference: 227			experimental reference: 307			
fluorine molecule [F$_2$]	38	$D_{\infty h}$	$^1\Sigma_g^+$	3.72	4.05	3.51	3.68	3.63	3.80	3.01 ± 0.07
		$D_{\infty h}$	$^2\Sigma_u^+$	(3.77)	(4.10)	(3.56)	(3.72)	(3.67)	(3.84)	
				theoretical reference: 227			experimental reference: 308			
propargyl radical [C$_3$H$_3$]	39	C_{2v}	$^2B_1$	0.97	1.48	0.64	0.93	1.11	1.68	0.918 ± 0.008
		C_s	$^1A'$	(0.98)	(1.49)	(0.65)	(0.94)	(1.12)	(1.69)	
				theoretical reference: 279			experimental reference: 309			
C$_3$H$_3$ [CH$_3$C$_2$]	39	C_s	$^2A'$	2.72	3.24	2.51	2.57	2.74	3.35	2.718 ± 0.008
		C_{3v}	$^1A_1$	(2.70)	(3.21)	(2.47)	(2.55)	(2.73)	(3.33)	
				theoretical reference: 279			experimental reference: 309			
dicarbon monoxide [C$_2$O]	40	$C_{\infty v}$	$^3\Sigma^-$	2.35	2.85	2.13	2.22	2.38	3.01	2.289 ± 0.018
		$C_{\infty v}$	$^2\Pi$	(2.33)	(2.84)	(2.12)	(2.20)	(2.36)	(3.00)	
				theoretical reference: 227			experimental reference: 310			
HCNN [HCN$_2$]	41	C_s	$^2A''$	1.70	2.22	1.33	1.67	1.84	2.52	1.685 ± 0.006
		C_s	$^1A'$	(1.68)	(2.20)	(1.31)	(1.66)	(1.83)	(2.51)	
				theoretical reference: 279			experimental reference: 311			
isocyanato radical [NCO]	42	$C_{\infty v}$	$^2\Pi$	3.56	4.10	3.36	3.39	3.57	4.29	3.609 ± 0.005
		$C_{\infty v}$	$^1\Sigma^+$	(3.54)	(4.08)	(3.34)	(3.37)	(3.55)	(4.27)	
				theoretical reference: 227			experimental reference: 293			
N$_3$ [N$_3$]	42	$D_{\infty h}$	$^2\Pi_g$	2.71	3.25	2.32	2.67	2.85	3.58	2.76 ± 0.04
		$D_{\infty h}$	$^1\Sigma_g^+$	(2.68)	(3.21)	(2.28)	(2.64)	(2.82)	(3.55)	
				theoretical reference: 227			experimental reference: 312			
CH$_2$CHO [CH$_2$CHO]	43	C_s	$^2A''$	1.79	2.31	1.45	1.75	1.92	2.61	1.8248 ± 0.0006
		C_s	$^1A'$	(1.81)	(2.33)	(1.47)	(1.77)	(1.95)	(2.63)	
				theoretical reference: 279			experimental reference: 313			

Table 8 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
acetyl radical [CH_3CO]	43	C_s	$^2A'$	0.43	0.85	0.11	0.45	0.54	1.01	0.423 ± 0.037
		C_s	$^1A'$	(0.50)	(0.92)	(0.18)	(0.51)	(0.60)	(1.07)	
				theoretical reference: 279			experimental reference: 314			
aluminum monoxide [AlO]	43	$C_{\infty v}$	$^2\Sigma^+$	2.57	3.09	2.46	2.39	2.60	3.09	2.60 ± 0.01
		$C_{\infty v}$	$^1\Sigma^+$	(2.57)	(3.09)	(2.46)	(2.39)	(2.60)	(3.10)	
				theoretical reference: 229			experimental reference: 315			
boron dioxide [BO_2]	43	$D_{\infty h}$	$^2\Pi_g$	4.34	4.90	4.27	4.06	4.26	4.98	4.32 ± 0.19
		$D_{\infty h}$	$^1\Sigma_g^+$	(4.29)	(4.85)	(4.17)	(4.03)	(4.23)	(4.95)	
				theoretical reference: 227			experimental references: 132, 316			
nitrogen dioxide [NO_2]	46	C_{2v}	$^2A_1$	2.37	2.80	2.31	2.18	2.23	2.74	2.273 ± 0.005
		C_{2v}	$^1A_1$	(2.39)	(2.82)	(2.33)	(2.20)	(2.26)	(2.76)	
				theoretical reference: 227			experimental reference: 317			
fluorosilylidyne [SiF]	47	$C_{\infty v}$	$^2\Pi$	0.98	1.55	0.82	0.86	1.13	1.50	0.81 ± 0.02
		$C_{\infty v}$	$^3\Sigma^-$	(0.99)	(1.56)	(0.83)	(0.87)	(1.14)	(1.51)	
				theoretical reference: 221			experimental reference: 318			
phosphorus monoxide [PO]	47	$C_{\infty v}$	$^2\Pi$	0.43	0.92	0.22	0.94	1.15	1.51	1.092 ± 0.010
		$C_{\infty v}$	$^1\Sigma^+$	(0.45)	(0.93)	(0.24)	(0.95)	(1.16)	(1.53)	
				theoretical reference: 229			experimental reference: 301			
sulfur monoxide [SO]	48	$C_{\infty v}$	$^3\Sigma^-$	1.27	1.76	1.04	1.14	1.29	1.75	1.125 ± 0.005
		$C_{\infty v}$	$^2\Pi$	(1.29)	(1.78)	(1.12)	(1.15)	(1.31)	(1.76)	
				theoretical reference: 229			experimental reference: 319			
ozone [O_3]	48	C_{2v}	$^1A_1$	2.75	3.14	2.92	2.43	2.44	2.78	2.1028 ± 0.0025
		C_{2v}	$^2B_1$	(2.79)	(3.18)	(2.97)	(2.46)	(2.47)	(2.82)	
				theoretical reference: 227			experimental reference: 320			
difluoromethylene [CF_2]	50	C_{2v}	$^1A_1$	0.56	0.98	0.36	0.49	0.55	0.81	0.179 ± 0.005
		C_{2v}	$^2B_1$	(0.62)	(1.04)	(0.42)	(0.55)	(0.60)	(0.86)	
				theoretical reference: 227			experimental reference: 321			
chlorine monoxide [ClO]	51	$C_{\infty v}$	$^2\Pi$	2.28	2.76	2.06	2.15	2.27	2.80	2.276 ± 0.006
		$C_{\infty v}$	$^1\Sigma^+$	(2.29)	(2.78)	(2.07)	(2.16)	(2.29)	(2.81)	
				theoretical reference: 229			experimental reference: 306			
sulfur fluoride [SF]	51	$C_{\infty v}$	$^2\Pi$	2.45	2.94	2.25	2.32	2.47	2.98	2.285 ± 0.006
		$C_{\infty v}$	$^1\Sigma^+$	theoretical reference: 220			experimental reference: 322			note: 3
chlorine monofluoride [ClF]	54	$C_{\infty v}$	$^1\Sigma^+$	2.96	3.35	2.74	2.91	2.94	3.10	2.86 ± 0.2
		$C_{\infty v}$	$^2\Sigma^+$	theoretical reference: 42			experimental reference: 323			note: 4
aluminum dimer [Al_2]	54	$D_{\infty h}$	$^3\Sigma_g^-$	1.54	2.15	1.46	1.34	1.66	2.05	1.46 ± 0.06
		$D_{\infty h}$	$^4\Sigma_g^-$	(1.54)	(2.15)	(1.46)	(1.34)	(1.67)	(2.05)	
				theoretical reference: 237			experimental reference: 324			
silicon dimer [Si_2]	56	$D_{\infty h}$	$^3\Sigma_g^-$	2.06	2.65	1.79	1.98	2.28	2.90	2.202 ± 0.010
		$D_{\infty h}$	$^2\Sigma_g^+$	(2.05)	(2.65)	(1.78)	(1.97)	(2.27)	(2.89)	
				theoretical reference: 230			experimental reference: 417			
Si_2H [Si_2H]	57	C_{2v}	$^2A_1$	2.31	2.86	2.20	2.13	2.38	2.87	2.31 ± 0.01
		C_{2v}	$^1A_1$	(2.31)	(2.87)	(2.21)	(2.13)	(2.38)	(2.87)	
				theoretical reference: 230			experimental reference: 418			note: 5
aluminum dioxide [AlO_2]	59	$D_{\infty h}$	$^2\Pi_g$	4.02	4.58	3.99	3.71	3.94	4.63	4.23 ± 0.01
		$D_{\infty h}$	$^1\Sigma_g^+$	(3.99)	(4.55)	(4.12)	(3.70)	(3.92)	(4.62)	
				theoretical reference: 229			experimental reference: 315			note: 6
silicon dioxide [SiO_2]	60	$D_{\infty h}$	$^1\Sigma_g^+$	2.21	2.72	2.13	2.03	2.20	2.60	2.1 ± 0.1
		C_{2v}	$^2A_1$	(2.25)	(2.76)	(2.16)	(2.06)	(2.23)	(2.63)	
				theoretical reference: 229			experimental reference: 327			
C_2F_2 [C_2F_2]	62	C_{2v}	$^1A_1$	2.49	3.03	2.29	2.38	2.57	3.01	2.255 ± 0.006
		C_{2v}	$^2B_2$	(2.52)	(3.06)	(2.32)	(2.42)	(2.60)	(3.04)	
				theoretical reference: 279			experimental reference: 328			note: 7
phosphorus dimer [P_2]	62	$D_{\infty h}$	$^1\Sigma_g^+$	0.78	1.34	0.70	0.60	0.85	1.20	0.589 ± 0.025
		$D_{\infty h}$	$^2\Pi_u$	(0.79)	(1.35)	(0.71)	(0.61)	(0.86)	(1.21)	
				theoretical reference: 237			experimental reference: 329			
phosphorus dioxide [PO_2]	63	C_{2v}	$^2A_1$	3.44	3.93	3.41	3.18	3.33	3.88	3.42 ± 0.01
		C_{2v}	$^1A_1$	(3.44)	(3.93)	(3.41)	(3.18)	(3.33)	(3.72)	
				theoretical reference: 229			experimental reference: 430			
sulfur dimer [S_2]	64	$D_{\infty h}$	$^3\Sigma_g^-$	1.81	2.34	1.71	1.63	1.82	2.27	1.670 ± 0.015
		$D_{\infty h}$	$^2\Pi_g$	(1.82)	(2.35)	(1.72)	(1.64)	(1.83)	(2.27)	
				theoretical reference: 237			experimental reference: 331			
sulfur dioxide [SO_2]	64	C_{2v}	$^1A_1$	1.58	2.06	1.55	1.37	1.50	1.87	1.107 ± 0.008
		C_{2v}	$^2B_1$	(1.77)	(2.25)	(1.75)	(1.54)	(1.68)	(2.05)	
				theoretical reference: 229			experimental reference: 298			
cyclopentadienyl radical [C_5H_5]	65	C_{2v}	$^2B_1$	1.73	2.28	1.46	1.62	1.84	2.52	1.804 ± 0.007
		D_{5h}	$^1A_1'$	(1.71)	(2.26)	(1.43)	(1.61)	(1.83)	(2.50)	
				theoretical reference: 215			experimental reference: 333			
difluorosilylene [SiF_2]	66	C_{2v}	$^1A_1$	0.56	1.07	0.39	0.45	0.65	0.96	0.1 ± 0.1
		C_{2v}	$^2B_1$	(0.58)	(1.10)	(0.42)	(0.47)	(0.67)	(0.98)	
				theoretical reference: 221			experimental reference: 318			

Table 8 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
pyrrolyl radical [C_4H_4N]	66	C_{2v}	$^2A_2$	2.07	2.62	1.79	1.97	2.19	2.88	2.39 ± 0.13
		C_{2v}	$^1A_1$	(2.07)	(2.62)	(1.78)	(1.98)	(2.19)	(2.87)	
				theoretical reference: 215			experimental reference: 434			
chlorine dioxide [ClO_2]	67	C_{2v}	$^2B_1$	2.41	2.85	2.45	2.15	2.22	2.64	2.140 ± 0.008
		C_{2v}	$^1A_1$	(2.45)	(2.88)	(2.49)	(2.17)	(2.24)	(2.66)	
				theoretical reference: 229			experimental reference: 306			
chlorine dimer [Cl_2]	70	$D_{\infty h}$	$^1\Sigma_g^+$	3.26	3.67	3.11	3.14	3.21	3.40	2.38 ± 0.10
		$D_{\infty h}$	$^2\Sigma_u^+$	(3.27)	(3.69)	(3.13)	(3.16)	(3.23)	(3.42)	
				theoretical reference: 237			experimental reference: 335			
C_6 [C_6]	72	$D_{\infty h}$	$^3\Sigma_g^-$	4.00	4.57	3.89	3.78	4.01	4.68	4.185 ± 0.006
		$D_{\infty h}$	$^2\Pi_u$	(4.02)	(4.59)	(3.91)	(3.80)	(4.04)	(4.71)	
				theoretical reference: 228			experimental reference: 307			
germanium atom [Ge]	73		^3P	1.33	1.94	1.16	1.21	1.53	1.97	1.232712 ± 1.5E−05
			^4S	theoretical reference: 224			experimental reference: 286			
triacetylene radical [C_6H]	73	$C_{\infty v}$	$^2\Pi$	3.65	4.23	3.48	3.45	3.69	4.35	3.809 ± 0.015
		$C_{\infty v}$	$^1\Sigma^+$	(3.66)	(4.24)	(3.50)	(3.48)	(3.72)	(4.38)	
				theoretical reference: 228			experimental reference: 336			note: 8
o-benzyne [C_6H_4]	76	C_{2v}	$^1A_1$	0.88	1.39	0.85	0.69	0.86	1.18	0.564 ± 0.007
		C_{2v}	$^2B_2$	(0.94)	(1.45)	(0.91)	(0.75)	(0.93)	(1.25)	
				theoretical reference: 215			experimental reference: 337			
phenyl radical [C_6H_5]	77	C_{2v}	$^2A_1$	1.01	1.50	0.75	0.95	1.10	1.64	1.096 ± 0.006
		C_{2v}	$^1A_1$	(1.07)	(1.56)	(0.81)	(1.01)	(1.16)	(1.69)	
				theoretical reference: 215			experimental reference: 120			
trans-dicyanoethylene [(*E*)-$C_2H_2(CN)_2$]	78	C_{2h}	^1A_g	1.53	2.09	1.35	1.40	1.61	2.13	1.249 ± 0.087
		C_{2h}	^2B_g	(1.60)	(2.16)	(1.44)	(1.47)	(1.68)	(2.19)	
				theoretical reference: 280			experimental reference: 338			
selenium atom [Se]	79		^3P	2.21	2.71	1.99	2.11	2.30	2.86	2.020767 ± 2E−05
			^2P	theoretical reference: 223			experimental reference: 450			
bromine atom [Br]	80		^2P	3.60	4.15	3.41	3.46	3.68	4.29	3.363588 ± 2E−06
			^1S	theoretical reference: 219			experimental reference: 339			note: 9
C_2F_3 [C_2F_3]	81	C_s	$^2A'$	2.43	2.85	2.20	2.35	2.41	2.85	2.06 ± 0.22
		C_s	$^1A'$	(2.48)	(2.90)	(2.25)	(2.40)	(2.46)	(2.90)	
				theoretical reference: 218			experimental reference: 340			note: 10
cyclopentanone enolate [C_5H_7O]	83	C_1	^2A	1.48	2.00	1.17	1.42	1.59	2.23	1.598 ± 0.007
		C_1	^1A	(1.52)	(2.04)	(1.20)	(1.46)	(1.63)	(2.26)	
				theoretical reference: 215			experimental reference: 341			
C_7 [C_7]	84	$D_{\infty h}$	$^1\Sigma_g^+$	3.43	4.03	3.58	3.10	3.36	3.90	3.358 ± 0.014
		$D_{\infty h}$	$^2\Pi_g$	(3.39)	(3.99)	(3.52)	(3.07)	(3.33)	(3.88)	
				theoretical reference: 228			experimental reference: 307			
trifluorosilyl radical [SiF_3]	85	C_{3v}	$^2A_1$	2.69	3.10	2.46	2.62	2.69	3.18	2.41 ± 0.22
		C_{3v}	$^1A_1$	(2.73)	(3.14)	(2.50)	(2.66)	(2.73)	(3.21)	
				theoretical reference: 221			experimental reference: 318			
sulfur trifluoride [SF_3]	89	C_s	$^2A'$	3.36	3.77	3.27	3.14	3.19	3.54	3.07 ± 0.2
		C_{2v}	$^1A_1$	theoretical reference: 220			experimental reference: 125			note: 11
germanium monofluoride [GeF]	92	$C_{\infty v}$	$^2\Pi$	1.15	1.71	1.02	1.01	1.26	1.63	1.02 ± 0.06
		$C_{\infty v}$	$^3\Sigma^-$	(1.16)	(1.71)	(1.03)	(1.02)	(1.27)	(1.64)	
				theoretical reference: 224			experimental reference: 342			note: 12
phenoxyl radical [C_6H_5O]	93	C_{2v}	$^2B_1$	2.16	2.72	1.85	2.06	2.28	2.93	2.253 ± 0.006
		C_{2v}	$^1A_1$	(2.18)	(2.75)	(1.86)	(2.09)	(2.32)	(2.96)	
				theoretical reference: 215			experimental reference: 120			
C_8 [C_8]	96	$D_{\infty h}$	$^3\Sigma_g^-$	4.18	4.76	4.10	3.93	4.18	4.83	4.379 ± 0.006
		$D_{\infty h}$	$^2\Pi_g$	(4.19)	(4.77)	(4.11)	(3.95)	(4.19)	(4.85)	
				theoretical reference: 228			experimental reference: 307			
bromine monoxide [BrO]	96	$C_{\infty v}$	$^2\Pi$	2.39	2.90	2.20	2.22	2.38	2.92	2.353 ± 0.006
		$C_{\infty v}$	$^1\Sigma^+$	(2.40)	(2.91)	(2.21)	(2.23)	(2.39)	(2.93)	
				theoretical reference: 234			experimental reference: 306			note: 13
cyclohexanone enolate [C_6H_9O]	97	C_1	^2A	1.40	1.92	1.09	1.35	1.53	2.16	1.526 ± 0.010
		C_1	^1A	(1.44)	(1.97)	(1.12)	(1.40)	(1.57)	(2.20)	
				theoretical reference: 215			experimental reference: 341			
maleic anhydride [$C_4H_2O_3$]	98	C_{2v}	$^1A_1$	1.74	2.28	1.54	1.62	1.81	2.33	1.44 ± 0.09
		C_{2v}	$^2A_2$	(1.80)	(2.34)	(1.60)	(1.68)	(1.87)	(2.39)	
				theoretical reference: 215			experimental reference: 343			
sulfur tetrafluoride [SF_4]	108	C_{2v}	$^1A_1$	2.45	2.77	1.99	2.62	2.54	2.56	2.35 ± 0.10
		C_{4v}	$^2A_1$	theoretical reference: 220			experimental reference: 344			note: 14
C_9 [C_9]	108	$D_{\infty h}$	$^1\Sigma_g^+$	3.73	4.33	3.94	3.38	3.64	4.20	3.684 ± 0.010
		$D_{\infty h}$	$^2\Pi_u$	(3.70)	(4.31)	(3.88)	(3.35)	(3.62)	(4.18)	
				theoretical reference: 228			experimental reference: 307			
1,1,1-trifluoroacetone enolate [$C_3H_2F_3O$]	111	C_s	$^2A''$	2.61	3.12	2.29	2.55	2.71	3.40	2.625 ± 0.010
		C_s	$^1A'$	(2.60)	(3.12)	(2.29)	(2.54)	(2.70)	(3.40)	
				theoretical reference: 228			experimental reference: 341			note: 15

Table 8 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
pentafluoroethyl radical [C_2F_5]	119	C_s	$^2A'$	1.94	2.35	1.70	1.92	1.94	2.37	1.81 ± 0.14
		C_s	$^1A'$	(2.03)	(2.42)	(1.77)	(2.00)	(2.01)	(2.44)	
				theoretical reference: 218			experimental reference: 345			note: 16
tetracyanoethylene [C_6N_4]	128	D_{2h}	^1A_g	3.51	4.10	3.46	3.28	3.51	4.08	3.17 ± 0.2
		D_{2h}	$^2B_{2g}$	(3.49)	(4.07)	(3.43)	(3.26)	(3.49)	(4.06)	
				theoretical reference: 228			experimental references: 338, 346			
germanium dimer [Ge_2]	146	$D_{\infty h}$	$^3\Sigma_g^-$	1.94	2.47	1.77	1.80	2.04	2.58	2.074 ± 0.001
		$D_{\infty h}$	$^2\Pi_u$	(1.93)	(2.47)	(1.76)	(1.80)	(2.04)	(2.61)	
				theoretical reference: 237			experimental reference: 347			note: 17
sulfur hexafluoride [SF_6]	146	O_h	$^1A_{1g}$	2.66	2.83	1.61	3.22	3.00	2.85	1.07 ± 0.07
		O_h	$^2A_{1g}$	theoretical reference: 220			experimental reference: 128			note: 18
selenium dimer [Se_2]	158	$D_{\infty h}$	$^3\Sigma_g^-$	1.96	2.48	1.88	1.75	1.95	2.40	1.94 ± 0.07
		$D_{\infty h}$	$^2\Pi_g$	(1.96)	(2.48)	(1.89)	(1.76)	(1.96)	(2.41)	
				theoretical reference: 237			experimental reference: 348			
bromine dimer [Br_2]	160	$D_{\infty h}$	$^1\Sigma_g^+$	3.10	3.55	3.01	2.95	3.06	3.28	2.51 ± 0.10
		$D_{\infty h}$	$^2\Sigma_u^+$	(3.12)	(3.56)	(3.02)	(2.97)	(3.07)	(3.29)	
				theoretical reference: 237			experimental references: 335, 349			
perinaphthenyl radical [$C_{13}H_9$]	165	D_{3h}	$^2A_1''$	1.29	1.86	0.92	1.23	1.47	2.07	1.07 ± 0.10
		D_{3h}	$^1A_1'$	(1.36)	(1.93)	(0.97)	(1.31)	(1.54)	(2.14)	
				theoretical reference: 43			experimental reference: 350			
anthracene [$C_{14}H_{10}$]	178	D_{2h}	^1A_g	0.58	1.16	0.30	0.53	0.78	1.29	0.530 ± 0.005
		D_{2h}	$^2B_{3u}$	(0.72)	(1.29)	(0.45)	(0.67)	(0.90)	(1.41)	
				theoretical reference: 43			experimental reference: 351			
selenium hexafluoride [SeF_6]	193	O_h	$^1A_{1g}$	3.95	4.16	3.13	4.39	4.11	4.13	2.9 ± 0.2
		O_h	$^2A_{2g}$	(4.10)	(4.30)	(3.31)	(4.52)	(4.24)	(4.27)	
				theoretical reference: 223			experimental reference: 125			note: 19
tetracene [$C_{18}H_{12}$]	228	D_{2h}	^1A_g	1.13	1.71	0.86	1.06	1.32	1.85	1.04 ± 0.04
		D_{2h}	$^2B_{1g}$	(1.24)	(1.83)	(0.96)	(1.18)	(1.43)	(1.95)	
				theoretical reference: 43			experimental reference: 352			

[a] Symmetry and state of neutral species listed first with that of the anion on the following line. Notes: (1) Revised EAs from ref 238. See also the discussion in the text. (2) CCSD(T)/aug-cc-pVTZ gives EA = 0.33 eV. See ref 361. (3) The BLYP/DZP ZPVE correction is +0.02 eV. LSDA and B3P86 results are from ref 237. (4) The BLYP ZPVE correction is +0.03 eV. LSDA and B3P86 results are from ref 237. (5) The hybrid density functionals (B3LYP, B3P86, and BHLYP) give the neutral gound state to be $^2B_1$. See ref 230 for discussion. (6) BHLYP exhibits orbital instability for the neutral species. See ref 229. (7) See ref 218 for additional theoretical work. (8) BLYP, BP86, and LSDA give bent C_s structures. See ref 228. (9) LSDA and B3P86 results are from ref 237. (10) LSDA result is from ref 237. (11) The BLYP/DZP ZPVE correction is +0.02 eV. LSDA and B3P86 results are from ref 237. See also refs 364 and 365 for additional experimental data. (12) LSDA and B3P86 results are from ref 239. No error given in ref 342. The error listed is a likely error based on the apparent resolution of the spectrum for GeF. (13) LSDA and B3P86 results are from ref 239. (14) The BLYP/DZP ZPVE correction is +0.09 eV. LSDA and B3P86 results are from ref 237. See also ref 364 for additional experimental data. (15) The neutral structure is a transition state with B3P86 and BP86. See ref 228. (16) See ref 132 for a revision of the experimental electron affinity value. The LSDA result is from ref 237. (17) See ref 372 for additional experimental work. (18) The BLYP/DZP ZPVE correction is +0.17 eV. LSDA and B3P86 results are from ref 237. DFT results improve with a larger basis (ref 275). EA = 0.92 eV with CCSD(T) (ref 276). (19) LSDA and B3P86 results are from ref 239.

Table 9. Theoretical Adiabatic Electron Affinities (eV) for 3 Atoms and 50 Molecules Excluded from Table 8. These Species Have either no Experimental Electron Affinity or an Uncertain Experimental Value (see the included notes). The ZPVE-Corrected Electron Affinities Are Listed in Parentheses[a]

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
beryllium atom [Be]	9		^1S	−0.19	0.31	−0.38	−0.25	−0.03	0.27	
			^2P	theoretical reference: 227						note: 1
nitrogen atom [N]	14		^4S	0.18	0.60	−0.32	0.30	0.38	0.75	−0.07 ± 0.02
			^3P	theoretical reference: 227			experimental reference: 289			
CF [CF]	31	$C_{\infty v}$	$^2\Pi$	0.71	1.21	0.47	0.66	0.81	1.22	3.2 ± 0.4
		$C_{\infty v}$	$^3\Sigma^-$	(0.74)	(1.24)	(0.51)	(0.69)	(0.84)	(1.25)	
				theoretical reference: 237			experimental reference: 353			note: 2
silane [SiH_4]	32	T_d	$^1A_1$	−0.74	−0.32	−0.91	−0.80	−0.64	−0.28	
		T_d	$^2A_1$	(−0.73)	(−0.30)	(−0.91)	(−0.79)	(−0.62)	(−0.26)	
				theoretical reference: 230						
C_2F [C_2F]	43	C_s	$^2A'$	3.16	3.66	2.97	2.98	3.14	3.78	3.4 ± 0.8
		$C_{\infty v}$	$^1\Sigma^+$	(3.16)	(3.66)	(2.97)	(2.99)	(3.15)	(3.77)	
				theoretical reference: 218			experimental reference: 354			note: 3
silicon monoxide [SiO]	44	$C_{\infty v}$	$^1\Sigma^+$	0.22	0.75	0.07	0.11	0.34	0.67	
		$C_{\infty v}$	$^2\Pi$	(0.39)	(0.76)	(0.08)	(0.12)	(0.35)	(0.68)	
				theoretical reference: 229						
nitrous oxide [N_2O]	44	$C_{\infty v}$	$^1\Sigma^+$	0.30	0.69	0.21	0.19	0.21	0.53	0.22 ± 0.10
		C_s	$^2A'$	(0.40)	(0.78)	(0.31)	(0.27)	(0.29)	(0.62)	
				theoretical reference: 227			experimental reference: 355			note: 4
phosphorus monofluoride [PF]	50	$C_{\infty v}$	$^3\Sigma^-$	0.95	1.41	0.71	0.87	1.02	1.47	
		$C_{\infty v}$	$^2\Pi$	(0.96)	(1.42)	(0.72)	(0.88)	(1.03)	(1.48)	
				theoretical reference: 222						note: 5
tricarbon monoxide [C_3O]	52	$C_{\infty v}$	$^1\Sigma^+$	1.29	1.81	1.24	1.11	1.28	1.69	1.34 ± 0.15
		C_s	$^2A'$	(1.36)	(1.88)	(1.31)	(1.18)	(1.34)	(1.76)	
				theoretical reference: 279			experimental reference: 278			note: 6

Table 9 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
cyanoethylene [C_2H_3CN]	53	C_s	$^1A'$	0.05	0.59	−0.16	−0.02	0.17	0.63	
		C_s	$^2A''$	(0.18)	(0.72)	(−0.03)	(0.09)	(0.29)	(0.74)	
				theoretical reference: 280						
Si_2H_2 [Si_2H_2]	58	C_{2v}	$^1A_1$	0.34	0.91	0.06	0.29	0.57	0.93	
		C_{2v}	$^2A_2$	(0.45)	(1.01)	(0.18)	(0.38)	(0.65)	(1.00)	
				theoretical reference: 230						note: 7
Si_2H_3 [Si_2H_3]	59	C_2	^2A	1.87	2.41	1.74	1.70	1.94	2.41	
		C_2	^1A	(1.88)	(2.43)	(1.75)	(1.72)	(1.95)	(2.42)	
				theoretical reference: 230						
disilene [Si_2H_4]	60	C_{2h}	^1A_g	1.28	1.83	1.16	1.13	1.36	1.68	
		C_{2h}	^2A_g	(1.34)	(1.89)	(1.23)	(1.19)	(1.42)	(1.74)	
				theoretical reference: 230						
disilanyl radical [Si_2H_5]	61	C_s	$^2A'$	1.80	2.32	1.56	1.71	1.92	2.46	
		C_s	$^1A'$	(1.85)	(2.37)	(1.61)	(1.77)	(1.97)	(2.50)	
				theoretical reference: 230						
disilane [Si_2H_6]	62	D_{3d}	$^1A_{1g}$	−0.61	−0.16	−0.88	−0.61	−0.42	−0.08	
		D_{3d}	$^2A_{2u}$	(−0.53)	(−0.08)	(−0.83)	(−0.50)	(−0.32)	(0.05)	
				theoretical reference: 230						
C_4O [C_4O]	64	$C_{\infty v}$	$^3\Sigma^-$	2.97	3.52	2.83	2.79	2.99	3.61	2.05 ± 0.15
		$C_{\infty v}$	$^2\Pi$	(2.98)	(3.52)	(2.83)	(2.79)	(2.99)	(3.61)	
				theoretical reference: 228			experimental reference: 278			note: 8
phosphorus difluoride [PF_2]	69	C_{2v}	$^2B_1$	0.99	1.44	0.75	0.90	1.02	1.46	
		C_{2v}	$^1A_1$	(1.01)	(1.46)	(0.78)	(0.93)	(1.05)	(1.49)	
				theoretical reference: 222						note: 9
sulfur difluoride [SF_2]	70	C_{2v}	$^1A_1$	2.00	2.40	1.69	2.04	2.08	2.25	
		$D_{\infty h}$	$^2\Pi_u$	theoretical reference: 220						note: 10
chlorine difluoride [ClF_2]	73	C_{2v}	$^2A_1$	4.94	5.39	4.93	4.62	4.71	5.13	
		$D_{\infty h}$	$^1\Sigma_g^+$	theoretical reference: 42						note: 11
1,1-dicyanoethylene [$C_2H_2(CN)_2$]	78	C_{2v}	$^1A_1$	1.36	1.92	1.12	1.23	1.45	1.94	
		C_{2v}	$^2B_1$	(1.46)	(2.02)	(1.31)	(1.32)	(1.54)	(2.02)	
				theoretical reference: 280						
benzene [C_6H_6]	78	D_{6h}	$^1A_{1g}$	−0.88	−0.47	−1.39	−1.44	−1.26	−7.41	−1.12 ± 0.03
		D_{6h}	$^2E_{2u}$	theoretical reference: 43			experimental reference: 356			note: 12
cis-dicyanoethylene [(*Z*)-$C_2H_2(CN)_2$]	78	C_{2v}	$^1A_1$	1.45	2.01	1.28	1.32	1.53	2.04	
		C_{2v}	$^2A_2$	(1.53)	(2.09)	(1.37)	(1.39)	(1.61)	(2.11)	
				theoretical reference: 280						
CF_3O [CF_3O]	85	C_s	$^2A'$	4.58	5.06	4.11	4.59	4.68	5.37	4.7 ± 0.13
		C_{3v}	$^1A_1$	(4.60)	(5.08)	(4.13)	(4.60)	(4.69)	(5.38)	
				theoretical reference: 232			experimental reference: 357			note: 13
phosphorus trifluoride [PF_3]	88	C_{3v}	$^1A_1$	0.19	0.62	−0.17	0.25	0.32	0.52	
		C_{2v}	$^2B_1$	(0.27)	(0.70)	(−0.08)	(0.33)	(0.39)	(0.59)	
				theoretical reference: 222						note: 14
chlorine trifluoride [ClF_3]	92	C_{2v}	$^1A_1$	4.41	4.71	4.32	4.31	4.24	4.25	
		C_{2v}	$^2A_1$	theoretical reference: 42						note: 15
selenium monofluoride [SeF]	98	$C_{\infty v}$	$^2\Pi$	2.52	3.02	2.37	2.39	2.53	3.04	
		$C_{\infty v}$	$^1\Sigma^+$	(2.53)	(3.03)	(2.38)	(2.40)	(2.54)	(3.05)	
				theoretical reference: 223						note: 16
chlorine tetroxide radical [ClO_4]	99	C_{2v}	$^2B_2$	5.31	5.83	5.42	4.84	5.01	5.69	
		T_d	$^1A_1$	(5.27)	(5.79)	(5.39)	(4.81)	(4.97)	(5.64)	
				theoretical reference: 233						
bromine monofluoride [BrF]	99	$C_{\infty v}$	$^1\Sigma^+$	2.80	3.23	2.64	2.71	2.79	3.00	
		$C_{\infty v}$	$^2\Sigma^+$	theoretical reference: 219						note: 17
tetrafluoroethylene [C_2F_4]	100	D_{2h}	^1A_g	0.32	0.78	0.09	0.32	0.32	0.46	
		C_{2h}	^2A_g	(0.43)	(0.79)	(0.21)	(0.43)	(0.42)	(0.55)	
				theoretical reference: 218						note: 18
tricyanoethylene [$C_2H(CN)_3$]	103	C_s	$^1A'$	2.59	3.17	2.48	2.41	2.63	3.17	
		C_s	$^2A''$	(2.64)	(3.22)	(2.54)	(2.46)	(2.68)	(3.21)	
				theoretical reference: 280						
tetrafluorosilane [SiF_4]	104	T_d	$^1A_1$	0.04	0.51	−0.29	0.08	0.20	0.50	
		C_{2v}	$^2A_1$	(0.11)	(0.58)	(−0.22)	(0.16)	(0.27)	(0.57)	
				theoretical reference: 221						note: 19
phosphorus tetrafluoride [PF_4]	107	D_{3h}	$^1A_1'$	3.45	3.83	3.17	3.40	3.41	3.83	
		C_{4v}	$^2A_1$	(3.50)	(3.88)	(3.23)	(3.45)	(3.46)	(3.88)	
				theoretical reference: 222						note: 20
chlorine tetrafluoride [ClF_4]	111	C_{4v}	$^2A_1$	5.88	6.26	5.73	5.60	5.61	5.94	
		D_{4h}	$^1A_{1g}$	theoretical reference: 42						note: 21
germanium difluoride [GeF_2]	111	C_{2v}	$^1A_1$	0.95	1.46	0.85	0.81	0.98	1.30	
		C_{2v}	$^2B_1$	(0.97)	(1.48)	(0.87)	(0.83)	(1.00)	(1.32)	
				theoretical reference: 224						note: 22
bromine dioxide [BrO_2]	112	C_{2v}	$^2B_1$	2.56	3.03	2.65	2.25	2.36	2.82	
		C_{2v}	$^1A_1$	(2.58)	(3.05)	(2.68)	(2.27)	(2.38)	(2.84)	
				theoretical reference: 234						note: 23
selenium difluoride [SeF_2]	117	C_{2v}	$^1A_1$	2.40	2.84	2.21	2.32	2.42	2.65	
		$D_{\infty h}$	$^2\Pi_u$	(2.43)	(2.87)	(2.24)	(2.35)	(2.45)	(2.69)	
				theoretical reference: 223						note: 24
bromine difluoride [BrF_2]	118	C_{2v}	$^2A_1$	4.71	5.19	4.78	4.34	4.47	5.10	
		$D_{\infty h}$	$^1\Sigma_g^+$	theoretical reference: 219						note: 25

Table 9 (Continued)

atom or molecule [molecular formula]	mol wt	sym	state	B3LYP	B3P86	BHLYP	BLYP	BP86	LSDA	expt
phosphorus pentafluoride [PF_5]	126	D_{3h}	$^1A'_1$	1.58	1.98	1.25	1.66	1.67	1.82	0.75 ± 0.15
		C_{4v}	$^2A_1$	(1.67)	(2.07)	(1.34)	(1.75)	(1.76)	(1.91)	
				theoretical reference: 222			experimental reference: 358			note: 26
sulfur pentafluoride [SF_5]	127	C_{4v}	$^2A_1$	4.70	5.02	4.29	4.74	4.69	4.98	
		C_{4v}	$^1A_1$	theoretical reference: 220						note: 27
naphthalene [$C_{10}H_8$]	128	D_{2h}	^1A_g	−0.20	0.35	−0.49	−0.23	−0.01	0.47	−0.19 ± 0.03
		D_{2h}	$^2B_{1g}$	(−0.04)	(0.51)	(−0.31)	(−0.07)	(0.15)	(0.62)	
				theoretical reference: 43			experimental reference: 356			note: 28
bromine trioxide [BrO_3]	128	C_{3v}	$^2A_1$	4.54	5.05	4.66	4.18	4.32	4.92	
		C_{3v}	$^1A_1$	(4.53)	(5.04)	(4.64)	(4.17)	(4.32)	(4.92)	
				theoretical reference: 234						note: 29
germanium trifluoride [GeF_3]	130	C_{3v}	$^2A_1$	3.94	4.33	3.72	3.82	3.86	4.34	
		C_{3v}	$^1A_1$	(3.97)	(4.36)	(3.75)	(3.84)	(3.88)	(4.36)	
				theoretical reference: 224						note: 30
chlorine pentafluoride [ClF_5]	130	C_{4v}	$^1A_1$	5.30	5.49	5.17	5.26	5.08	4.94	
		C_{4v}	$^2A_1$	theoretical reference: 42						note: 31
selenium trifluoride [SeF_3]	136	C_{2v}	$^2B_1$	3.41	3.85	3.39	3.14	3.22	3.61	
		C_{2v}	$^1A_1$	(3.43)	(3.87)	(3.41)	(3.16)	(3.24)	(3.64)	
				theoretical reference: 223						note: 32
bromine trifluoride [BrF_3]	137	C_{2v}	$^1A_1$	3.89	4.23	3.77	3.76	3.74	3.84	
		C_{2v}	$^2A_1$	theoretical reference: 219						note: 33
bromine tetroxide [BrO_4]	144	C_{2v}	$^2B_1$	5.59	6.15	5.64	5.09	5.28	5.98	
		T_d	$^1A_1$	(5.55)	(6.11)	(5.61)	(5.06)	(5.24)	(5.94)	
				theoretical reference: 234						note: 34
germanium tetrafluoride [GeF_4]	149	T_d	$^1A_1$	1.81	2.20	1.46	1.89	1.90	2.15	
		C_{2v}	$^2A_1$	(1.87)	(2.26)	(1.52)	(1.95)	(1.96)	(2.21)	
				theoretical reference: 224						note: 35
chlorine hexafluoride [ClF_6]	149	O_h	$^2A_{1g}$	6.17	6.46	5.51	6.39	6.30	6.49	
		O_h	$^1A_{1g}$	theoretical reference: 42						note: 36
selenium tetrafluoride [SeF_4]	155	C_{2v}	$^1A_1$	2.87	3.21	2.50	2.92	2.89	3.01	1.7 ± 0.1
		C_{4v}	$^2A_1$	(2.95)	(3.29)	(2.58)	(2.99)	(2.96)	(3.08)	
				theoretical reference: 223			experimental reference: 359			note: 37
bromine tetrafluoride [BrF_4]	156	C_{4v}	$^2A_1$	5.58	5.98	5.58	5.21	5.25	5.62	
		D_{4h}	$^1A_{1g}$	theoretical reference: 219						note: 38
selenium pentafluoride [SeF_5]	174	C_{4v}	$^2A_1$	5.44	5.80	5.23	5.30	5.30	5.69	5.1 ± 0.4
		C_{4v}	$^1A_1$	(5.48)	(5.84)	(5.28)	(5.33)	(5.33)	(5.73)	
				theoretical reference: 223			experimental reference: 125			note: 39
bromine pentafluoride [BrF_5]	175	C_{4v}	$^1A_1$	4.48	4.72	4.24	4.44	4.32	4.29	
		C_{4v}	$^2A_1$	theoretical reference: 219						note: 40
bromine hexafluoride [BrF_6]	194	O_h	$^2A_{1g}$	6.10	6.41	5.59	6.19	6.12	6.39	
		O_h	$^1A_{1g}$	theoretical reference: 219						note: 41

[a] Symmetry and state of neutral species listed first with that of the anion on the following line. Notes: (1) Theoretical results suggest an EA of less than 0 eV. See ref 360. (2) Recent CCSD(T) results predict an EA of 0.40 eV. See ref 268. (3) The LSDA result is from ref 237. (4) Recent QCISD(T)/aug-cc-pVDZ computations suggest EA(N_2O) = −0.15 eV. See ref 270. (5) Revised EAs from ref 238. See the experimental estimates in ref 222. EA by G2 methods ∼0.68 eV (ref 362). CCSD(T)/aug-cc-pVQZ EA = 0.73 (ref 269). (6) CCSD(T)/aug-cc-pVTZ EA = 0.93 eV (ref 172). (7) BHLYP and B3LYP exhibit orbital symmetry breaking problems. See ref 230. (8) Recent CCSD(T) results predict an EA of 2.99 eV. See ref 172. (9) Revised EAs from ref 238. See the experimental estimates in ref 222. EA by G2 methods ∼0.75 eV (ref 362). CCSD(T)/aug-cc-pVQZ EA = 0.74 (ref 269). (10) The BLYP/DZP ZPVE correction is +0.04 eV. LSDA and B3P86 results are from ref 237. (11) The BLYP ZPVE correction is −0.01 eV. LSDA and B3P86 results from ref 237. See ref 363 for experimental estimates. (12) All density functional results are VAEs. Experimental VAE value determined by electron transmission spectroscopy. (13) LSDA and B3P86 results are from ref 237. The experimental value is an estimate based on the F−CF_2O bond strength. (14) Revised EAs from ref 238. EA by G2 methods ∼−0.36 eV (ref 362). (15) The BLYP ZPVE correction is +0.05 eV. LSDA and B3P86 results are from ref 237. See ref 363 for experimental estimates. (16) LSDA and B3P86 results are from ref 239. (17) The B3LYP ZPVE correction is +0.03 eV. LSDA and B3P86 results are from ref 237. (18) The LSDA result is from ref 237. (19) The experimental EA is less than 0 eV. See ref 318. (20) Revised EAs from ref 238. EA by G2 methods ∼3.14 eV (ref 362). (21) The BLYP ZPVE correction is +0.02 eV. LSDA and B3P86 results are from ref 237. (22) LSDA and B3P86 results are from ref 239. For experimental estimates, see ref 366. (23) LSDA and B3P86 results are from ref 239. For experimental estimates, see ref 306. For theoretical work on BrOO, see ref 234. (24) LSDA and B3P86 results are from ref 239. (25) The B3LYP ZPVE correction is −0.003 eV. LSDA and B3P86 results are from ref 237. The LSDA value is a VDE, as no optimized neutral species was found with this method. (26) Revised EAs from ref 238. EA by G2 methods ∼0.93 eV (ref 362). High-level CCSD(T) EA = 1.02 eV (ref 276). (27) The BLYP/DZP ZPVE correction is +0.05 eV. LSDA and B3P86 results are from ref 237. See refs 344, 364, and 367−369 for experimental estimates. (28) VAE value determined by electron transmission spectroscopy. (29) LSDA and B3P86 results are from ref 239. For theoretical work on BrOOO, see ref 234. (30) LSDA and B3P86 results are from ref 239. For experimental estimates, see refs 366 and 370. Other theoretical results give EA = 3.5−3.7 eV; see ref 371. (31) The BLYP ZPVE correction is +0.09 eV. LSDA and B3P86 results are from ref 237. (32) LSDA and B3P86 results are from ref 239. With a larger integration grid DFT predicts the neutral species to be C_s; see ref 223. (33) The B3LYP ZPVE correction is +0.06 eV. LSDA and B3P86 results are from ref 237. (34) LSDA and B3P86 results are from ref 239. BHLYP predicts a C_s ($^2A''$) structure for the neutral species. (35) LSDA and B3P86 results are from ref 239. (36) The BLYP ZPVE correction is +0.05 eV. LSDA and B3P86 results are from ref 237. (37) LSDA and B3P86 results are from ref 239. (38) The B3LYP ZPVE correction is +0.03 eV. LSDA and B3P86 results are from ref 237. (39) LSDA and B3P86 results are from ref 239. (40) The B3LYP ZPVE correction is +0.10 eV. LSDA and B3P86 results are from ref 237. (41) The B3LYP ZPVE correction is +0.05 eV. LSDA and B3P86 results are from ref 237.

B. Review of Experimental Photoelectron Electron Affinities, Table 10

Table 10. Experimental Atomic and Molecular Affinities Determined by Photoelectron Spectroscopy[a]

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
1	H	0.75419 ± 0.00002	$(1s)\ {}^2S_{1/2}$	←	$(1s^2)\ {}^1S_0$	ThD	47
2	D	0.75459 ± 0.00007	$(1s)\ {}^2S_{1/2}$	←	$(1s^2)\ {}^1S_0$	ThD	47
7	Li	0.618 ± 0.0005	$(2s)\ {}^2S_{1/2}$	←	$(2s^2)\ {}^1S_0$	ThD	282
8	LiH	0.342 ± 0.012	${}^1\Sigma^+$	←	${}^2\Sigma^+$	PES	283
9	LiD	0.337 ± 0.012	${}^1\Sigma^+$	←	${}^2\Sigma^+$	PES	283
10	BeH	0.70 ± 0.10	${}^2\Sigma^+$	←		ThD	284
11	B	0.279723 ± 0.000025	$(2p)\ {}^2P_{1/2}$	←	$(2p^2)\ {}^3P_0$	ThD	285
12	C	1.262119 ± 0.000020	$(2p^2)\ {}^3P_0$	←	$(2p^3)\ {}^4S_{3/2}$	ThD	286
13	CH	1.238 ± 0.008	${}^2\Pi$	←	${}^3\Sigma^-$	PES	373
14	Li_2	0.437 ± 0.009	${}^1\Sigma_g^+$	←	${}^2\Sigma_u^+$	PES	374
14	BH_3	0.038 ± 0.015	${}^1A_1'$	←	${}^2A_2''$	PES	288
14	CH_2	0.652 ± 0.006	${}^3B_1$	←	${}^2B_1$	PES	94
15	NH	0.370 ± 0.004	${}^3\Sigma^-$	←	${}^2\Pi$	ThD	103
15	CH_3	0.080 ± 0.030	${}^2A_2''$	←	${}^1A_1'$	PES	290
16	CD_2	0.645 ± 0.006	${}^3B_1$	←	${}^2B_1$	PES	94
16	O	1.4611100 ± 0.00000007	$(2p^4)\ {}^3P_2$	←	$(2p^5)\ {}^2P_{3/2}$	ThD	40
16	NH_2	0.771 ± 0.005	${}^2B_1$	←	${}^1A_1$	PES	291
17	BD_3	0.027 ± 0.014	${}^1A_1'$	←	${}^2A_2''$	PES	288
17	OH	1.827653 ± 0.000004	${}^2\Pi$	←	${}^1\Sigma^+$	ThD	553
18	$H(NH_3)$	1.114 ± 0.010				PES	375
18	OD	1.825548 ± 0.000037	${}^2\Pi$	←	${}^1\Sigma^+$	ThD	292
19	F	3.401290 ± 0.000003	$(2p^5)\ {}^2P_{3/2}$	←	$(2p^6)\ {}^1S_0$	ThD	40
19	$OH(H_2)$	1.53				PES	376
20	$OD(H_2)$	1.53				PES	376
21	FH_2	$\cong 3.66$				PES	377
23	Na	0.547930 ± 0.000025	$(3s^1)\ {}^2S_{1/2}$	←	$(3s^2)\ {}^1S_0$	ThD	39
24	C_2	3.269 ± 0.006	${}^1\Sigma_g^+$	←	${}^2\Sigma_g^+$	PES	272
25	$C\equiv CH$	2.969 ± 0.006	${}^2\Sigma^+$	←	${}^1\Sigma^+$	PES	272
25	MgH	1.05 ± 0.06	${}^2\Sigma^+$	←		ThD	284
25	BN	3.160 ± 0.005	${}^3\Sigma^-$	←	${}^2\Sigma^+$	PES	378
26	${}^{13}C_2$	3.270 ± 0.010	${}^1\Sigma_g^+$	←	${}^2\Sigma_g^+$	PES	272
26	$C\equiv CD$	2.973 ± 0.006	${}^2\Sigma^+$	←	${}^1\Sigma^+$	PES	272
26	$C{=}CH_2$	0.490 ± 0.006	${}^1A_1$	←	${}^2B_2$	PES	379
26	$C\equiv N$	3.862 ± 0.004	${}^2\Sigma^+$	←	${}^1\Sigma^+$	PES	293
27	Al	0.43283 ± 0.00005	$(3p)\ {}^2P_{1/2}$	←	$(3p^2)\ {}^3P_0$	ThD	294
27	BO	2.508 ± 0.008	${}^2\Sigma^+$	←	${}^1\Sigma^-$	PES	169
27	$C{=}CHD$	0.492 ± 0.006	${}^1A'$	←	${}^2A'$	PES	379
27	$CH_2{=}CH$	0.667 ± 0.024	${}^2A'$	←	${}^1A'$	PES	118
28	Si	1.389521 ± 0.000020	$(3p^2)\ {}^3P_0$	←	$(3p^3)\ {}^4S_{3/2}$	ThD	286
28	${}^{13}C_2D$	2.971 ± 0.006	${}^2\Sigma^+$	←	${}^1\Sigma^+$	PES	272
28	$C{=}CD_2$	0.492 ± 0.006	${}^1A_1$	←	${}^2B_1$	PES	379
28	$CH_2{=}N$	0.511 ± 0.008	${}^2B_2$	←	${}^1A_1$	PES	295
29	HCO	0.313 ± 0.005	${}^2A'$	←	${}^1A'$	PES	296
29	SiH	1.277 ± 0.009	${}^2\Pi$	←	${}^3\Sigma^-$	PES	380
29	CH_3N	0.022 ± 0.009	${}^3A_2$	←	${}^2E$	PES	381
30	$CD_2{=}N$	0.498 ± 0.011	${}^2B_2$	←	${}^1A_1$	PES	295
30	DCO	0.301 ± 0.005	${}^2A'$	←	${}^1A'$	PES	296
30	NO	0.026 ± 0.005	${}^2\Pi$	←	${}^3\Sigma^-$	PES	111
30	SiH_2	1.124 ± 0.020	${}^1A_1$	←	${}^2B_1$	PES	380
31	HNO	0.338 ± 0.015	${}^1A'$	←	${}^2A'$	PES	300
31	P	0.7464 ± 0.0004	$(3p^3)\ {}^4S_{3/2}$	←	$(3p^4)\ {}^3P_2$	ThD	297
31	SiH_3	1.406 ± 0.014	${}^2A_1$	←	${}^1A_1$	PES	332
31	CH_3O	1.572 ± 0.004	${}^2E$	←	${}^1A_1$	PES	299
32	DNO	0.330 ± 0.015	${}^1A'$	←	${}^2A'$	PES	300
32	HCF	0.542 ± 0.005	${}^1A'$	←	${}^2A'$	PES	302
32	O_2	0.451 ± 0.007	${}^3\Sigma_g^-$	←	${}^2\Pi_g$	PES	111
32	PH	1.028 ± 0.010	${}^3\Sigma^-$	←	${}^2\Pi$	PES	301
32	S	2.077103 ± 0.000003	$(3p^4)\ {}^3P_2$	←	$(3p^5)\ {}^2P_{3/2}$	ThD	40
33	DCF	0.535 ± 0.005	${}^1A'$	←	${}^2A'$	PES	302
33	HOO	1.078 ± 0.006	${}^2A''$	←	${}^1A'$	PES	102
33	PH_2	1.271 ± 0.010	${}^2B_1$	←	${}^1A_1$	PES	301
33	SH	2.317 ± 0.002	${}^2\Pi$	←	${}^1\Sigma^+$	ThD	304
34	DOO	1.077 ± 0.005	${}^2A''$	←	${}^1A'$	PES	382
34	SD	2.315 ± 0.002	${}^2\Pi$	←	${}^1\Sigma^+$	ThD	304
34	SiD_3	1.386 ± 0.022	${}^2A_1$	←	${}^1A_1$	PES	332
34	CD_3O	1.559 ± 0.004	${}^2E$	←	${}^1A_1$	PES	299
34	$OH(NH_3)$	2.35 ± 0.07				PES	383
35	Cl	3.612724 ± 0.00003	$(3p^5)\ {}^2P_{3/2}$	←	$(3p^6)\ {}^1S_0$	ThD	305
35	FO	2.272 ± 0.006	${}^2\Pi$	←	${}^1\Sigma^+$	PES	306
36	C_3	1.995 ± 0.025	${}^1\Sigma_g^+$	←	${}^2\Pi_g$	PES	307
36	BNB	3.098 ± 0.010	${}^2\Sigma_u^+$	←	${}^1\Sigma_g^+$	PES	384
37	C_3H	1.858 ± 0.023				PES	278

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
38	$CH_2{=}C{=}C$	1.794 ± 0.008	$^1A_1$	←	$^2B_1$	PES	309
39	$CH_2C{\equiv}CH$	0.918 ± 0.008	$^2B_1$	←	$^1A'$	PES	309
39	$CH_3C{\equiv}C$	2.718 ± 0.008		←	$^1A_1$	PES	309
39	K	0.50147 ± 0.0001	$(4s)\ ^2S_{1/2}$	←	$(4s^2)\ ^1S_0$	ThD	385
40	Ca	0.043 ± 0.007	$(4s^2)\ ^1S_0$	←	$(4s^24p)\ ^2P_{1/2}$	ThD	386
40	$(HF)_2$	0.063 ± 0.003				PES	387
40	CCO	2.289 ± 0.018	$^3\Sigma^-$	←	$^2\Pi$	PES	310
40	CH_2CN	1.543 ± 0.014	$^2B_1$	←	$^1A_1$	PES	388
40	CH_2NC	1.059 ± 0.024	$^2B_1$	←	$^1A_1$	PES	389
40	CN_2	1.771 ± 0.010	$^3\Sigma^-$	←	$^2\Pi$	PES	311
41	CaH	0.93 ± 0.05	$^2\Sigma^+$	←		ThD	284
41	CH_2CHCH_2	0.481 ± 0.008	$^2A_2$	←	$^1A_1$	PES	390
41	HCCO	2.350 ± 0.020	$^2A''$	←	$^1A'$	PES	391
41	HCN_2	1.685 ± 0.006	$^2A''$	←	$^1A'$	PES	311
42	CD_2CN	1.538 ± 0.012	$^2B_1$	←	$^1A_1$	PES	388
42	CD_2NC	1.070 ± 0.024	$^2B_1$	←	$^1A_1$	PES	389
42	DCCO	2.35 ± 0.02	$^2A''$	←	$^1A'$	PES	391
42	DCN_2	1.678 ± 0.006	$^2A''$	←	$^1A'$	PES	311
42	LiCl	0.593 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
42	N_3	2.7 ± 0.1	$^2\Pi_g$	←	$^1\Sigma_g^+$	ThD	393
42	NaF	0.520 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
42	NCO	3.609 ± 0.005	$^2\Pi$	←	$^1\Sigma^+$	PES	293
43	AlO	2.60 ± 0.01	$^2\Sigma^+$	←		PES	315
43	$CH_2{=}SiH$	2.010 ± 0.010	$^1A'$	←	$^2A''$	PES	394
43	CH_2CHO	$1.8248^{+0.0002}_{-0.0006}$	$^2A''$	←	$^1A'$	ThD	313
43	CH_3CH_2N	0.56 ± 0.01	$^3A''$	←	$^2A''$	ThD	395
43	CH_3CO	0.423 ± 0.037	$^2A'$	←	$^1A'$	PES	314
43	CH_3Si	0.852 ± 0.010	^2E	←	$^1A_1$	PES	394
44	$C{=}CHF$	1.718 ± 0.006	$^1A'$	←	$^2A''$	PES	328
44	CH_2DCO	0.418 ± 0.038	$^2A'$	←	$^1A'$	PES	314
44	CS	0.205 ± 0.021	$^1\Sigma^+$	←	$^2\Pi$	PES	396
45	CH_3CH_2O	1.712 ± 0.004	$^2A''$	←	$^1A'$	PES	299
45	CH_3SiH_2	1.196 ± 0.035	$^2A'$	←	$^1A'$	ThD	397
45	HCO_2	3.498 ± 0.015	$^2A_1$	←	$^1A_1$	PES	398
45	Sc	0.189 ± 0.020	$(3d4s^2)\ ^2D_{3/2}$	←	$(3d4s^24p)\ ^{13}D$	PES	399
46	DCO_2	3.512 ± 0.015	$^2B_2$	←	$^1A_1$	PES	398
46	CD_2CDCD_2	0.464 ± 0.006	$^2A_2$	←	$^1A_1$	PES	390
46	CD_2CDO	$1.8148^{+0.0002}_{-0.0006}$	$^2A''$	←	$1A'$	ThD	313
46	CH_2S	0.465 ± 0.023	$^1A_1$	←	$^2B_1$	PES	331
46	Na_2	0.430 ± 0.015	$^1\Sigma_g^+$	←	$^2\Pi$	PES	400
46	NO_2	2.273 ± 0.005	$^2A_1$	←	$^1A_1$	PES	317
46	NS	1.194 ± 0.011	$^2\Pi$	←	$^1\Sigma^+$	PES	396
47	CH_3CD_2O	1.712 ± 0.007	$^2A''$	←	$^1A'$	PES	401
47	CH_3PH	0.94 ± 0.02	$^2A''$	←	$^1A'$	ThD	402
47	CH_3S	1.867 ± 0.004	^2E	←	$^1A_1$	PES	403
47	PO	1.092 ± 0.010	$^2\Pi$	←	$^1\Sigma^+$	PES	301
47	BBNB	2.919 ± 0.010	$^1\Sigma^+$	←		PES	384
47	CH_3OO	1.161 ± 0.005	$^2A''$	←	$^1A'$	PES	404
48	$NO(H_2O)$	0.75 ± 0.05				PES	405
48	C_4	3.882 ± 0.010	$^1\Sigma_g^+$	←	$^2\Sigma_g^+$	PES	307
48	CD_3CH_2O	1.709 ± 0.007	$^2A''$	←	$^1A'$	PES	401
48	HCCl	1.210 ± 0.005	$^1A'$	←	$^2A'$	PES	302
48	O_3	2.1028 ± 0.0025	$^1A_1$	←	$^2B_1$	ThD	320
48	SO	1.125 ± 0.005	$^3\Sigma^-$	←	$^2\Pi$	PES	319
48	Ti	0.080 ± 0.014	$(3d^24s^2)\ ^3F_2$	←	$(3d^34s^2)\ ^4F_{3/2}$	PES	406
49	$HC{\equiv}CC{\equiv}C$	3.558 ± 0.015	$^2\Sigma^+$	←	$^1\Sigma^+$	PES	336
50	$DC{\equiv}CC{\equiv}C$	3.552 ± 0.015	$^2\Sigma^+$	←	$^1\Sigma^+$	PES	336
50	$NO(D_2O)$	0.80 ± 0.05				PES	405
50	CD_3CD_2O	1.699 ± 0.004	$^2A''$	←	$^1A'$	PES	299
50	CD_3S	1.858 ± 0.006	^2E	←	$^1A_1$	ThD	407
50	CF_2	0.179 ± 0.005	$^1A_1$	←	$^2B_1$	PES	321
50	CD_3OO	1.154 ± 0.004	$^2A''$	←	$^1A'$	PES	404
51	ClO	2.276 ± 0.006	$^2\Pi$	←	$^1\Sigma^+$	PES	306
51	SF	2.285 ± 0.006	$^2\Pi$	←	$^1\Sigma^+$	PES	322
51	V	0.526 ± 0.012	$(3d^34s)\ ^4F_{3/2}$	←	$(3d^44s^2)\ ^5D_0$	PES	406
52	Cr	0.67584 ± 0.00012	$(3d^54s)\ ^7S_3$	←	$(3d^54s^2)\ ^6S_{5/2}$	ThD	408
52	C_3O	0.93 ± 0.10	$^1\Sigma^+$	←	$^2\Pi$	PES	278, 172
52	$C{=}CHCH{=}CH_2$	0.914 ± 0.015	$^1A'$	←	$^2A''$	PES	409
52	OHCl	$\cong 4.2$				PES	410
53	CrH	0.563 ± 0.010				PES	411
54	$C(CH_2)_3$ [trimethylenemethane] (TMM) (**1**)	0.431 ± 0.006	$^3A_2'$	←	$^2A_2$	PES	412
54	CH_3CHCN	1.247 ± 0.012	$^1A'$	←	$^2A''$	PES	413
54	Al_2	1.46 ± 0.06				PES	324

Table 10 (Continued)

m/z	species	EA/eV	M	←	M$^-$	exptl	ref
55	$CH_3C(CH_2)_2$	0.505 ± 0.006	$^2A_2$	←	$^1A_1$	PES	390
55	AlSi	1.32 ± 0.05	$^4\Sigma^-$	←	$^3\Sigma^-$	PES	414
56	$C{=}CDCD{=}CD_2$	0.909 ± 0.015	$^1A'$	←	$^2A''$	PES	409
56	Fe	0.151 ± 0.003	$(3d^6 4s^2)\ ^5D_4$	←	$(3d^7 4s^2)\ ^4F_{9/2}$	PES	415
56	MnH	0.869 ± 0.010	$^7\Sigma^+$	←	$^6\Delta$	PES	416
56	Si_2	2.202 ± 0.010	$^3\Sigma_g^-$	←	$^2\Sigma_g^+$	PES	417
57	CH_3CHCHO	1.621 ± 0.006	$^2A''$	←	$^1A'$	ThD	341
57	CH_3COCH_2	1.758 ± 0.019	$^2A''$	←	$^1A'$	ThD	341
57	Si_2H	2.31 ± 0.01	$^1A_1$	←	$^2A_1$	PES	418
57	FeH	0.934 ± 0.011	$^4\Delta$	←	$^5\Delta$	PES	416
57	MnD	0.866 ± 0.010	$^7\Sigma^+$	←	$^6\Delta$	PES	416
57	MnH_2	0.444 ± 0.016	$^6\Sigma^+$	←		PES	419
58	$(CH_3)_2Si$	1.07 ± 0.02	$^1A'$	←	$^2A''$	ThD	468
58	FeD	0.932 ± 0.015	$^4\Delta$	←	$^5\Delta$	PES	416
58	FeH_2	1.049 ± 0.014				PES	419
58	NaCl	0.727 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
58	NCS	3.537 ± 0.005	$^2\Pi$	←	$^1\Sigma^+$	PES	293
59	Co	0.6633 ± 0.0006	$(3d^7 4s^2)\ ^4F_{9/2}$	←	$(3d^8 4s^2)\ ^3F_4$	ThD	421
59	Ni	1.15716 ± 0.00012	$(3d^8 4s^2)\ ^3F_4$	←	$(3d^9 4s^2)\ ^2D_{5/2}$	ThD	421
59	AlO_2	4.23 ± 0.01	$^2\Pi_g$	←		PES	315
59	$(CH_3)_2SiH$	1.07 ± 0.02	$^2A'_1$	←	$^1A'_1$	ThD	468
59	MgCl	1.589 ± 0.011	$^2\Sigma^+$	←		PES	392
59	MnD_2	0.465 ± 0.014	$^6\Sigma^+$	←		PES	419
59	$(CH_3)_2CHO$	1.847 ± 0.004	$^2A'_1$	←	$^1A'_1$	PES	299
60	SiO_2	2.1 ± 0.1				PES	327
60	C_5	2.839 ± 0.008	$^1\Sigma_g^+$	←	$^2\Pi$	PES	307
60	CH_2NO_2	2.475 ± 0.010	$^2A''$	←	$^1A'$	PES	422
60	CO_3	$2.69^{+0.07}_{-0.14}$				PES	423
60	CoH	0.671 ± 0.010	$^2\Phi$	←	$^3\Phi$	PES	411
60	NiH	0.481 ± 0.007	$^2\Delta$	←	$^3\Delta$	PES	411
61	CH_2CFO	2.22 ± 0.09	$^2A'$	←	$^1A'$	ThD	424
61	CH_3NO_2	0.26 ± 0.08	$^1A'$	←		PES	425
61	CH_3CH_2S	1.953 ± 0.006	$^2A''$	←	$^1A'$	ThD	407
61	CH_3SCH_2	0.868 ± 0.051	$^2A''$	←	$^1A'$	PES	331
61	CoD	0.68 ± 0.01	$^2\Phi$	←	$^3\Phi$	PES	411
61	CoH_2	1.450 ± 0.014				PES	419
61	NiD	0.477 ± 0.007	$^2\Delta$	←	$^3\Delta$	PES	411
61	$OH(N_2O)$	2.12 ± 0.02				PES	426
61	NiH_2	1.934 ± 0.008				PES	419
61	CH_3CH_2OO	1.186 ± 0.004	$^2A''$	←	$^1A'$	PES	404
62	$CD_2C(CD_3)CD_2$	0.493 ± 0.008	$^2A_2$	←	$^1A_1$	PES	390
62	$C{=}CF_2$	2.255 ± 0.006	$^1A_1$	←	$^2B_1$	PES	328
62	NaK	0.465 ± 0.030	$^1\Sigma^+$	←		PES	427
62	NO_3	3.937 ± 0.014	$^2A'_2$	←	$^1A'_1$	PES	428
62	P_2	0.589 ± 0.025	$^1\Sigma_g^+$	←		PES	329
63	$CH_3O(CH_3OH)$	2.26 ± 0.08				PES	429
63	CoD_2	1.465 ± 0.013	^4F	←		PES	419
63	NiD_2	1.926 ± 0.007	^3D	←		PES	419
63	PO_2	3.42 ± 0.01				PES	430
63	Al_3C	2.56 ± 0.06				PES	431
64	TiO	1.30 ± 0.03	$^3\Delta$	←	$^1\Sigma^+$	PES	432
64	Cu	1.23579 ± 0.00004	$(3d^{10} 4s)\ ^2S_{1/2}$	←	$(3d^{10} 4s^2)\ ^1S_0$	ThD	408
64	CD_3NO_2	0.24 ± 0.08	$^1A'$	←		PES	425
64	C_4O	2.99 ± 0.10	$^3\Sigma^-$	←	$^2\Pi$	PES	278, 172
64	S_2	1.670 ± 0.015	$^3\Sigma_g^-$	←	$^2\Pi_g$	PES	331
64	SO_2	1.107 ± 0.008	$^1A_1$	←	$^2B_1$	PES	298
65	C_5H_5 [cyclopentadienyl] (**2**)	1.786 ± 0.020	$^2E''_1$	←	$^1A_1$	PES	433
65	HS_2	1.907 ± 0.023	$^2A''$	←	$^1A'$	PES	331
66	$NO(H_2O)_2$	1.43 ± 0.06				PES	405
66	C_4H_4N [pyrrolyl] (**3**)	$\sim 2.39 \pm 0.13$	$^2A_1$	←	$^1A_1$	ThD	434
66	DS_2	1.912 ± 0.015	$^2A''$	←	$^1A'$	PES	331
67	ZnH	~ 0.95	$^2\Sigma^+$	←		ThD	284
67	VO	1.229 ± 0.008	$^4\Sigma^-$	←	$^5\Pi$	PES	435
67	OClO	2.140 ± 0.008	$^2B_1$	←	$^1A_1$	PES	306
68	CrO	1.221 ± 0.006	$^5\Pi$	←	$^4\Pi$	PES	436
68	OCCCO	0.85 ± 0.15	$^1\Sigma_g^+$	←	$^2\Pi$	PES	278
69	C_4H_5O [cyclobutanone enoyl] (**4**)	1.801 ± 0.008	$^2A''$	←	$^1A'$	ThD	341
69	CF_3	~ 2.01	$^2A_1$	←	$^1A_1$	ThD	437
69	Na_3	1.019 ± 0.060				PES	400
70	Ga	0.41 ± 0.04	$(4p)\ ^2P_{1/2}$	←	$(4p^2)\ ^3P_0$	PES	438
70	$NO(Ar)_1$	0.095				PES	429
71	$HCOC(CH_2CH_3)H$	1.67 ± 0.05				ThD	424

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
72	$CH_3COC(CH_3)D$	1.67 ± 0.05				ThD	424
72	C_6	4.185 ± 0.006	$^3\Sigma_g^-$	←	$^2\Sigma_g^+$	PES	307
72	TiC_2	1.542 ± 0.020				PES	440
72	FeO	1.4945 ± 0.0001	$^5\Delta_4$	←	$^4\Delta_{7/2}$	PES	554
73	Ge	1.232712 ± 0.00015	$(4p^2)\ ^3P_0$	←	$(4p^3)\ ^4S_{3/2}$	ThD	286
73	$(CH_3)_3CO$	1.909 ± 0.004	^2E	←	$^1A_1'$	PES	299
73	$CH_3CD_2COCH_2$	1.75 ± 0.06				ThD	424
73	CH_3OCOCH_2	1.80 ± 0.06				ThD	424
73	HC_6	3.809 ± 0.015	$^2\Pi$	←		PES	336
74	DC_6	3.805 ± 0.015	$^2\Pi$	←		PES	336
74	KCl	0.582 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
74	$NO(N_2O)$	0.258 ± 0.009	$^2\Pi$	←	$^3\Sigma^-$	PES	442
74	AlC_4	2.65 ± 0.06				PES	443
75	NiO	1.470 ± 0.003	$^3\Sigma^-$	←	$^2\Pi_{3/2}$	PES	444
75	$(CH_3)_2CHS$	2.02 ± 0.02				ThD	407
75	As	0.814 ± 0.008	$(4p^3)\ ^4S_{3/2}$	←	$(4p^4)\ ^3P_2$	PES	445
75	$(CH_3)_2PCH_2$	1.53 ± 0.01				ThD	446
75	$CH_3CH_2CH_2S$	2.00 ± 0.02				ThD	407
76	AsH	1.0 ± 0.1	$^2\Sigma^+$	←		ThD	284
76	C_6H_4 [*o*-benzyne] (**5**)	0.564 ± 0.007	$^1A_1$	←	$^2B_2$	PES	337
76	C_6H_4 [*p*-benzyne] (**6**)	1.265 ± 0.008	$^1A_1$	←	$^2B_2$	PES	337
76	CS_2	<0.800	$^1\Sigma^+$	←	$^2B_1$	PES	447, 333
76	GeH_3	$\leq 1.74 \pm 0.04$	$^2A_1$	←	$^1A_1$	ThD	448
76	$LiCl_2$	5.92 ± 0.04				PES	449
77	C_6H_5 [phenyl] (**7**)	1.096 ± 0.006	$^2A_1$	←	$^1A_1$	PES	120
78	K_2	0.493 ± 0.012	$^1\Sigma_g^+$	←	$^2\Pi$	PES	400
79	Se	2.02067 ± 0.00002	$(4p^4)\ ^3P_2$	←	$(4p^5)\ ^2P_{3/2}$	ThD	450
79	$CH_3C_5H_4$ [methylcyclopentadienyl] (**8**)	$\leq 1.67 \pm 0.04$				ThD	334
79	CH_3S_2	1.757 ± 0.022	$^2A''$	←	$^1A'$	PES	331
80	FeC_2	1.91 ± 0.10				PES	452
80	TiO_2	1.59 ± 0.03				PES	432
80	$(CH_2)_2CC(CH_2)_2$ [tetramethyleneethane] (TME) (**9**)	0.855 ± 0.010	^1A	←	$^2B_3$	PES	453
80	Br	3.363588 ± 0.000002	$(4p^5)\ ^2P_{3/2}$	←	$(4p^6)\ ^1S_0$	ThD	339
80	C_6D_4 [*o*-benzyne-*d*$_4$] (**5**)	0.551 ± 0.010	$^1A_1$	←	$^2B_2$	PES	454
80	CuO	1.777 ± 0.006	$^2\Pi_{3/2}$	←		PES	455
80	S_2O	1.877 ± 0.008	$^1A_1$	←	^3A	PES	298
80	SeH	2.21 ± 0.03	$^2\Pi$	←	$^1\Sigma^+$	ThD	456
80	ZnO	2.088 ± 0.010				PES	457
81	FeC_2H	1.41 ± 0.05				PES	452
81	Al_3	1.90 ± 0.01				PES	458
82	CCl_2	1.603 ± 0.008	$^1A_1$	←	$^2B_1$	PES	321
82	CD_3S_2	1.748 ± 0.022	$^2A''$	←	$^1A'$	PES	331
82	$(CH_3)_3CCH{=}C$	0.645 ± 0.015	$^1A'$	←	$^2A'$	PES	459
83	VO_2	2.03 ± 0.01	$^2A_1$	←	$^1A_1$	PES	435
83	ClO_3	4.25 ± 0.10	$^2A_1$	←	$^1A_1$	PES	63
83	$(CH_3)_2CC(CH_3){=}CH_2$ [2-(isopropenyl)allyl] (**10**)	0.654 ± 0.010	$^2A''$	←	$^1A'$	PES	453
83	C_5H_7O [cyclopentanone enoyl] (**11**)	1.598 ± 0.007	$^2A''$	←	$^1A'$	ThD	341
84	C_7	3.358 ± 0.014	$^1\Sigma_g^+$	←	$^2\Pi_g$	PES	307
84	FeCO	1.157 ± 0.005				PES	460
84	TiC_3	1.561 ± 0.015				PES	440
84	Si_3	2.3018 ± 0.0009	$^1A_1$	←	$^2A_1$	PES	461
85	Rb	0.48592 ± 0.00002	$(5s)\ ^2S_{1/2}$	←	$(5s^2)\ ^1S_0$	ThD	462
85	$CH_3CH_2COCHCH_3$	1.68 ± 0.05				ThD	424
85	Si_3H	2.53 ± 0.01	$^1A_1$	←	$^2B_2$	PES	418
85	SiF_3	$<2.95 \pm 0.10$	^2A	←	^1A	ThD	437
86	Al_2O_2	1.88 ± 0.03	^1A_g	←		PES	463
87	$(CH_3)_3CCH_2O$	1.93 ± 0.05				ThD	464
87	$(CH_3)_3SiN$	1.43 ± 0.10	$^3A_2$	←	^2E	ThD	465
87	$(CH_3)_3SiCH_2$	0.95 ± 0.013	^2A		^1A	ThD	465
87	$Ni(CO)$	0.804 ± 0.012				PES	466
88	FeO_2	2.36 ± 0.03				PES	439
88	$(CD_2)_2CC(CD_2)_2$	0.842 ± 0.010	^1A	←	$^2B_3$	PES	453
88	Sr	0.05206 ± 0.00006	$(5s^2)\ ^1S_0$	←	$(5s^25p^1)\ ^2P_{1/2}$	ThD	467
88	FeO_2	2.358 ± 0.03				PES	441
89	$C_4H_9O_2$ [tetrahydropyran-2-oxy] (**12**)	2.15 ± 0.11				ThD	468
89	$(CH_3)_3COO$	1.196 ± 0.011	$^2A''$	←	$^1A'$	PES	102
89	$(CH_3)_3CS$	2.07 ± 0.02	^2E	←	$^1A_1$	ThD	407
89	$CH_3CH_2CH_2CH_2S$	2.03 ± 0.02				ThD	407
89	Y	0.307 ± 0.012	$(4d5s^2)\ ^2D_{3/2}$	←	$(4d5s^25p)\ ^1D_2$	PES	406
91	C_7H_7 [quadricyclan-2-yl] (**13**)	0.868 ± 0.0006				PES	469
91	C_7H_7 [quadricyclan-1-yl] (**14**)	0.962 ± 0.0006				PES	469
91	C_7H_7 [2,5-norbornadiene-2-yl] (**15**)	1.286 ± 0.0006				PES	469

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
91	C_7H_7 [cycloheptatrienyl] (**16**)	0.390 ± 0.004				PES	469
91	$C_6H_5CH_2$	0.912 ± 0.006	$^2B_1$	←	$^1A_1$	PES	120
91	C_6H_5N	1.45 ± 0.02	$^3A_2$	←	$^2B_1$	ThD	470
91	$HC\equiv CCH_2CH_2CHC\equiv CH$	1.14 ± 0.006				PES	469
91	$HC\equiv CCH_2CH_2CH_2C\equiv C$	3.046 ± 0.006				PES	469
91	Zr	0.427 ± 0.014	$(4d^25s^2)\ ^3F_2$	←	$(4d^35s^2)\ ^4F_{3/2}$	PES	406
91	ONiO	3.05 ± 0.01	$^3\Sigma_g^-$	←		PES	471
91	$Ni(O_2)$	0.82 ± 0.03				PES	471
91	AsO	1.286 ± 0.008		←	$^3\Sigma^-$	PES	472
92	FeC_3	1.69 ± 0.08				PES	473
92	C_5O_2	1.2 ± 0.2				PES	333
92	C_6H_5NH [phenylamino] (**17**)	1.70 ± 0.03				ThD	474
92	Na_4	0.91 ± 0.15				PES	400
93	FeC_3H	1.58 ± 0.06				PES	473
93	C_6H_5O [phenoxy] (**18**)	2.253 ± 0.006	$^2B_1$	←	$^1A_1$	PES	120
93	HCBr	1.454 ± 0.005				PES	302
93	Nb	0.894 ± 0.025	$(4d^45s)\ ^6D_{1/2}$	←	$(4d^45s^2)\ ^5D_0$	PES	406
93	$CH_2{=}CHCH{=}CHCH{=}CHCH_2$	1.27 ± 0.03				ThD	475
93	$NaCl_2$	5.86 ± 0.06				PES	449
95	SeO	1.456± 0.02	$^3\Sigma^-$	←	$^2\Pi$	PES	476
96	TiO_3	4.20 ± 0.01				PES	432
96	Mo	0.7472 ± 0.0002	$(4d^55s)\ ^7S_3$	←	$(4d^55s^2)\ ^6S_{5/2}$	ThD	408
96	BrO	2.353 ± 0.006	$^2\Pi$	←	$^1\Sigma^+$	PES	306
96	C_8	4.379 ± 0.006	$^1\Sigma_g^+$	←	$^2\Sigma_g^+$	PES	307
96	TiC_4	1.494 ± 0.020				PES	440
96	S_3	2.093 ± 0.025	$^1A_1$	←	$^2B_1$	PES	298
96	C_6D_5N	1.44 ± 0.02	$^3A_2$	←	$^2B_1$	ThD	470
97	Al_3O (*T*)	1.57 ± 0.06	$^2B_2$	←		PES	458
97	Al_3O (*Y*)	1.14 ± 0.06	$^2A_1$	←		PES	458
97	HC_8	3.966 ± 0.010	$^2\Pi$	←		PES	336
97	C_6H_9O [cyclohexanone enoyl] (**19**)	1.526 ± 0.010	^1A	←	^2A	ThD	341
97	Al_3O	1.57 ± 0.01				PES	458
99	VO_3	4.36 ± 0.05	$^2A_1$	←	$^1A_1$	PES	435
99	ClO_4	5.25 ± 0.10	$^2B_2$	←	$^1A_1$	PES	63
99	$(CH_3)_3CCHCHO$	1.82 ± 0.06				ThD	424
99	$(CH_3)_3CCOCH_2$	$1.755^{+0.05}_{-0.005}$	$^2A''$	←	$^1A'$	ThD	341
100	Si_3O	1.76 ± 0.08				PES	477
100	GaP	1.96 ± 0.08				PES	12
101	CuO_2	3.46 ± 0.04				PES	478
101	$Cu(O_2)$	1.503 ± 0.010				PES	478
101	Ru	1.04638 ± 0.00025	$(4d^75s)\ ^5F_5$	←	$(4d^75s^2)\ ^4F_{9/2}$	ThD	479
102	Al_2O_3	3.71 ± 0.03				PES	463
102	C_8H_6 [1,2-dehydrocyclooctatetraene] (**20**)	1.044 ± 0.008				PES	480
103	C_8H_7 [cyclooctatetraenyl] (**21**)	1.091 ± 0.008				PES	480
103	$CH_3CH_2CH_2CH_2CH_2S$	2.09 ± 0.02				ThD	407
103	NaBr	0.788 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
104	Si_2O_3	0.9 ± 0.1				PES	327
104	FeO_3	3.26 ± 0.04				PES	439
104	Rh	1.14289 ± 0.00020	$(4d^85s)\ ^4F_{9/2}$	←	$(4d^85s^2)\ ^3F_4$	ThD	421
104	c-C_8H_8 [cyclooctatetraene]	0.55 ± 0.02	$^1A_{1g}$	←	$^2B_{2u}$	PES	480
104	Cr_2	0.505 ± 0.005				PES	481
104	*m*-$(CH_2)C_6H_4(CH_2)$ [*m*-xylylene] (**22**)	0.909 ± 0.008	$^3B_2$	←	$^2B_1$	PES	482
104	FeO_3	3.261 ± 0.05				PES	441
105	FeC_4H	1.67 ± 0.06				PES	473
105	Cl_3	5.14 ± 0.50				ThD	483
105	Cr_2H	1.474 ± 0.005				PES	484
105	$OH(N_2O)_2$	2.38 ± 0.02				PES	426
106	GeO_2	2.50 ± 0.10				PES	327
107	Pd	0.56214 ± 0.00012	$(4d^{10})\ ^1S_0$	←	$(4d^{10}5s)\ ^2S_{1/2}$	ThD	421
107	$(C_6H_5)SiH_2$	1.439 ± 0.004				ThD	397
107	$C_6H_5CH_2O$	2.14 ± 0.02				ThD	485
107	*o*-$CH_3C_6H_4O$ [*o*-methylphenoxy] (**23**)	<2.36 ± 0.06				ThD	486
108	Ag	1.30447 ± 0.00002	$(4d^{10}5s)\ ^2S_{1/2}$	←	$(4d^{10}5s^2)\ ^1S_0$	ThD	408
108	C_9	3.684 ± 0.010	$^1\Sigma_g^+$	←	$^2\Pi_g$	PES	307
108	*o*-OC_6H_4O [*o*-quinone] (**24**)	~1.62	^1A	←		ThD	487
108	TiC_5	1.748 ± 0.050				PES	440
108	MoC	1.358 ± 0.010				PES	488
108	Al_4	2.20 ± 0.06				PES	324
108	*p*-OC_6H_4O [*p*-quinone] (**25**)	1.860 ± 0.005				ThD	489
109	C_6H_5PH	1.52 ± 0.04				ThD	402
109	C_6H_5S	<2.47 ± 0.06	$^2B_1$	←	$^1A_1$	ThD	486
109	*o*-$FC_6H_4CH_2$ [*o*-fluorobenzyl] (**26**)	1.091 ± 0.008	$^2A''$	←	$^1A'$	PES	490
109	*m*-$FC_6H_4CH_2$ [*m*-fluorobenzyl] (**27**)	1.173 ± 0.008	$^2A''$	←	$^1A'$	PES	490

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M$^-$	exptl	ref
109	*p*-$\mathrm{FC_6H_4CH_2}$ [*p*-fluorobenzyl] (**28**)	0.937 ± 0.008	$^2B_1$	←	$^1A_1$	PES	490
111	$\mathrm{C_7H_{11}O}$ [cycloheptanone enoyl] (**29**)	$1.444^{+0.02}_{-0.002}$	^2A	←	^1A	ThD	341
111	$\mathrm{CF_3COCH_2}$	2.625 ± 0.010	$^2A''$	←	$^1A'$	ThD	341
111	$\mathrm{C_7H_{11}O}$ (**30**) [1,4-(dimethyl)cyclopentanone enoyl]	1.49 ± 0.04				ThD	491
111	$\mathrm{SeO_2}$	1.823 ± 0.050	$^1A_1$	←	$^2B_1$	PES	348
111	$\mathrm{C_4H_5N_3O}$ [cytosine] (**31**)	0.085 ± 0.008				PES	492
112	MoO	1.285 ± 0.006	$^5\Pi$	←	$^4\Pi$	PES	493
112	$\mathrm{Fe(CO)_2}$	1.22 ± 0.02				PES	494
112	$\mathrm{Fe_2}$	0.902 ± 0.008				PES	415
112	$\mathrm{Si_4}$	2.13 ± 0.01	^1A_g	←	$^2B_{2g}$	PES	495
112	$\mathrm{C_5H_6N_2O_2}$ [uracil] (**32**)	0.093 ± 0.007				PES	496
113	$\mathrm{Si_4H}$	2.68 ± 0.01	$^1A'$	←	$^2A'$	PES	418
113	$\mathrm{CH_3CH_2CH_2COC(CH_2CH_3)H}$	1.72 ± 0.06				ThD	424
113	$\mathrm{(CH_3)_2CHCOC(CH_3)_2}$	1.47 ± 0.04				ThD	424
113	$\mathrm{Al_3O_2}$	2.18 ± 0.01				PES	458
113	$\mathrm{Al_3O_2}$ (iso)	1.6 ± 0.1				PES	458
114	NO(Kr)	0.136				PES	429
115	$\mathrm{VO_4}$	4.0 ± 0.1				PES	435
115	c-$\mathrm{C_6H_{11}P}$ (**33**)	1.03 ± 0.02				ThD	402
115	In	0.404 ± 0.009	(5p) $^2P_{1/2}$	←	(5p^2) $^3S_0$	ThD	497
115	$\mathrm{Na_5}$	1.10 ± 0.10				PES	400
115	$\mathrm{Ni(CO)_2}$	0.643 ± 0.014				PES	466
116	$\mathrm{Si_3O_2}$	1.81 ± 0.09				PES	477
117	$\mathrm{Ni_2}$	0.926 ± 0.010				PES	498
117	$\mathrm{OCuO_2}$	3.19 ± 0.04				PES	451
117	$\mathrm{K_3}$	0.956 ± 0.050				PES	400
118	$\mathrm{Co_2}$	1.110 ± 0.008				PES	415
118	$\mathrm{[(CH_3)_2SiHSi(CH_3)_2}$	1.40 ± 0.03				ThD	468
118	$\mathrm{Al_2O_4}$	3.98 ± 0.03				PES	463
118	$\mathrm{NO(N_2O)_2}$	0.513 ± 0.022	$^2\Pi$	←	$^3\Sigma^-$	PES	442
119	Sn	1.112067 ± 0.00015	(5p^2) $^3P_0$	←	(5p^3) $^4S_{3/2}$	ThD	286
119	$\mathrm{C_6H_5COCH_2}$	$2.057^{+0.005}_{-0.010}$	$^2A''$	←	$^1A'$	ThD	500
119	KBr	0.642 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
120	$\mathrm{Si_2O_4}$	2.6 ± 0.1				PES	327
120	$\mathrm{FeO_4}$	3.30 ± 0.04				PES	439
120	$\mathrm{C_{10}}$	4.5	$^1\Sigma_g^+$	←	$^2\Sigma_g^+$	PES	501
120	$\mathrm{FeS_2}$	3.28 ± 0.14				PES	502
120	RbCl	0.543 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
121	$\mathrm{(C_6H_5)SiH(CH_3)}$	1.335 ± 0.039				ThD	397
122	Sb	1.047402 ± 0.000020	(5p^3) $^4S_{3/2}$	←	(5p^4) $^3P_2$	ThD	503
123	$\mathrm{C_6H_5NO_2}$	1.00 ± 0.01	$^1A_1$	←	$^2B_1$	PES	504
125	$\mathrm{C_8H_{13}O}$ [cyclooctanone enoyl] (**34**)	1.63 ± 0.06				ThD	491
125	KRb	0.486 ± 0.020	$^1\Sigma^+$	←		PES	427
125	*o*-$\mathrm{ClC_6H_4CH_2}$	1.257 ± 0.008	$^2A''$	←	$^1A'$	PES	490
125	*m*-$\mathrm{ClC_6H_4CH_2}$	1.272 ± 0.008	$^2A''$	←	$^1A'$	PES	490
125	*p*-$\mathrm{ClC_6H_4CH_2}$	1.174 ± 0.008	$^2B_1$	←	$^1A_1$	PES	490
126	$\mathrm{C_5N_2O_2H_6}$ [thymine] (**35**)	0.062 ± 0.008				PES	492
127	$\mathrm{C_6H_5CH_2O(HF)}$	≤3.05 ± 0.06				PES	485
127	$\mathrm{Cu_2}$	0.836 ± 0.007	$^1\Sigma_g^+$	←	$^2\Sigma_u^+$	PES	505
127	I	3.059038 ± 0.000010	(5p^5) $^2P_{3/2}$	←	(5p^6) $^1S_0$	ThD	506
127	*o*-$\mathrm{ClC_6H_4O}$[*o*-chlorophenoxy] (**36**)	<2.58 ± 0.08				ThD	486
128	Te	1.970876 ± 0.000007	(5p^4) $^3P_2$	←	(5p^5) $^2P_{3/2}$	ThD	507
128	$\mathrm{Ti_2O_4}$	2.10 ± 0.08				PES	432
128	$\mathrm{(SO_2)_2}$	1.96 ± 0.03				PES	508
128	$\mathrm{Fe_2O}$	1.641 ± 0.03				PES	441
129	$\mathrm{Al_3O_3}$	2.80 ± 0.02				PES	458
129	$\mathrm{Al_3O_3}$(iso)	2.07 ± 0.02				PES	458
129	TeH	2.102 ± 0.015	$^2\Pi$	←	$^1\Sigma^+$	PES	509
131	$\mathrm{GaP_2}$	1.78 ± 0.08				PES	12
132	$\mathrm{Si_3O_3}$	0.6 ± 0.1				PES	477
132	$\mathrm{C_{11}}$	3.913 ± 0.008	$^1\Sigma_g^+$	←	$^2\Pi$	PES	307
132	PdCN	2.543 ± 0.007				PES	510
133	$\mathrm{OCuO(O_2)}$	3.53 ± 0.04				PES	451
133	Cs	0.47164 ± 0.00006	(6s) $^2S_{1/2}$	←	(6s^2) $^1S_0$	ThD	511
134	$\mathrm{Al_2O_5}$	3.75 ± 0.03				PES	463
134	*m*-$\mathrm{CH_3C_6H_4COCH_2}$	$2.030^{+0.005}_{-0.010}$				ThD	500
134	PdCO	0.604 ± 0.010				PES	510
135	$\mathrm{Si_4Na}$	1.30 ± 0.05	$^2B_2$	←	^1A	PES	512
135	$\mathrm{Al_5}$	2.25 ± 0.06				PES	324
135	SnO	0.598 ± 0.006	$^1\Sigma^+$	←	$^2\Pi_{1/2}$	PES	513
136	$\mathrm{Cr(CO)_3}$	1.349 ± 0.006		←		PES	514
137	Ba	0.14462 ± 0.00006	(6s^2) $^1S_0$	←	(6s^{2}6p^1) $^2S_{1/2}$	ThD	515
138	*m*-$\mathrm{FC_6H_4COCH_2}$ [*m*-fluoroacetophenone enoyl] (**37**)	$2.218^{+0.005}_{-0.010}$				ThD	500

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
138	*p*-$FC_6H_4COCH_2$ [*p*-fluoroacetophenone enoyl] (**38**)	$2.176^{+0.005}_{-0.010}$				ThD	500
139	La	0.47 ± 0.02	$(5d^16s^2)\ ^2D_{3/2}$	←	$(5d^26s^2)\ ^3F_2$	ThD	516
139	$C_9H_{15}O$ [cyclononanone enoyl] (**39**)	1.69 ± 0.06				ThD	491
140	Ce	0.700 ± 0.010	$4f^15d^16s^2$	←	$4f^15d^16s^26p^1$	ThD	517
140	Si_5	2.59 ± 0.02	$^1A_1'$	←	$^2A_2''$	PES	495
140	$Fe(CO)_3$	1.8 ± 0.2				PES	494
140	HCI	1.680 ± 0.005				PES	302
143	IO	2.378 ± 0.006	$^2\Pi$	←	$^1\Sigma^+$	PES	306
143	$Ni(CO)_3$	1.077 ± 0.013				PES	466
144	Ti_3	1.17 ± 0.08				PES	518
144	Fe_2O_2	2.36 ± 0.05				PES	439
144	C_{12}	4.6	$^3\Sigma_g^-$			PES	501
144	TeO	1.697 ± 0.022	$^3\Sigma^-$	←		PES	519
145	Al_3O_4	3.58 ± 0.08				PES	458
145	Al_3O_4 (iso)	1.75 ± 0.06				PES	458
145	$Co(CO)_2NO$	1.73 ± 0.03				PES	520
146	Ge_2	2.074 ± 0.001				PES	347
146	InP	1.95 ± 0.05				PES	521
148	Si_3O_4	0.46 ± 0.07				PES	477
149	$OCuO_2(O_2)$	3.21 ± 0.04				PES	451
149	CsO	1.84 ± 0.15	$^2\Sigma^+$	←	$^1\Sigma^+$	PES	522
149	$OH(N_2O)_3$	2.60 ± 0.02				PES	426
150	NaI	0.865 ± 0.010	$^1\Sigma^+$	←		PES	392
150	As_2	0.739 ± 0.001				PES	445
152	FeS_3	2.64 ± 0.08				PES	502
152	$(CS_2)_2$	1.071 ± 0.032				PES	429
153	V_3	1.01 ± 0.06				PES	523
153	$C_{10}H_{17}O$ [cyclodecanone enoyl] (**40**)	1.83 ± 0.06				ThD	491
154	Cu_2O	1.10 ± 0.03				PES	524
156	C_{13}	4.2	$^1\Sigma_g^+$	←		PES	501
156	K_4	0.83 ± 0.12				PES	400
156	Cr_3	1.36 ± 0.08				PES	525
158	Se_2	1.94 ± 0.07	$^3\Sigma_g^-$	←	$^2\Pi_g$	PES	348
159	OIO	2.577 ± 0.008				PES	306
159	$[(CH_3)_3Si]_2CH$	1.561 ± 0.009				ThD	468
160	Fe_2O_3	3.06 ± 0.04				PES	439
160	TeO_2	>2.2				PES	348
161	Al_3O_5	4.92 ± 0.08				PES	458
161	$(CH_3)_3CHCOCHC_6H_5$	2.10 ± 0.08				ThD	424
161	NO(Xe)	0.204	$^2\Pi$	←	$^3\Sigma^-$	PES	429
162	GaP_3	1.95 ± 0.08				PES	12
162	Al_6	2.63 ± 0.06				PES	324
163	Si_5Na	2.45 ± 0.05	$^2B_1$	←	$^1A_1$	PES	512
164	Si_3O_5	<2.5				PES	477
164	$LiBr_2$	5.42 ± 0.03				PES	449
165	$OCuO(O_2)_2$	3.53 ± 0.04				PES	451
165	$C_{13}H_9$ [perinaphthyl] (**41**)	1.07 ± 0.10				ThD	350
166	KI	0.728 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
168	Fe_3	1.47 ± 0.08				PES	526
168	Si_6	2.00 ± 0.03	$^1A_{1g}$	←	$^2B_2$	PES	512
168	C_{14}	4.6	$^3\Sigma_g^-$	←		PES	501
168	CsCl	0.455 ± 0.010	$^1\Sigma^+$	←	$^2\Sigma^+$	PES	392
168	$Fe(CO)_4$	2.4 ± 0.3				PES	494
170	Cu_2O_2	2.12 ± 0.03				PES	524
170	*o*-$BrC_6H_4CH_2$	1.308 ± 0.008	$^2A''$	←	$^1A'$	PES	490
170	*m*-$BrC_6H_4CH_2$	1.307 ± 0.008	$^2A''$	←	$^1A'$	PES	490
170	*p*-$BrC_6H_4CH_2$	1.229 ± 0.008	$^2B_1$	←	$^1A_1$	PES	490
171	$I(CO_2)$	3.225 ± 0.001				PES	527
171	Rb_2	0.498 ± 0.015	$^1\Sigma_g^+$	←	$^2\Pi$	PES	400
171	Ga_2P	2.42 ± 0.08				PES	12
175	*p*-$(CH_3)_3CC_6H_4COCH_2$ [*p*-*tert*-butylacetophenone enoyl] (**42**)	$2.032^{+0.005}_{-0.010}$				ThD	468
176	Fe_2O_4	3.56 ± 0.04				PES	439
176	Fe_2S_2	2.15 ± 0.83				PES	502
176	$[(CH_3)_3Si]_2SiH$	1.94 ± 0.08				ThD	468
176	Ni_3	1.41 ± 0.05				ThD	528
177	Co_3	1.54 ± 0.08				PES	499
177	InP_2	1.617 ± 0.001				PES	521
177	Ge_2O_2	0.625 ± 0.050				PES	529
178	$C_{14}H_{10}$ [anthracene] (**43**)	0.530 ± 0.005				PES	351
180	Si_3O_6	<3.1				PES	477
180	C_{15}	4.2	$^1\Sigma_g^+$	←		PES	501

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M$^-$	exptl	ref
180	$Mo(CO)_3$	1.337 ± 0.006				PES	514
181	$C_{12}H_{21}O$ [cyclododecanone enoyl] (**44**)	1.9 ± 0.07				ThD	491
181	Ta	0.323 ± 0.012	$(5d^36s^2)\ ^4F_{3/2}$	←	$(5d^46s^2)\ ^5D_0$	PES	406
181	$NaBr_2$	5.36 ± 0.06				PES	449
183	$I(CO)_2$	3.225 ± 0.001				PES	527
184	FeS_4	2.95 ± 0.33				PES	502
184	W	0.817 ± 0.004	$(5d^46s^2)\ ^5D_0$	←	$(5d^56s^2)\ ^6S_{5/2}$	PES	514
184	Fe_3O	1.42 ± 0.05				PES	441
186	Cu_2O_2	3.03 ± 0.03				PES	524
189	Al_7	2.43 ± 0.06				PES	324
190	Os	1.07780 ± 0.00012	$(5d^66s^2)\ ^5D_4$	←	$(5d^76s^2)\ ^4F_{9/2}$	ThD	530
191	Si_6Na	1.90 ± 0.05	$^2B_1$	←	$^1A_1$	PES	512
191	Cu_3	2.27 ± 0.10				PES	505
192	Ti_4	1.21 ± 0.08				PES	518
192	Fe_2O_5	3.88 ± 0.04				PES	439
192	C_{16}	4.7	$^3\Sigma_g^-$	←		PES	501
192	Ir	1.56436 ± 0.00015	$(5d^76s^2)\ ^4F_{9/2}$	←	$(5d^86s^2)\ ^3F_4$	ThD	531
193	$OH(N_2O)_4$	>2.80				PES	426
193	GaP_4	3.48 ± 0.08				PES	12
195	Pt	2.125 10 ± 0.00005	$(5d^96s)\ ^3D_3$	←	$(5d^96s^2)\ ^2D_{5/2}$	ThD	531
195	K_5	0.95 ± 0.10				PES	400
196	Ge_2O_3	2.43 ± 0.10				PES	327
196	$C_{14}H_{10}(H_2O)$ [anthracene, H_2O]	0.770 ± 0.005				PES	351
196	Si_7	1.85 ± 0.02	$^1A_1'$	←	$^2A_2''$	PES	495
196	WC	1.022 ± 0.010				PES	488
197	Au	2.30863 ± 0.00003	$(5d^{10}6s)\ ^3S_{1/2}$	←	$(5d^{10}6s^2)\ ^1S_0$	ThD	532
198	$(H_2O)_{11}$	0.75				PES	52
200	Fe_3O_2	1.80 ± 0.06				PES	441
202	Cu_2O_2	2.94 ± 0.03				PES	524
202	Ga_2P_2	1.86 ± 0.08				PES	12
204	V_4	1.32 ± 0.07				PES	523
204	Tl	0.377 ± 0.013	$(6s^26p)\ ^2P_{1/2}$	←	$(6p^2)\ ^3P_0$	ThD	533
207	Pb	0.365 ± 0.008	$(6p^2)\ ^3P_0$	←	$(6p^3)\ ^4S_{3/2}$	PES	534
208	Fe_2S_3	2.93 ± 0.19				PES	502
208	InP_3	1.86 ± 0.05				PES	521
208	Cr_4	1.28 ± 0.08				PES	525
209	Bi	0.942362 ± 0.000013	$(6p^3)\ ^4S_{3/2}$	←	$(6p^4)\ ^3P_2$	PES	535
213	Pd_2	1.685 ± 0.008	$^3\Sigma_u^+$	←	$^2\Sigma_u^+$	PES	498
216	Ag_2	1.023 ± 0.007				PES	505
216	FeS_5	2.99 ± 0.29				PES	502
216	$(H_2O)_{12}$	0.83				PES	52
216	Al_8	2.35 ± 0.06				PES	324
216	Fe_3O_3	2.19 ± 0.06				PES	441
218	Ge_3	2.23 ± 0.01				PES	347
218	RbCs	0.478 ± 0.020	$^1\Sigma^+$	←		PES	427
218	$[(CH_3)C_5H_4]Mn(CO)_3$ (**45**)	0.5 ± 0.1				PES	444
219	Si_7Na	1.94 ± 0.05	$^2B_1$	←	$^1A_1$	PES	512
224	Fe_4	1.72 ± 0.08				PES	526
224	PbO	0.722 ± 0.006	$^1\Sigma^+$	←		PES	537
225	As_3	1.45 ± 0.01				PES	445
230	In_2	1.27 ± 0.10				PES	538
232	Ni_4	1.45 ± 0.08				PES	539
232	Fe_3S_2	2.50 ± 0.79				PES	502
232	WO_3	$3.33^{+0.08}_{-0.15}$				ThD	540
232	Fe_3O_4	2.56 ± 0.06				PES	441
233	Ga_2P_3	3.03 ± 0.08				PES	12
234	$(H_2O)_{13}$	0.88				PES	52
235	K_6	0.95 ± 0.10				PES	400
236	Co_4	1.75 ± 0.08				PES	499
237	$OH(N_2O)_5$	>2.92				PES	426
237	Se_3	>2.2				PES	348
237	Sn_2	1.962 ± 0.010				PES	541
239	InP_4	3.22 ± 0.05				PES	521
240	Ti_5	1.16 ± 0.08				PES	518
240	Ti_3O_6	2.90 ± 0.01				PES	432
240	Ti_3C_8	2.5 ± 0.2				PES	542
240	Fe_2S_4	3.41 ± 0.40				PES	502
240	Ga_3P	1.88 ± 0.08				PES	12
240	Fe_4O	1.73 ± 0.05				PES	441
243	Al_9	2.85 ± 0.06				PES	324
244	Sb_2	1.282 ± 0.008	$^1\Sigma_g^+$	←		PES	543
247	$[(CH_3)_3Si]_3Si$	2.03 ± 0.09				ThD	468
248	FeS_6	3.21 ± 0.22				PES	502

Table 10 (Continued)

m/z	species	EA/eV	M	←	M^-	exptl	ref
248	Fe_3O_5	3.80 ± 0.10				PES	441
252	$C_{20}H_{12}$ [perylene] (**46**)	0.973 ± 0.005				PES	447
252	$(H_2O)_{14}$	0.83				PES	52
254	Cu_4	1.32 ± 0.10				PES	505
254	I_2	2.524 ± 0.005	$^1\Sigma_g^+$	←	$^2\Sigma_u^+$	PES	544
255	V_5	1.27 ± 0.08				PES	545
255	Te_2	1.92 ± 0.07	$^3\Sigma_g^-$	←	$^2\Pi_g$	PES	348
256	Rb_3	0.920 ± 0.030				PES	400
256	Fe_4O_2	2.05 ± 0.05				PES	441
260	Cr_5	1.58 ± 0.08				PES	525
260	LiI_2	4.88 ± 0.03				PES	449
261	In_2P	2.400 ± 0.001				PES	546
263	Fe_3S_3	2.92 ± 0.07				PES	502
264	Ga_2P_4	2.40 ± 0.08				PES	12
266	Cs_2	0.469 ± 0.015	$^1\Sigma_g^+$	←	$^2\Pi$	PES	400
268	$W(CO)_3$	1.859 ± 0.006				PES	514
270	$(H_2O)_{15}$	0.97				PES	52
270	Al_{20}	2.70 ± 0.06				PES	324
271	Ga_3P_2	3.03 ± 0.08				PES	12
272	Fe_2S_5	3.35 ± 0.43				PES	502
272	Fe_4O_3	2.40 ± 0.07				PES	441
274	K_7	1.05 ± 0.10				PES	400
277	NaI_2	4.84 ± 0.06				PES	449
280	Fe_5	1.81 ± 0.08				PES	526
287	Fe_4S_2	1.92 ± 0.23				PES	502
288	Ti_6	1.31 ± 0.08				PES	518
288	Ti_4C_8	1.8 ± 0.2				PES	542
288	Fe_4O_4	2.69 ± 0.07				PES	441
290	Ni_5	1.61 ± 0.08				PES	539
290	Ge_4	1.94 ± 0.05				PES	347
292	In_2P_2	1.68 ± 0.05				PES	521
295	Co_5	1.66 ± 0.08				PES	499
295	Fe_3S_4	3.22 ± 0.33				PES	502
297	Al_{11}	2.87 ± 0.06				PES	324
300	As_4	<0.8				PES	445
300	$C_{24}H_{12}$ [coronene] (**47**)	0.47 ± 0.09				PES	277
302	Ga_3P_3	2.50 ± 0.08				PES	12
304	Fe_2S_6	3.29 ± 0.34				PES	502
304	Fe_4O_5	3.02 ± 0.05				PES	441
306	V_6	1.32 ± 0.08				PES	545
309	Ga_4P	2.09 ± 0.08				PES	12
312	Cr_6	1.97 ± 0.08				PES	525
318	Cu_5	1.82 ± 0.05				PES	505
319	Fe_4S_3	2.24 ± 0.42				PES	502
319	Pd_3	≤1.5 ± 0.1				PES	528
320	Ti_4O_8	3.3 ± 0.02				PES	432
320	Fe_4O_6	3.35 ± 0.06				PES	441
323	In_2P_3	2.72 ± 0.05				PES	521
324	Ag_3	2.36 ± 0.01				PES	505
324	Al_{12}	2.75 ± 0.06				PES	324
326	SnPb	1.569 ± 0.008				PES	541
327	Fe_3S_5	3.25 ± 0.37				PES	502
333	Ga_3P_4	3.12 ± 0.08				PES	12
336	Fe_6	1.51 ± 0.08				PES	526
336	Ti_7	1.16 ± 0.08				PES	518
340	Ga_4P_2	2.16 ± 0.08				PES	12
342	$(H_2O)_{19}$	1.12				PES	52
343	Fe_5S_2	1.79 ± 0.07				PES	502
348	Ni_6	1.84 ± 0.08				PES	539
351	Fe_4S_4	2.04 ± 0.04				PES	502
351	Al_{13}	3.62 ± 0.06				PES	324
354	Co_6	1.62 ± 0.08				PES	499
354	In_2P_4	1.08 ± 0.05				PES	521
357	V_7	1.36 ± 0.08				PES	545
359	Fe_3S_6	3.09 ± 0.34				PES	502
363	Ge_5	2.51 ± 0.05				PES	347
364	Cr_7	1.73 ± 0.08				PES	525
365	Sb_3	1.85 ± 0.03				PES	543
371	Ga_4P_3	2.88 ± 0.08				PES	12
372	Re_2	1.571 ± 0.008				PES	547
375	Fe_5S_3	2.13 ± 0.25				PES	502
375	In_3P	1.77 ± 0.05				PES	521
375	As_5	∼1.7				PES	445

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
378	Al_{14}	2.60 ± 0.06				PES	324
381	I_3	4.226 ± 0.013	$^2B_2$	←	$^1A_1$	PES	548
381	Cu_6	1.82 ± 0.05				PES	505
383	Fe_4S_5	3.29 ± 0.12				PES	502
383	Te_3	<2.7				PES	348
384	Ti_8	1.46 ± 0.08				PES	518
390	Pt_2	1.898 ± 0.008	$^3\Sigma_g$ $(O^+{}_g)$	←		PES	498
392	Fe_7	1.39 ± 0.08				PES	526
394	Au_2	1.938 ± 0.007	$^1\Sigma_g^+$	←		PES	505
399	Fe_6S_2	1.87 ± 0.47				PES	502
399	Cs_3	0.864 ± 0.030				PES	400
402	Ga_4P_4	2.33 ± 0.15				PES	12
405	Al_{15}	2.90 ± 0.06				PES	324
406	Ni_7	1.86 ± 0.08				PES	539
406	In_3P_2	2.07 ± 0.05				PES	521
407	Fe_5S_4	2.66 ± 0.27				PES	502
408	V_8	1.46 ± 0.08				PES	545
409	Tl_2	$0.95^{+0.05}{}_{-0.10}$				PES	538
411	Ga_5P_2	2.37 ± 0.08				PES	12
413	Co_7	1.65 ± 0.08				PES	499
414	Pb_2	1.366 ± 0.010				PES	541
415	Fe_4S_6	3.29 ± 0.38				PES	502
416	Cr_8	1.59 ± 0.08				PES	525
418	Bi_2	1.271 ± 0.008				PES	549
431	Fe_6S_3	2.17 ± 0.36				PES	502
431	Ag_4	1.51 ± 0.10				PES	505
432	Ti_9	1.55 ± 0.08				PES	518
432	Al_{16}	2.87 ± 0.06				PES	324
433	Ga_4P_5	2.47 ± 0.15				PES	12
436	Ge_6	2.06 ± 0.05				PES	347
437	In_3P_3	1.30 ± 0.05				PES	521
439	Fe_5S_5	2.83 ± 0.16				PES	502
442	Ga_5P_3	2.67 ± 0.15				PES	12
444	Ti_6C_{13}	2.2 ± 0.2				PES	542
445	Cu_7	1.98 ± 0.15				PES	505
448	Fe_8	1.66 ± 0.08				PES	526
455	Fe_7S_2	1.70 ± 0.20				PES	502
459	V_9	1.58 ± 0.08				PES	545
459	In_4	$1.7^{+0.15}_{-0.35}$				PES	538
459	Al_7	2.90 ± 0.06				PES	324
463	Fe_6S_4	2.22 ± 0.23				PES	502
464	Ni_8	1.92 ± 0.08				PES	539
468	In_3P_4	2.72 ± 0.05				PES	521
468	Cr_9	1.78 ± 0.08				PES	525
471	Fe_5S_6	3.42 ± 0.36				PES	502
472	Co_8	1.68 ± 0.08				PES	499
473	Ga_5P_4	3.11 ± 0.15				PES	12
480	Ti_{10}	1.67 ± 0.08				PES	518
486	Al_{18}	2.57 ± 0.06				PES	324
487	Fe_7S_3	2.06 ± 0.16				PES	502
487	Sb_4	$<1.00 \pm 0.10$				PES	543
490	In_4P	1.88 ± 0.05				PES	521
492	Ti_7C_{13}	2.1 ± 0.2				PES	542
495	Fe_6S_5	2.82 ± 0.30				PES	502
504	Fe_9	1.75 ± 0.08				PES	526
504	Ga_5P_5	2.81 ± 0.08				PES	12
508	Cu_8	1.41 ± 0.10				PES	505
508	Ge_7	1.80 ± 0.05				PES	347
510	V_{10}	1.67 ± 0.08				PES	545
511	Fe_8S_2	1.80 ± 0.18				PES	502
511	Ga_6P_3	3.05 ± 0.08				PES	12
513	Al_{19}	3.12 ± 0.06				PES	324
519	Fe_7S_4	2.15 ± 0.10				PES	502
520	Cr_{10}	1.68 ± 0.08				PES	525
521	In_4P_2	2.00 ± 0.05				PES	521
522	Ni_9	1.95 ± 0.08				PES	539
527	Fe_6S_6	3.00 ± 0.32				PES	502
528	Ti_8C_{12}	1.05 ± 0.05				PES	550
528	Ti_{11}	1.69 ± 0.08				PES	518
531	Co_9	1.77 ± 0.08				PES	499
535	Ga_5P_6	3.27 ± 0.15				PES	12
539	Ag_5	1.98 ± 0.05				PES	505
540	Al_{20}	2.86 ± 0.06				PES	324
542	Ga_6P_4	2.83 ± 0.15				PES	12
543	Fe_8S_3	2.02 ± 0.08				PES	502

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M^-	exptl	ref
551	Fe_7S_5	2.77 ± 0.28				PES	502
552	V_8C_{12}	1.80 ± 0.08				PES	550
552	In_4P_3	2.43 ± 0.05				PES	521
560	Cr_8C_{12}	2.28 ± 0.08				PES	550
560	Fe_{10}	1.85 ± 0.08				PES	526
561	V_{11}	1.65 ± 0.08				PES	545
567	Al_{21}	3.30 ± 0.06				PES	324
572	Cu_9	2.25 ± 0.10				PES	505
572	Cr_{11}	1.73 ± 0.08				PES	525
573	Ga_6P_5	2.97 ± 0.15				PES	12
574	In_5	$1.9^{+0.2}_{-0.3}$				PES	538
575	Fe_8S_4	2.42 ± 0.12				PES	502
576	Ti_{12}	1.74 ± 0.08				PES	518
580	Ni_{10}	2.00 ± 0.08				PES	539
581	Ge_8	2.41 ± 0.05				PES	347
583	Fe_7S_6	2.77 ± 0.18				PES	502
583	In_4P_4	2.07 ± 0.05				PES	521
583	Fe_7S_6	2.60 ± 0.16				PES	502
585	Pt_3	1.87 ± 0.02				PES	528
590	Co_{10}	1.97 ± 0.08				PES	499
591	Au_3	$3.40 - 3.95$				PES	505
594	Al_{22}	3.22 ± 0.06				PES	324
600	$[C_{24}H_{12}]_2$ $[\text{coronene}]_2$ (**47**)	0.67 ± 0.09				PES	277
604	Ga_6P_6	2.74 ± 0.15				PES	12
607	Fe_8S_5	2.42 ± 0.20				PES	502
612	V_{12}	1.48 ± 0.08				PES	545
612	Ti_9C_{15}	1.8 ± 0.2				PES	542
613	Tl_3	1.1 ± 0.3				PES	538
616	Fe_{11}	2.00 ± 0.08				PES	526
621	Al_{23}	3.45 ± 0.06				PES	324
624	Ti_{13}	1.82 ± 0.08				PES	518
624	Cr_{12}	1.79 ± 0.08				PES	525
627	Bi_3	1.60 ± 0.03				PES	549
635	Cu_{10}	1.91 ± 0.10				PES	505
638	Ni_{11}	2.01 ± 0.08				PES	539
644	Ga_7P_5	2.95 ± 0.08				PES	12
647	Ag_6	1.92 ± 0.10				PES	505
648	Al_{24}	2.80 ± 0.06				PES	324
649	Co_{11}	2.06 ± 0.08				PES	499
653	Ge_9	2.86 ± 0.05				PES	347
663	V_{13}	1.59 ± 0.08				PES	545
672	Fe_{12}	2.12 ± 0.08				PES	526
672	Ti_{14}	1.9 ± 0.08				PES	518
675	Ga_7P_6	3.39 ± 0.15				PES	12
675	Al_{25}	3.34 ± 0.06				PES	324
676	Cr_{13}	1.80 ± 0.08				PES	525
689	In_6	$1.75^{+0.1}_{-0.2}$				PES	538
696	Ni_{12}	2.07 ± 0.08				PES	539
702	Al_{26}	2.88 ± 0.06				PES	324
706	Ga_7P_7	2.81 ± 0.15				PES	12
708	Co_{12}	2.12 ± 0.08				PES	499
714	V_{14}	1.69 ± 0.08				PES	545
720	Ti_{15}	1.9 ± 0.08				PES	518
720	C_{60}	2.666 ± 0.001				ThD	551
726	Ge_{10}	$2.5 \pm 0.1{-}0.2$				PES	347
728	Fe_{13}	2.20 ± 0.08				PES	526
728	Cr_{14}	1.96 ± 0.08				PES	525
729	Al_{27}	3.32 ± 0.06				PES	324
744	Ga_8P_6	3.11 ± 0.15				PES	12
754	Ni_{13}	2.12 ± 0.08				PES	539
755	Ag_7	2.30 ± 0.10				PES	505
756	Al_{28}	2.90 ± 0.06				PES	324
765	V_{15}	1.72 ± 0.08				PES	545
767	Co_{13}	2.20 ± 0.08				PES	499
768	Ti_{16}	1.9 ± 0.08				PES	518
775	Ga_8P_7	3.33 ± 0.15				PES	12
780	Cr_{15}	1.96 ± 0.08				PES	525
783	Al_{29}	3.32 ± 0.06				PES	324
784	Fe_{14}	2.23 ± 0.08				PES	526
788	Au_4	2.60 ± 0.10				PES	505
798	Ge_{11}	$2.5 \pm 0.1{-}0.2$				PES	347
804	In_7	$2.1^{+0.15}_{-0.20}$				PES	538
806	Ga_8P_8	3.04 ± 0.15				PES	12
810	Al_{30}	3.05 ± 0.06				PES	324
812	Ni_{14}	2.20 ± 0.08				PES	539

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M$^-$	exptl	ref
816	V_{16}	1.72 ± 0.08				PES	545
816	Ti_{17}	1.9 ± 0.08				PES	518
817	Tl_4	$1.65^{+0.10}_{-0.15}$				PES	538
826	Co_{14}	2.30 ± 0.08				PES	499
832	Cr_{16}	2.13 ± 0.08				PES	525
836	Bi_4	1.05 ± 0.10				PES	549
837	Al_{31}	3.22 ± 0.06				PES	324
840	Fe_{15}	2.25 ± 0.08				PES	526
840	C_{70}	2.676 ± 0.001				ThD	551
844	Ga_9P_7	3.00 ± 0.15				PES	12
863	Ag_8	1.48 ± 0.10				PES	505
864	Zr_8C_{12}	1.02 ± 0.06				PES	550
864	Ti_{18}	1.9 ± 0.08				PES	518
864	Al_{32}	2.96 ± 0.06				PES	324
867	V_{17}	1.88 ± 0.08				PES	545
870	Ni_{15}	2.29 ± 0.08				PES	539
871	Ge_{12}	2.4 ± 0.1−0.2				PES	347
875	Ga_9P_8	2.97 ± 0.15				PES	12
884	Cr_{17}	2.10 ± 0.08				PES	525
885	Co_{15}	2.30 ± 0.08				PES	499
888	Nb_8C_{12}	1.65 ± 0.06				PES	550
891	Al_{33}	3.40 ± 0.06				PES	324
896	Fe_{16}	2.01 ± 0.08				PES	526
900	Ga_9P_9	2.92 ± 0.15				PES	12
912	Ti_{19}	1.97 ± 0.08				PES	518
918	V_{18}	1.91 ± 0.08				PES	545
918	Al_{34}	3.12 ± 0.06				PES	324
919	In_8	$2.04^{+0.05}_{-0.10}$				PES	538
928	Ni_{16}	2.37 ± 0.08				PES	539
936	Cr_{18}	2.13 ± 0.08				PES	525
944	Co_{16}	2.32 ± 0.08				PES	499
944	Ge_{13}	2.9 ± 0.1−0.2				PES	347
945	Al_{35}	3.37 ± 0.06				PES	324
952	Fe_{17}	2.06 ± 0.08				PES	526
960	Ti_{20}	1.95 ± 0.08				PES	518
969	V_{19}	1.93 ± 0.08				PES	545
971	Ag_9	2.32 ± 0.10				PES	505
972	Al_{36}	2.58 ± 0.06				PES	324
985	Au_5	2.93 ± 0.10				PES	505
986	Ni_{17}	2.43 ± 0.08				PES	539
988	Cr_{19}	2.13 ± 0.08				PES	525
999	Al_{37}	3.45 ± 0.06				PES	324
1003	Co_{17}	2.40 ± 0.08				PES	499
1008	Fe_{18}	2.14 ± 0.08				PES	526
1008	Ti_{21}	2.04 ± 0.08				PES	518
1016	Ge_{14}	2.8 ± 0.1−0.2				PES	347
1020	V_{20}	1.97 ± 0.08				PES	545
1022	Tl_5	$1.75^{+0.15}_{-0.20}$				PES	538
1026	Al_{38}	2.95 ± 0.06				PES	324
1033	In_9	2.05 ± 0.20				PES	538
1040	Cr_{20}	2.20 ± 0.08				PES	525
1044	Ni_{18}	2.48 ± 0.08				PES	539
1053	Al_{39}	3.40 ± 0.06				PES	324
1056	Ti_{22}	2.04 ± 0.08				PES	518
1062	Co_{18}	2.40 ± 0.08				PES	499
1064	Fe_{19}	2.01 ± 0.08				PES	526
1071	V_{21}	2.00 ± 0.08				PES	545
1079	Ag_{10}	2.03 ± 0.10				PES	505
1080	Al_{40}	3.26 ± 0.06				PES	324
1092	Cr_{21}	2.20 ± 0.08				PES	525
1102	Ni_{19}	2.47 ± 0.08				PES	539
1104	Ti_{23}	2.04 ± 0.08				PES	518
1107	Al_{41}	3.18 ± 0.06				PES	324
1120	Fe_{20}	2.01 ± 0.08				PES	526
1121	Co_{19}	2.40 ± 0.08				PES	499
1122	V_{22}	2.05 ± 0.08				PES	545
1134	Al_{42}	2.93 ± 0.06				PES	324
1144	Cr_{22}	2.20 ± 0.08				PES	525
1148	Ge_{15}	2.7 ± 0.1−0.2				PES	347
1148	In_{10}	2.13 ± 0.20				PES	538
1152	Ti_{24}	2.1 ± 0.08				PES	518
1160	Ni_{20}	2.52 ± 0.08				PES	539
1161	Al_{43}	3.20 ± 0.06				PES	324
1173	V_{23}	2.05 ± 0.08				PES	545
1176	Fe_{21}	2.11 ± 0.08				PES	526

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M^-	exptl	ref
1180	Co_{20}	2.40 ± 0.08				PES	499
1182	Au_6	2.051 ± 0.002				PES	552
1188	Al_{44}	2.89 ± 0.06				PES	324
1196	Cr_{23}	2.22 ± 0.08				PES	525
1200	Ti_{25}	2.1 ± 0.08				PES	518
1215	Al_{45}	3.15 ± 0.06				PES	324
1218	Ni_{21}	2.56 ± 0.08				PES	539
1224	V_{24}	2.14 ± 0.08				PES	545
1226	Tl_6	1.73 ± 0.20				PES	538
1232	Fe_{22}	2.15 ± 0.08				PES	526
1239	Co_{21}	2.40 ± 0.08				PES	499
1242	Al_{46}	3.02 ± 0.06				PES	324
1248	Ti_{26}	2.11 ± 0.08				PES	518
1248	Cr_{24}	2.20 ± 0.08				PES	525
1263	In_{11}	$2.34^{+0.15}_{-0.25}$				PES	538
1269	Al_{47}	3.06 ± 0.06				PES	324
1275	V_{25}	2.15 ± 0.08				PES	545
1276	Ni_{22}	2.58 ± 0.08				PES	539
1288	Fe_{23}	2.04 ± 0.08				PES	526
1296	Ti_{27}	2.12 ± 0.08				PES	518
1296	Al_{48}	3.22 ± 0.06				PES	324
1298	Co_{22}	2.40 ± 0.08				PES	499
1300	Cr_{25}	2.20 ± 0.08				PES	525
1323	Al_{49}	3.30 ± 0.06				PES	324
1326	V_{26}	2.19 ± 0.08				PES	545
1334	Ni_{23}	2.59 ± 0.08				PES	539
1344	Fe_{24}	2.13 ± 0.08				PES	526
1344	Ti_{28}	2.13 ± 0.08				PES	518
1350	Al_{50}	3.20 ± 0.06				PES	324
1352	Cr_{26}	2.20 ± 0.08				PES	525
1357	Co_{23}	2.40 ± 0.08				PES	477
1377	V_{27}	2.24 ± 0.08				PES	545
1377	Al_{51}	3.41 ± 0.06				PES	324
1378	In_{12}	$2.28^{+0.2}_{-0.2}$				PES	538
1392	Ti_{29}	2.15 ± 0.08				PES	518
1392	Ni_{24}	2.61 ± 0.08				PES	539
1404	Al_{52}	2.98 ± 0.06				PES	324
1404	Cr_{27}	2.27 ± 0.08				PES	525
1428	V_{28}	2.24 ± 0.08				PES	545
1431	Tl_7	$1.87^{+0.15}_{-0.30}$				PES	538
1431	Al_{53}	3.40 ± 0.06				PES	324
1440	Ti_{30}	2.19 ± 0.08				PES	518
1450	Ni_{25}	2.64 ± 0.08				PES	539
1456	Cr_{28}	2.27 ± 0.08				PES	525
1458	Al_{54}	2.93 ± 0.06				PES	324
1479	V_{29}	2.25 ± 0.08				PES	545
1485	Al_{55}	3.41 ± 0.06				PES	324
1488	Ti_{31}	2.19 ± 0.08				PES	518
1508	Ni_{26}	2.69 ± 0.08				PES	539
1508	Cr_{29}	2.29 ± 0.08				PES	525
1512	Al_{56}	3.20 ± 0.06				PES	324
1530	V_{30}	2.24 ± 0.08				PES	545
1536	Ti_{32}	2.20 ± 0.08				PES	518
1539	Al_{57}	3.30 ± 0.06				PES	324
1560	Cr_{30}	2.31 ± 0.08				PES	525
1566	Ni_{27}	2.70 ± 0.08				PES	539
1566	Al_{58}	3.15 ± 0.06				PES	324
1581	V_{31}	2.26 ± 0.08				PES	545
1584	Ti_{33}	2.21 ± 0.08				PES	518
1593	Al_{59}	3.33 ± 0.06				PES	324
1607	In_{14}	$2.2^{+0.2}_{-0.3}$				PES	538
1612	Cr_{31}	2.32 ± 0.08				PES	525
1620	Al_{60}	3.18 ± 0.06				PES	324
1624	Ni_{28}	2.72 ± 0.08				PES	539
1632	V_{32}	2.34 ± 0.08				PES	545
1632	Ti_{34}	2.23 ± 0.08				PES	518
1635	Tl_8	$1.66^{+0.30}_{-0.35}$				PES	538
1647	Al_{61}	3.31 ± 0.06				PES	324
1664	Cr_{32}	2.32 ± 0.08				PES	525
1674	Al_{62}	3.15 ± 0.06				PES	324
1680	Ti_{35}	2.23 ± 0.08				PES	518
1682	Ni_{29}	2.75 ± 0.08				PES	539
1683	V_{33}	2.35 ± 0.08				PES	545
1701	Al_{63}	3.34 ± 0.06				PES	324
1716	Cr_{33}	2.34 ± 0.08				PES	525
1722	In_{15}	2.21 ± 0.25				PES	538
1728	Ti_{36}	2.23 ± 0.08				PES	518
1728	Al_{64}	3.30 ± 0.06				PES	324

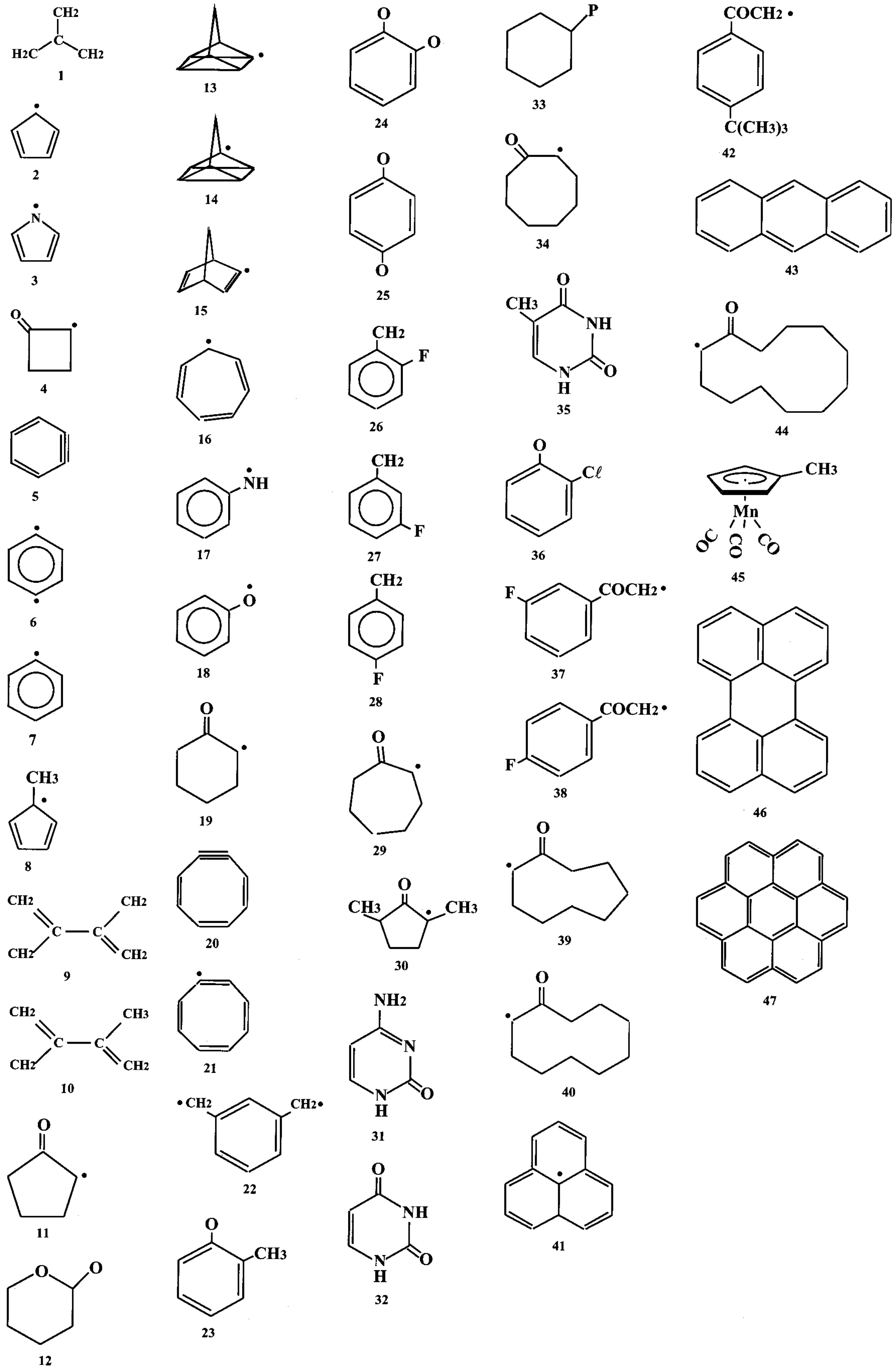
Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M⁻	exptl	ref
1734	V_{34}	2.35 ± 0.08				PES	545
1740	Ni_{30}	2.79 ± 0.08				PES	539
1755	Al_{65}	3.31 ± 0.06				PES	324
1768	Cr_{34}	2.34 ± 0.08				PES	525
1776	Ti_{37}	2.25 ± 0.08				PES	518
1782	Al_{66}	2.90 ± 0.06				PES	324
1785	V_{35}	2.35 ± 0.08				PES	545
1809	Al_{67}	3.26 ± 0.06				PES	324
1820	Cr_{35}	2.38 ± 0.08				PES	525
1824	Ti_{38}	2.26 ± 0.08				PES	518
1836	V_{36}	2.34 ± 0.08				PES	545
1836	Al_{68}	3.01 ± 0.06				PES	324
1839	Tl_{9}	1.87 ± 0.32				PES	538
1863	Al_{69}	3.40 ± 0.06				PES	324
1872	Ti_{39}	2.30 ± 0.08				PES	518
1872	Cr_{36}	2.38 ± 0.08				PES	525
1887	V_{37}	2.39 ± 0.08				PES	545
1890	Al_{70}	3.42 ± 0.06				PES	324
1917	Al_{71}	3.55 ± 0.06				PES	324
1920	Ti_{40}	2.33 ± 0.08				PES	518
1924	Cr_{37}	2.38 ± 0.08				PES	525
1938	V_{38}	2.39 ± 0.08				PES	545
1944	Al_{72}	3.38 ± 0.06				PES	324
1971	Al_{73}	3.50 ± 0.06				PES	324
1976	Cr_{38}	2.38 ± 0.08				PES	525
1989	V_{39}	2.38 ± 0.08				PES	545
1998	Al_{74}	3.16 ± 0.06				PES	324
2025	Al_{75}	3.4 ± 0.06				PES	324
2028	Cr_{39}	2.38 ± 0.08				PES	525
2030	Ni_{35}	2.92 ± 0.08				PES	539
2040	V_{40}	2.39 ± 0.08				PES	545
2044	Tl_{10}	$1.88^{+0.25}_{-0.28}$				PES	538
2052	Al_{76}	3.38 ± 0.06				PES	324
2079	Al_{77}	3.40 ± 0.06				PES	324
2080	Cr_{40}	2.39 ± 0.08				PES	525
2091	V_{41}	2.43 ± 0.08				PES	545
2106	Al_{78}	3.40 ± 0.06				PES	324
2132	Cr_{41}	2.40 ± 0.08				PES	525
2133	Al_{79}	3.41 ± 0.06				PES	324
2142	V_{42}	2.45 ± 0.08				PES	545
2160	Ti_{45}	2.41 ± 0.08				PES	518
2160	Al_{80}	3.40 ± 0.06				PES	324
2184	Cr_{42}	2.41 ± 0.08				PES	525
2187	Al_{81}	3.38 ± 0.06				PES	324
2193	V_{43}	2.44 ± 0.08				PES	545
2214	Al_{82}	3.40 ± 0.06				PES	324
2241	Al_{83}	3.42 ± 0.06				PES	324
2244	V_{44}	2.46 ± 0.08				PES	545
2248	Tl_{11}	2.01 ± 0.25				PES	538
2268	Al_{84}	3.40 ± 0.06				PES	324
2295	V_{45}	2.46 ± 0.08				PES	545
2295	Al_{85}	3.42 ± 0.06				PES	324
2320	Ni_{40}	2.96 ± 0.08				PES	539
2322	Al_{86}	3.44 ± 0.06				PES	324
2340	Cr_{45}	2.48 ± 0.08				PES	525
2346	V_{46}	2.49 ± 0.08				PES	545
2349	Al_{87}	3.44 ± 0.06				PES	324
2376	Al_{88}	3.46 ± 0.06				PES	324
2397	V_{47}	2.50 ± 0.08				PES	545
2400	Ti_{50}	2.42 ± 0.08				PES	518
2403	Al_{89}	3.47 ± 0.06				PES	324
2430	Al_{90}	3.36 ± 0.06				PES	324
2448	V_{48}	2.53 ± 0.08				PES	545
2452	Tl_{12}	$2.05^{+0.15}_{-0.40}$				PES	538
2457	Al_{91}	3.40 ± 0.06				PES	324
2484	Al_{92}	3.45 ± 0.06				PES	324
2499	V_{49}	2.54 ± 0.08				PES	545
2511	Al_{93}	3.42 ± 0.06				PES	324
2538	Al_{94}	3.44 ± 0.06				PES	324
2550	V_{50}	2.55 ± 0.08				PES	545
2565	Al_{95}	3.46 ± 0.06				PES	324
2592	Al_{96}	3.45 ± 0.06				PES	324
2600	Cr_{50}	2.48 ± 0.08				PES	525
2601	V_{51}	2.56 ± 0.08				PES	545
2619	Al_{97}	3.45 ± 0.06				PES	324

Table 10 (Continued)

m/*z*	species	EA/eV	M	←	M$^-$	exptl	ref
2640	Ti_{55}	2.51 ± 0.08				PES	518
2646	Al_{98}	3.44 ± 0.06				PES	324
2652	V_{52}	2.56 ± 0.08				PES	545
2657	Tl_{13}	1.94 ± 0.30				PES	538
2668	Ni_{46}	3.06 ± 0.08				PES	539
2673	Al_{99}	3.50 ± 0.06				PES	324
2700	Al_{100}	3.36 ± 0.06				PES	324
2703	V_{53}	2.56 ± 0.08				PES	545
2727	Al_{101}	3.40 ± 0.06				PES	324
2754	V_{54}	2.56 ± 0.08				PES	545
2754	Al_{102}	3.45 ± 0.06				PES	324
2781	Al_{103}	3.48 ± 0.06				PES	324
2805	V_{55}	2.58 ± 0.08				PES	545
2808	Al_{104}	3.50 ± 0.06				PES	324
2835	Al_{105}	3.51 ± 0.06				PES	324
2856	V_{56}	2.57 ± 0.08				PES	545
2860	Cr_{55}	2.53 ± 0.08				PES	525
2861	Tl_{14}	$2.00^{+0.05}_{-0.40}$				PES	538
2862	Al_{106}	3.52 ± 0.06				PES	324
2880	Ti_{60}	2.51 ± 0.08				PES	518
2889	Al_{107}	3.55 ± 0.06				PES	324
2900	Ni_{50}	3.11 ± 0.08				PES	539
2916	Al_{108}	3.56 ± 0.06				PES	324
2943	Al_{109}	3.56 ± 0.06				PES	324
2970	Al_{110}	3.56 ± 0.06				PES	324
2997	Al_{111}	3.55 ± 0.06				PES	324
3024	Al_{112}	3.55 ± 0.06				PES	324
3051	Al_{113}	3.60 ± 0.06				PES	324
3060	V_{60}	2.63 ± 0.08				PES	545
3066	Tl_{15}	$2.17^{+0.15}_{-0.30}$				PES	538
3078	Al_{114}	3.60 ± 0.06				PES	324
3105	Al_{115}	3.60 ± 0.06				PES	324
3120	Ti_{65}	2.58 ± 0.08				PES	518
3132	Al_{116}	3.60 ± 0.06				PES	324
3159	Al_{117}	3.60 ± 0.06				PES	324
3186	Al_{118}	3.60 ± 0.06				PES	324
3213	Al_{119}	3.60 ± 0.06				PES	324
3240	Al_{120}	3.60 ± 0.06				PES	324
3267	Al_{121}	3.60 ± 0.06				PES	324
3270	Tl_{16}	$2.17^{+0.15}_{-0.40}$				PES	538
3294	Al_{122}	3.60 ± 0.06				PES	324
3315	V_{65}	2.67 ± 0.08				PES	545
3321	Al_{123}	3.60 ± 0.06				PES	324
3348	Al_{124}	3.60 ± 0.06				PES	324
3375	Al_{125}	3.60 ± 0.06				PES	324
3402	Al_{126}	3.60 ± 0.06				PES	324
3429	Al_{127}	3.58 ± 0.06				PES	324
3456	Al_{128}	3.58 ± 0.06				PES	324
3474	Tl_{17}	$2.2^{+0.25}_{-0.35}$				PES	538
3483	Al_{129}	3.58 ± 0.06				PES	324
3510	Al_{130}	3.58 ± 0.06				PES	324
3537	Al_{131}	3.58 ± 0.06				PES	324
3564	Al_{132}	3.58 ± 0.06				PES	324
3591	Al_{133}	3.56 ± 0.06				PES	324
3618	Al_{134}	3.55 ± 0.06				PES	324
3645	Al_{135}	3.55 ± 0.06				PES	324
3672	Al_{136}	3.60 ± 0.06				PES	324
3679	Tl_{18}	$2.1^{+0.2}_{-0.3}$				PES	538
3699	Al_{137}	3.58 ± 0.06				PES	324
3726	Al_{138}	3.59 ± 0.06				PES	324
3753	Al_{139}	3.58 ± 0.06				PES	324
3780	Al_{140}	3.56 ± 0.06				PES	324
3807	Al_{141}	3.58 ± 0.06				PES	324
3834	Al_{142}	3.60 ± 0.06				PES	324
3861	Al_{143}	3.61 ± 0.06				PES	324
3883	Tl_{19}	$2.15^{+0.25}_{-0.25}$				PES	538
3888	Al_{144}	3.61 ± 0.06				PES	324
3915	Al_{145}	3.61 ± 0.06				PES	324
3942	Al_{146}	3.61 ± 0.06				PES	324
3969	Al_{147}	3.61 ± 0.06				PES	324
3996	Al_{148}	3.61 ± 0.06				PES	324

Chart 2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H2C
C
CH2
1
2
N
3
O
4
5
6
7
CH3
8
CH2
CH2
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CH2
CH2
9
CH2
CH3
C
C
CH2
CH2
10
O
11
O
O
12
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14
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NH
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21
•CH2
CH2•
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O
CH3
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24
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25
CH2
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26
CH2
F
27
CH2
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CH3
NH
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35
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Cℓ
36
F
COCH2•
37
COCH2•
F
38
O
39
O
40
41
COCH2•
C(CH3)3
42
43
O
44
CH3
Mn
OC
CO
CO
45
46
47

VIII. Supporting Information

Table 11 giving the same experimental EAs as listed in Table 10, but instead arranged in order of increasing EAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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