Gas Phase Stabilities of Small Anions: Theory and Experiment in Cooperation

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Contents

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I. Introduction

There have appeared a series of excellent reviews dealing with various aspects of anion chemistry during the last decade. Although most of these articles deal with experimental investigations on negatively charged systems, there are some profound presentations of the theoretical aspects. Gutsev and Boldyrev[1] have considered the metal halide anions, Simons and Jordan[2] have reviewed the ab initio approaches for anion structure analysis, and Simons and Gutowski[3] have presented a special survey on double Rydberg molecular anions. The most important contributions, dealing with the experimental aspects, are cited in short. Kebarle and Chowdhury[4] considered electron affinities with special emphasis

on electron-transfer reactions, Wetzel and Brauman[5] have given an overview on the photodetachment spectroscopy of trapped anions, Squires[6] reviewed the gas phase chemistry of transition-metal negative ions, and Jordan and Burrow[7] dealt with temporary anion states of hydrocarbon molecules. Compton[8] has concentrated on ion photoreactions, and Oster et al.[9] worked out the formation and decomposition of negative ions following low-energy electron capture using electron transmission spectroscopy. A collection of high quality calculations on negative ions has been given by Botschwina.[10] Ziegler[11] has reviewed the density functional method and its application to some negative ions. A very excellent review with a main thrust somewhat similar to the present, which covers the most important literature up to 1989, has been published by Bates.[12] Professor Compton has provided the references of two forthcoming reviews on atomic negative ions[13a] and multiply charged negative ions.[13b]

Since these publications cover a wide range of theoretical and experimental aspects of negative ion chemistry, the purpose of our review is to consider and collect paradigmatically most recent theoretical and experimental results on atomic and molecular anions and not to sample all available data. Special emphasis is also laid on bound excited molecular anion states and important aspects of doubly and higher negatively charged systems are discussed. Our selected topics are stable gas phase anions, and therefore, we mainly concentrate on adiabatic electron affinities, which are not the only but certainly the key quantities to judge the stabilities of free anions. Whenever possible we try to juxtapose theoretical and experimental information, which nicely demonstrates the sibling rivalry as well as the mutual stimulations of both research areas on each other.

This review is based on the literature until early 1994.

II. General Considerations on Atomic Anions

The periodic table of the elements (PT) can be considered as *the omphalic taxonomy*, which portrays the chemists' as well as the physicists' conceptual view of systematization of the atomic ground states. Although one can argue about the most appropriate representation, which depends on the hierarchy of aspects imposed on this classification scheme, the nowadays accepted form reflects various systematic changes across the periods and the columns of the PT. Ground state configurations, atomic (and many cationic) radii, and ionization potentials are examples of such more or less *smoothly* varying features, which allow one to infer characteristic trends through the system.

A glance at Figure 1, which shows the entries of the PT, loaded with the corresponding electron affinity values (EA) in numeric and graphical form, reveals, that there is no such clear periodic or systematic group pattern within the main group elements, as found for example for ionization potentials, even though there are several characteristic trends. Expectedly, those atoms with completely filled valence shells, such as the noble gases, exhibit no electron affinities. The group 2 elements can be

Figure 1. Periodic table which shows the electron affinities (in eV). The numbers above each column represent the group numbers. Each entry is also loaded with a black square the area of which is proportional to the corresponding EA value. (All data are taken from ref 20 except as follows: Ca, ref 60; Sr and Ba, ref 61.)

termed as "pseudo-noble", since they share the reluctance to electron attachment with the noble gas atoms, and therefore, the light members have no bound stable anion states. This homology can be attributed to the filled s-subshells and the completely filled shells in the group 2 and group 18 elements, respectively, which would force an additional electron to occupy an orbital of the next subshell in the former and even the next higher $(n+1)$ shell in the latter. Despite this general feature it is invalid to infer the corollary that these systems could not provide negatively charged states, since anions like He^-, Be^-, etc. are well known. One has to remember, however, that all these corresond to excited metastable species with lifetimes of the order of milliseconds or as short as femtoseconds, as delineated in sections III.B and III.C. On account of their ns^2np^5 ground state configurations the halogen atoms (group 17) exhibit the largest electron-binding propensities, since they need only one more electron to complete their valence shells. The corresponding EA's decrease monotonically from Cl to At, although this decrease is not very pronounced. A parallel trend exists for group 16, where the EA values are also rather large and decrease from S to Po. A maximum in the electron attachment capability with respect to their adjacent neighbors is seen in group 14, and a rationale for this can be found in the ns^2np^2 ground state configurations of the neutral atoms, which adopt the favored ns^2np^3 ($^4S^o$) configurations in their corresponding anions.

In agreement with these group trends there are characteristic periodic variations in the EA values, which increase according to (group 2) < (group 13) < (group 14) and in an analogous fashion (group 15) < (group 16) < (group 17). The elements of the first period are exceptional with respect to the binding of an excess electron, since, apart from the alkaline metals, all these first entry atoms exhibit smaller EA's than their next heavier congeners. This special behavior is often attributed to the small spatial dimensions of the first row elements, which is a significant drawback for anion formation on account of a more severe Coulomb repulsion. This may also be the reason that the N atom is a white spot within Figure 1, since its atomic radius is as small as for O and the excess electron has to enter an already occupied 2p orbital. The EA of P also corroborates that the ground state configuration of the small group 15 elements is infavorable for electron attachment.

While in most main groups a top-down (starting from period 2) decrease in the EA's is observed, a different trend becomes apparent within the group 11 elements (similar to group 15), where the electron attachment energy increases down the column and thus the gold atom does not only have the largest EA within this group but it exhibits the largest electron affinity of all non-main group elements within the PT. A rationale for this unexpected feature can be derived from the study of relativistic effects on the electronic structure and will be discussed in more detail in section III.D.

Among all known atomic anions there are only very few like C^- or Si^- which have excited states. The ^2D_u state of C^- exhibits a binding energy of 0.025 eV. The corresponding value for Si^- is 0.53 eV and even the ^2P_u state is stable by 0.03 eV, but it is obvious that these excited anion states are rather loosely bound. It is characteristic that the few known atomic anion states all correspond to higher multiplet components of the respective ground state configurations. It can be stated quite generally that, apart from metastable or resonance states (for a very short discussion on resonances see section VIII.B), bound excited atomic anion states can be expected solely for those belonging to the anion ground state multiplet. The potential function of the atomic anion decays too rapidly with increasing distance from the nucleus as to allow the binding of an electron in higher excited configurations.

III. Some Interesting Atomic Anions

A. H⁻

The hydrogen atom is the only atomic system whose electron affinity is more precisely known theoretically than experimentally. It is the smallest and most simple negative ion and served as target for many theoretical studies. It has a $^1S^e$ bound state and, since the electron−electron repulsion and the electron−nucleus attraction of the additional electron are of comparable magnitude, highly correlated wavefunctions are necessary for a proper description. Pekeris[14] has performed a Hylleraas-type variational calculation and arrived at an EA value of 6083.04 ± 0.01 cm⁻¹. This result is 0.05 cm⁻¹ lower than that reported by Aashamar,[15] who evaluated the EA using

Hylleraas−Scherr−Knight variational perturbation wave functions including relativistic corrections. There has been a series of experimental studies on the binding energy of H⁻ starting as early as 1953. Feldman[16] derived 6081 ± 16 cm⁻¹ from photodetachment threshold studies, whereas McCulloh and Walker[17] arrived via a thermochemical cycle at a lower bound on the EA which turns out to be virtually the same. Chupka et al.[18] succeeded in improving the accuracy and obtained 6083 (+11,−3) cm⁻¹, while Scherk[19] determined 6085.5 ± 3.3 cm⁻¹ from H⁻ decay rates in an electric field. The reason for the rather significant deviations of the experimental results in the range of some centimeter⁻¹ is 2-fold. On the one hand in a H⁻ photodetachment an s electron escapes as a p wave, which has a zero slope in the cross section at threshold and makes precise measurements very difficult, on the other hand the hydrogen hyperfine structure yields two detachment thresholds within 0.05 cm⁻¹. On the basis of previous results[20,21] Lineberger and co-workers[22] recently attempted a high precision threshold−photodetachment analysis and determined electron affinities of 6082.99 and 6086.2 cm⁻¹ for H and D, which are accurate to 0.15 and 0.6 cm⁻¹, respectively. This value for H⁻ is in excellent agreement with the 6083.04 cm⁻¹ predicted by Pekeris.

A second bound state with even parity, $(2p)^2\ ^3P^e$, is believed to exist, and it ought to exhibit a very small EA of 9.5 meV with respect to the H (2p) threshold.[23] The series of shape resonances in the H⁻ continuum, due to the long-range dipole interaction, represent doubly or higher excited hydride ion states, which have been extensively studied.[24]

B. Noble Gas Anions

Sixteen years after the first mass spectroscopic detection of the He anion by Von Hiby,[25] Holøien and Midtdal[26] presented a plausible explanation for the rather long lifetime of He⁻. They argued that the $^4P^o_{5/2}$ state of the $(1s2s2p)\ ^4P^o$ multiplet is stable against autoionization to $(1s2s)\ ^4S$ He* and calculated a relative stability of 0.075 eV. This result is in complete conformity with the experimentally derived 0.080 eV by Brehm et al.[27] and the 0.0774 eV calculated by Bunge and Bunge.[28] Several experimental groups[29−31] conjectured that long-lived ^2P states of this anion might exist too. A very careful theoretical analysis of Nicolaides et al.[32] on bound states and decay mechanisms in He⁻ revealed that the only bound states of this system, $^4P^o$ and $^4S^o$, are 19.74 and 59.33 eV above the He ^1S ground state, respectively, and thus 0.0774 and 0.33 eV below the $(1s2s)\ ^3S$ and $(2p)^2\ ^3P$ excited states of the neutral atom. Both anion states can detach to the adjacent continuum on account of spin-dependent forces, but there are further decay mechanisms such as non-relativistic radiative autodetachment for $^4S^o$ and relativistic radiative autodetachment for $^4P^o$. Brage and Froese Fischer[33] performed a reanalysis of He⁻ bound states and predict lifetimes of 405, 11.8, and 10.7 μs for the $^5/_2$, $^3/_2$, and $^1/_2$ $^4P^o$ components, respectively, which are in good agreement with the corresponding experimental data.[34] It is interesting to note that the very long lifetime of the $J = ^5/_2$He⁻ state cannot be attributed to the fact that it decays

through two-body relativistic effects, since these interactions are larger in this system than the one-body effects, but is due to the weak interaction with the continuum, which corresponds to high-l quantum numbers.

A compendium of various Wannier resonances for He$^-$ and H$^-$ can be found in the review of Bates.[12]

Much less is known about the negative ion states of the heavier rare gas atoms. While no bound state is known for Ne$^-$, Bunge et al.[35] calculated a stability of 0.135 eV for ^{4}S^e Ar$^-$ with respect to the ^{3}P^o excited state of Ar. Bae et al.[36] observed the Ar$^-$ ion in the gas phase and determined a lifetime of 260 ± 25 ns. They could, however, not obtain any signals for Kr$^-$ and Xe$^-$, whence they concluded that these anions either do not form or are very short lived (≤50 ns). In contrast to these assumptions, Haberland et al.[37] succeeded in identifying Xe$^-$ in their negative ion mass spectra and deduced an unusually long lifetime ≥10^{-4} s. This peculiarity raised the question whether Xe$^-$ might have attached the extra electron in the ground state rather than in a metastable state. Guo et al.[38] performed a local-spin-density-functional study on a series of atomic anions, and they report stable ground state anions $ns^2np^6(n+1)s^1$ for all members of group 18. This is quite surprising, since all experimental evidence rules out ground state binding for angular momentum $l = 0$ in Xe$^-$, although bound states for $l > 1$, where the electron is temporarily captured by an angular momentum barrier, would not be at variance with the experiment. Prompted by this controversy, Nicolaides and Aspromallis[39] reanalyzed the attachment of an electron to He and Xe, and they are convinced on account of their results that ground state binding does not occur for any angular momentum $0 \leq l \leq 3$. Thus the electronic structure of Xe$^-$ is still an open question.

C. Alkaline Earth Metals

Since the ground states of the neutral atoms have a "closed shell structure" of the form ns^2, in close analogy to the noble gas atoms, it has been believed until very recently,[20] that none of these atoms would actually bind an extra electron in its ground state.

However, metastable states of Be$^-$, in analogy to He$^-$, have been known for rather a long time. Weiss[40] used superposition techniques with an analytic basis to study alkali and alkali earth metal anions and was in fact the first who predicted a positive electron affinity for the triplet excited (2s2p) ^{3}P state of Be and postulated the existence of a metastable (2s2p^2) ^{4}P^e state of Be$^-$. Beck et al.[41] studied the three state system (^{4}P^e, ^{4}S^o, and ^{6}S^o) of Be$^-$, and Bae and Peterson[42] and Kvale et al.[43] succeeded to observe the metastable Be$^-$ ion. Bunge et al.[44] investigated bound negative ion states for various atoms and they confirmed that Be$^-$ is unstable. Moreover they worked out that the ^{4}P states are imbedded in the 2s^2kl ^{2}D and ^{2}S continua and may autoionize via spin−orbit interactions with the 2s2p^2 ^{2}D and ^{2}S states. In analogy to He$^-$ the long-lived component (>100 μs) was believed to be the ^{4}P$_{5/2}$ state, but Aspromallis et al.[45] could show theoretically that this component corresponds to ^{4}P$_{3/2}$, and Gaarsted and Andersen[46] were able to

observe the electric dipole transitions between the ^{4}P^e and the ^{4}S^o states. According to these theoretical as well as experimental findings the existence of a metastable Be$^-$ is beyond doubt. The most accurate experimental binding energy with respect to Be(^{3}P^o) is found as 261 ± 10 meV[47] and the lifetime is determined to 45 ± 5 μs.[48]

Although there are similar calculations and theoretical predictions[49,50] for the (3s3p^2) ^{4}P^e and (3p^3) ^{4}S^o states of Mg$^-$, the corresponding transitions could not yet be detected.[51] Froese Fischer[52] found out by MCSCF calculations that the (3s^{2}3p) ^{3}P "ground state" in Mg$^-$, is in fact unbound.

In the light of these findings for the Be$^-$ and Mg$^-$ anions, MCSCF investigations[52,53] on Ca$^-$ revealed the surprising result that this anion should have a bound (4s^{2}4p) ^{2}P ground state, and Pegg et al.[54] could verify experimentally the bound nature of this state. Froese Fischer[53] demonstrated that the Ca$^-$ ground state is very peculiar, since its stability is accounted for by electron correlation of 4s^2, especially by the unfilled 3d shell. These correlation contributions increase the polarizability of the 4s^2 electron pair and, thus, favor the attachment of the excess electron in the 4p orbital. Considering isoelectronic structures of Ca$^-$ and Sc, one could expect the (3d^{1}4s^2) ^{2}D state to be the ground state of the Ca$^-$ ion. It could be shown, however, that this electronic state is unbound.[53] The theoretically derived electron affinities for the Ca ground state are obtained as approximately 0.1 eV,[55−57] and are in fact very small. The most recent photodetachment[58] and electric field dissociation[59] experiments suggest a substantially smaller EA of 18.4 and 17.5 meV, respectively, corroborated by model potential calculations with B-spline basis sets, which yield 17.7 meV.[60] This development delineates the ordeal in assessing reliable EA's for these ns^2 atoms. Although further bound states cannot be ruled out completely, their existence is highly unlikely on theoretical grounds, and it would be extremely difficult to identify them experimentally among the various possible metastable states.

The heavier alkaline earth anions have not yet been detected in gas phase experiments but several theoretical investigations predict Sr$^-$ (5s^{2}5p) and Ba$^-$ (6s^{2}6p) to be bound: Gribakin et al.[61] by the Dyson equation, Vosko et al.[62] using the local density functional approach, Froese Fischer[53] employing the MCSCF method, and Johnson et al.[55] by means of the relativistic Dyson equation. All these theoretical studies agree that the stabilities of group 2 anions, where an electron is attached to a closed shell ns^2 atom, are governed by the atomic dipole polarizabilities α_d. Since these α_d values increase down the group as 170, 190, and 270 au for Ca, Sr, and Ba, respectively,[61] EA(Ca) < EA(Sr) < EA(Ba) is found in all investigations and is, therefore, undoubted. The actually calculated electron affinity values, however, differ significantly with respect to the different methodological approaches. Usage of the Dyson equation with the self-energy calculated to the second order provides 0.202 (Sr) and 0.220 eV (Ba). These computed values are certainly too high, since even the EA of Ca is overshot by a factor of 2, and a more refined treatment with third order corrections to the

self-energy leads to significantly smaller respective values of 0.129 and 0.144 eV.[61] There are, however, other factors, which can further diminish the binding strength.

Froese Fischer[53] performed a "valence-only" MC-SCF study on the Sr⁻ and Ba⁻ ions and found that these anions are stable by 0.128 and 0.277 eV, respectively. The relativistic shift (including mass–velocity, spin–spin contact, and Darwin terms) reduces the corresponding values by 0.022 and 0.129 eV, and thus corrected EA's of 0.106 (Sr) and 0.148 eV (Ba) are obtained. Despite the fact that these data given for the relativistic corrections conform to the expectation that they should increase with increasing nuclear charge, their actual significance is hard to estimate, since they have been evaluated without accounting for core polarization effects. It has been verified at least for the alkali anions that the relativistic corrections to the EA decrease upon inclusion of core polarization.[53]

Dzuba et al.[63] investigated the binding energies and the fine structure intervals ΔE_{fs} $np_{1/2}-np_{3/2}$ for the alkaline earth anions by relativistic many body perturbation theory. They calculate ΔE_{fs} values of 0.007, 0.022, and 0.057 eV for Ca⁻, Sr⁻, and Ba⁻, respectively, which indicates that the $p_{1/2}$ and $p_{3/2}$ components both are bound for these anions. The lifetimes of the metastable $np_{3/2}$ states, which decay by M1 transitions to the corresponding $np_{1/2}$ ground states, have been estimated as 635000 (Ca⁻), 19800 (Sr⁻), and 2700 s (Ba⁻). Due to these enormously high lifetimes of the metastable anion states it seems necessary to consider them in EA measurements.

The Ra atom is very special within the group 2 atoms, since its dipole polarizability is only 206 au, and consequently, the calculated EA value is only 0.148 eV. The corresponding ΔE_{fs}, however, amounts to 0.166 eV, which exceeds the ground state stability, so that the $7p_{3/2}$ level of Ra⁻ appears in the continuum.[63]

A recent core–valence MCSCF study by Sundholm and Olsen,[64] including relativistic effects, resulted in a "best theoretical" EA of 7.2 ± 5 meV for Ca, which is in favor of a "small" (18 meV) rather than the "large" (>43 meV) value. In the event that this small value should turn out to be correct for Ca, the binding energies calculated hitherto for Sr⁻ and Ba⁻ might be too large and should be reconsidered theoretically as well as measured in the gas phase.

D. Some Aspects of Transition Element Anions (Groups 3 and 11)

This paragraph is not intended to give a thorough discussion but should only sketch paradigmatically the most prominent features and trends. As can be seen from Figure 1, two-thirds of these atoms have electron affinities below 1 eV and quite often the EA's for the period 4 elements are either maximum or rather similar to those of the 5th period. Exceptions to this pattern are, however, groups 9–11, where the heaviest members have values that are at least 1 eV larger than those of their lighter congeners. None of the group 12 elements forms a stable anion for the fact that the $(n-1)d^{10}ns^2$ electronic structures of these systems are intimately related to the earth alkaline atoms, but their dipole polarizabilities are below 70

au, which is too small to allow for stationary negative ion states (compare section III.C). The complications arising in the theoretical treatment of transition metal EA's and difficulties in understanding the binding mechanisms will be paradigmatically demonstrated only for group 3 and group 11; the former exhibit very small, and the latter the largest electron affinities within this family.

At first we will turn our attention to the leftmost proponents, i.e. group 3. Until 1981 scandium and yttrium were believed to have EA's smaller than zero. Feigerle et al.[65] detected the Sc⁻ ground state and proposed the tentative assignment $(3d4s^24p)$ ^1D and ^3D, with the respective electron affinities of 0.189 and 0.042 eV. CI calculations done by Jeung[66] corroborated this assumption and yielded an EA value of 0.14 eV for the ^1D state, which is in favorable agreement with that observed experimentally for the lowest state. Froese Fischer et al.,[53] employing MCSCF methods, arrived at 0.152 eV, which is slightly better than Jeung's result, whereas their density functional approaches predict 0.452 and 0.193 eV for the ^1D and ^3D states of Sc⁻, respectively, and hence strongly overestimate the corresponding experimental data by factors of 2–5. There are, however, no high-quality calculations on Y and Y⁻, so no reliable theoretical EA values are available, although at least one bound negative ion state is expected. It has to be noted that on account of the $3d4s^24p$ and the $4d5s^25p$ ground state configurations of Sc⁻ and Y⁻, respectively, there are large state manifolds, i.e. 60 LS states, corresponding to $^3F^o$, $^1F^o$, $^3D^o$, $^1D^o$, $^3P^o$, and $^1P^o$, and not much is known about all these possible states, since only two of them, $^1D^o$ (ground state) and $^3D^o$, have been identified to date. Furthermore, it has to be stressed that the isoelectronic comparison Sc⁻ ↔ Ti or Y⁻ ↔ Zr does not furnish the electronic structures of the anions. Ti and Zr have even-parity ground states, and the lowest-lying odd-parity states originate from the $3d^2$-$4s4p$ and $4d^25s5p$ configurations, respectively, which is obviously disparate to the group 3 anions.

La⁻ is very special within group 3, since Vosko et al.[67] could show theoretically that not only the odd-parity $(5d6s^26p)$ but also the even-parity $(5d^26s^2)$ states should be stable.

The Dirac–Fock and density functional calculations of Vosko and Chevary[68] yielded the result that Lu⁻ is stable by some 0.19 ± 0.10 eV. The ground state corresponds to the odd-parity Xe $4f^{14}5d6s^26p$ rather than the even-parity Xe $4f^{14}5d^26s^2$ configuration, as expected from the isoelectronicity with Hf. Garwan[69] detected the Lu⁻ ion by accelerator mass spectrometry and determined its detachment energy as ≥0.1 eV, but the experimental verification of the ground state parity is not provided. Due to the electronic structure of Lu⁻ it is concluded that this anion is very similar to Sc⁻ and Y⁻. Since the neutral Lu⁰ atom has a $5d6s^2$ valence configuration, which conforms to the $(n-1)dns^2$ valence configurations of Sc($n=4$), Y($n=5$), and La($n=6$), it has been argued that Lu should be considered as a group 3 element rather than a lanthanide.[68]

Another important aspect is the highly electronegative systems, i.e. group 11. The lightest coinage metal anion, Cu⁻ has been studied in several theo-

retical investigations. Bauschlicher et al.[70] used very large Slater-type basis sets and obtained a nonrelativistic EA value of 1.06 eV, which is approximately 0.17 eV smaller than the experimental value. Marian[71] reinvestigated the EA of Cu and realized that the relativistic and the correlation contributions are not independent. The relativistic improvement of the EA amounts to 0.08 eV, and this effect is rationalized by the contraction of the 4s orbital. Since the differential correlation is mainly dominated by 4s–3d correlation effects, the anion, which has two electrons in the 4s orbital, gains more correlation energy when the valence s orbital gets spatially closer to the 3d shell than does the lonely 4s electron in Cu.

Apart from the halogen atoms, platinum and gold exhibit the largest electron affinities, and gold has the most pronounced propensity of all transition elements to attach an extra electron. This specifically high binding energy of 2.309 ± 0.005 eV[20] in Au⁻ cannot be explained when relativistic effects are ignored, since at the nonrelativistic level of theory silver and gold are found to have rather similar values of about 1.2 eV.[72] The peculiarity in several properties of gold can be attributed to the contraction of the 6s orbital due to the mass–velocity effect, which roots in the relativistic contraction of the 1s electrons. The rationale for this can be provided by the qualitative argument that the expectation value for the velocity of an 1s electron can be approximated as $\langle v \rangle \approx Z\alpha c$, leading to a relativistic electron mass which is some 22–25% larger than the rest mass and this difference is far from negligible. As a consequence of this increase in the electron mass the Bohr radius a_0 shrinks by the same amount and, for reasons of orthogonality, all higher s orbitals appear contracted with respect to their nonrelativistic counterparts. Concomitant to the s-shell stabilization the p-shell orbitals become spatially more extended and less stable, and this is the reason why the 6s–6p energy gap in Pt, Au, and Hg is significantly larger than the 5s–5p gap in the lighter homologues Pd, Ag, and Cd. In order to understand the outstanding EA of the gold atom, we have to consider its ground state configuration, which can be termed as Xe $4f^{14}5d^{10}6s^1$. As a consequence of the relativistic s-shell contraction discussed above, the 6s level is so stable that, according to Pyykkö and Desclaux,[73] "it feels good" if an extra electron closes this shell, or in other words, it is relativity which makes gold behave almost as a halogen. A quantification of the relativistic influence has been provided by a few high quality calculations[74,75] which reveal that the relativistic EA of the gold atom exceeds its nonrelativistic value by about 1 eV. From this theoretical finding the authors conclude that relativistic as well as correlation effects have to be accounted for, if the theoretic binding energies should not be too far away from the experiment. The finding that electron correlation has a vital influence on the calculated EA seems surprising at first, but appears rather plausible, since the relativistic contraction of the 6s electrons increases the valence–valence as well as the valence–core electron correlation.[74] These investigations clearly demonstrate that relativistic effects may, in some cases, also provoke drastic changes in the electron correlation contributions.

IV. Shapes and Sizes of Atomic Anions

The only theoretical concept to date that could be applied systematically to derive quantitative theoretical information on the spatial extension or radii of negatively charged systems has been the analysis of the electrostatic potential (ESP). At a point r it is defined as

$$V(r) = \sum_{A=1}^{N_A} Z_A/|r - R_A| - \int \mathrm{d}^3 r' \, \varrho(r')/|r - r'|$$

where N_A is the number of nuclei, Z_A the charge of nucleus A located at R_A, and $\varrho(r')$ denoted the electron density. Weinstein et al.[76] realized for the first time that the ESP of spherically symmetric systems (i.e. atoms; $N_A = 1$) are completely devoid of maxima due to the Poisson equation

$$V''(r) + \frac{2}{r} V'(r) = 4\pi \varrho(r)$$

The single and double primes symbolize the first and second derivatives with respect to r. The necessary and sufficient conditions for $V(r)$ to be a maximum are $V'(r) = 0$ and $V''(r) < 0$, which cannot occur, however, since $\varrho(r) > 0$ holds for any arbitrary r and thus maxima in the ESP are strictly forbidden. Gadre and Pathak[77] generalized this theorem for molecular electrostatic potentials (MESP), which were also found to lack any maxima, but minima and saddle points may provoke a rich topographical structure.

For the atomic anions Sen and Politzer[78,79] succeeded in deriving physically meaningful ionic radii defined by r_m, the position where $V(r)$ takes a minimum. r_m has a special significance, since for a nucleus with charge Z, we obtain the relation

$$4\pi \int_0^{r_m} r'^2 \varrho(r') \, \mathrm{d}r' = Z$$

and, for the reason that such an anion carries $Z + 1$ electrons, we necessarily have the condition that

$$4\pi \int_{r_m}^{\infty} r'^2 \varrho(r') \, \mathrm{d}r' = 1$$

Alternatively we can state that the anion radii defined by r_m treat all negatively charged atoms on an equal footing by the fact that there are Z electrons within the sphere of radius r_m. Table 1 contains the theoretical and experimental anion radii as given in ref 78. Since $\varrho(r)$ is a monotonically decreasing function of r, Prasad and Sen[80] exploited this property to prove that r_m is bounded from above in terms of the square root of the expectation value $\langle r^2 \rangle$. In particular they worked out the inequality

$$r_m \leq \frac{2}{3}\sqrt{\langle r^2 \rangle}$$

and the examples shown in Table 1 confirm that this bound is rigorously valid for all atomic anions investigated.

V. Accurate EA's from Ab Initio Methods

A. Connecting Theory and Experiment

While the electron affinities for atoms pose no serious principal problems, there are different data

Table 1. Comparison of Theoretical (r_m^{calc}) and Experimental (r_m^{exp}) "Radii" and the Radial Expectation Values $\langle r^2 \rangle^{1/2}$ for Some Atomic Anions[a] (Adapted from Ref 78)

ion	r_m^{calc}	r_m^{exp}	$\frac{2}{3}\langle r^2 \rangle^{1/2}$
H⁻	1.11		1.45
Na⁻	2.69	2.77[b]	3.23
K⁻	3.19	3.30[b]	3.92
Rb⁻	3.33	3.27[b]	4.22
Cs⁻	3.53	3.60[b]	4.72
F⁻	1.08	1.15[c]	1.42
Cl⁻	1.63	1.67[c]	2.21
Br⁻	1.79	1.82[c]	2.59
I⁻	2.05	2.06[c]	3.13
Al⁻	2.45		3.11
Si⁻	2.09		2.66
P⁻	1.94		2.50
S⁻	1.76		2.33

[a] All data in Å. [b] Huang, R. W.; Wang, D. L.; Dye, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 5707. [c] Shannon, R. D. *Acta Cryst. Sec. A* **1976**, *32*, 751.

for molecular systems, which may be employed to characterize their stabilities or to be compared to experimental values. We use the abbreviations r_e and $\bar{r}_e$ for the optimized geometries for the neutral molecule and the anion, respectively, and $E_0(x)$ and $E_-(y)$ for their corresponding energies at the geometries x and y. Then we have

$$\text{EA} = E_0(r_e) - E_-(\bar{r}_e)$$

$$\text{VAE} = E_0(r_e) - E_-(r_e)$$

$$\text{VDE} = E_0(\bar{r}_e) - E_-(\bar{r}_e) = \text{VIP}$$

EA denotes the adiabatic electron affinity, VAE the vertical attachment energy of the neutral ground state, and VDE is the vertical detachment energy, which is often also denoted as VIP, the vertical ionization potential of the anion. VDE and VIP will be used synonymously in our paper, which is frequently used in the literature for anions, due to the fact that no confusion can occur in this respect. Since EA is computed as energy difference of two minima, it has no significance unless the neutral and the anion species both are stable. The VAE and VDE quantities can only be defined in the case of a stable neutral and a stable negatively charged species, respectively. Both yield information on the energetic separations of the potential energy surfaces (PES) for the neutral and the anion electronic states. In the event that the three energies are well defined, |EA − VAE| and |EA − VDE| (which can also be written as |EA − VIP| in our notation) provide insight in the potential energy surfaces of the anion and the neutral species, respectively, and both yield measures for the geometry changes, which are often denoted as "adiabatic corrections".

For photodetachment experiments VIP is the most readily accessible value, provided the detached species is not highly unstable. When the adiabatic corrections are small it is frequently possible to observe the T_{00} transitions $M(\nu=0) \leftarrow M^-(\nu=0)$, and in this case the EA value can be directly derived from the spectrum. Otherwise, there are bands with long vibrational progressions and the T_{00} transition may be missing for the reason of vanishingly small Franck−Condon factors.

B. Methodological Approaches

The ab initio determination of electron affinities to within *chemical accuracy* (i.e. accurate to ∼0.04 eV or less) has remained a very difficult task and, therefore, most attempts on highly precise theoretical values have focused on light atoms or a few diatomic molecules. Especially some members of the second period of the PT such as C, O, and F, have been chosen very frequently to study the abilities of the different levels of theoretical sophistication.

The theoretical approaches with a broad use comprise single configuration SCF or Hartree−Fock (HF), and various post-SCF methods such as Møller−Plesset perturbation theory of different orders (MP2, MP3, MP4), multiconfiguration SCF (MCSCF), multireference singles−doubles CI (MRCI), and various coupled cluster (CC) approaches. The post-SCF methods are designed to calculate the electron correlation contribution to the total energy, at least for the "chemically relevant" electrons, which is by definition neglected in the Hartree−Fock ansatz. The MP-n methods, which start with a single reference configuration, are widely used but unfortunately the results converge only slowly with increasing order n of the perturbation expansion. Due to the rather limited number of configurations used to span the wave function, the MCSCF methods can in general only account for a small portion of the correlation energy, which is commonly denoted as static or nondynamical correlation. The remaining dynamical correlation contributions can subsequently be computed from a single reference or multireference wave function via CI or CC methods. The variationally optimized CI wave functions normally comprise all single and double substitutions with respect to the reference wave function. Correlation energy contributions of higher order (especially quadruple) substitutions can be approximated by $E_Q = (1 - w)|E_{ref} - E_{MRCI}|$, where w denotes the weight of the reference function in the MRCI expansion, and the such obtained result is termed by MRCI+Q. These theoretical approaches allow one to account for a large portion of the correlation energy. All methods cited above determine the total energy of a specific electronic state for a given geometry, and hence, the electron affinities are obtained indirectly by taking the energy difference from two independent calculations on the neutral and the negatively charged system. The calculated EA's are, however, not only governed by the methodology employed but depend also crucially on the basis sets used. The electron densities of anions are in general much more diffuse than in the neutral molecules, and quite elaborate basis sets, including spatially extended basis functions as well as functions corresponding to large l quantum numbers, together with highly sophisticated computational procedures have to be employed, in order to assess a good estimate of the charged-neutral differential correlation energy. This is by no means trivial, since the correlation effects often strongly exceed the EA values, so that small errors in the differential correlation contributions can cause large percentage errors in the electron affinities. A further drawback lies in the molecular orbital (MO) basis, which is mostly determined at a theoretical level which incorporates either no or only a small

Table 2. Electron Affinities EA (w) (in eV) Calculated with the Weights w of the Reference Space in the MRCI and MRCI+Q Approaches (Adapted from Ref 88)

atom	weight (w)	MRCI	MRCI+Q	exp[b]	error (%)
B	0.9721	0.278	0.273	0.280	2.5
C	0.9808	1.267	1.264	1.268	0.3
O	0.9839	1.453	1.454	1.462	0.5
F	0.9835	3.363	3.363	3.399	1.1

[a] Deviations between experimental and MRCI+Q estimates are given in %. [b] Reference 20.

portion of electron correlation (normally SCF, MC-SCF at best). Consequently, the associated MO's (especially from SCF calculations) are too diffuse and the corresponding low-level EA values are often negative. These shortcomings in the orbital bases, which are used in constructing the reference wave-functions, may be a nuisance in calculating correlation energies.

Sasaki and Yoshimine[81] were the first to use a very large Slater-type basis (10s9p8d8f6g4h2i), which can be considered to be of high quality, but their rather limited configuration space (CI) prevented the calculated EA values for C, O, and F to come in better than 0.5 eV agreement with the experimental data. Even the inclusion of selected triple and quadruple substitutions rendered only a marginal improvement, so that the calculated EA values remained 0.15–0.34 eV too small. Botch and Dunning[82] increased the reference space for the C atom by including the $2p^2 \rightarrow 3p^2$ excitations and taking into account all single and double substitutions with respect to these reference wave functions (MRCI). Notwithstanding the fact that they employed a much smaller contracted (4s4p3d) Gaussian-type basis set, the accuracy of their calculations is comparable to that of ref 81. Feller and Davidson[83] used a (8s5p4d2f1g) contracted Gaussian basis and large MCSCF reference wave functions to estimate the contributions of the triple and quadruple excitations to the differential correlation energy and arrived at 1.22 and 1.29 eV for carbon and oxygen, respectively. The authors extended these calculations[84] by employing even larger basis sets and adopting a 0.05 eV correction, which they estimated as the deficiency for fully exploiting their configuration space, they obtained 1.36 eV for the oxygen atom. Bauschlicher et al.[85,86] investigated the O^- and F^- systems and concluded, in conformity with other groups, that the calculated electron affinities can be obtained to chemical accuracy only if the differential correlation energies are recovered to a very high degree. Noro and Yoshimine[87] proposed a selected reference MRCI procedure using curves of energy versus weight w of reference configurations in the CI wave function to determine the lowest necessary level of electron correlation needed to arrive at reliable EA's and to establish error bars. This approach may, however, be very time consuming, since various energies for different weights must be evaluated to be sure that the actual result is close to the extrapolated one. They applied this approach, using a (13s11p6d5f5g5h) contracted Gaussian basis set to demonstrate that the EAs of B, C, O, and F can be evaluated to within an error of 0.04 eV.[88] Table 2, which is adapted from ref 88, compiles their results on these four atoms. The weights w of the

references in the CI wavefunctions exceed 98% for C, O, and F and pinpoint the high quality of these calculations. The fact that the MRCI and MRCI+Q values hardly differ is a strong indicator that the corresponding EA(w) are *cum grano salis* constant already for these weights, since both entries must become equal for $w = 1.0$, which corresponds to the full CI electron affinity. The most important additional components in the reference wave functions are the $2p^2 \rightarrow 3p^2$ configurations and the $2s^2 \rightarrow 2p^2$ "near degeneracy" excitations in boron and carbon, and the $2s \rightarrow 3d$ excitations in oxygen and fluorine. Reference 88 represents a very careful analysis of the differential correlation contributions to the EA values and their data are within 0.01 eV of the full CI limit for the (large) chosen basis set. The invested computational effort, however, clearly demonstrates that this high level of accuracy is an extremely demanding task already for relatively small atoms. Such precision for calculated electron affinities is far from routine and cannot be attained for heavier atoms and even less for molecules.

The basis set problem has been relieved a little bit by the advent of the atomic natural orbital (ANO) contraction scheme.[89] The contraction coefficients for these ANO basis functions are selected as to diagonalize the first order density matrix of the corresponding atomic CI or MRCI wave function. Despite the high degree of contraction and their reduced sizes, the results are hardly degraded with respect to the completely uncontracted primitive basis set. Due to the reduced basis set dimension a higher level of electron correlation can be achieved more easily, which is especially advantageous for EA calculation.

Kendall et al.[90] made a very careful revisitation of the electron affinities of B, C, O, and F. They employed correlation-consistent basis sets according to Dunning,[91] successively augmented by diffuse sp sets and polarization functions up to $l = 4$. The correlation energies were evaluated at the MRCI+Q level of theory, using large MCSCF wave functions of increasing complexity, the best of which afford total energies rather close to the corresponding full CI values. With this systematic procedure they arrive at EA's, which are in fact of the same quality as those of Noro et al.,[88] although, on account of the generally contracted basis sets used, these more recent results have been obtained with significantly reduced computational effort.

The group of Roos[92] has performed a very systematic study on the EA of O_2 using elaborate ANO basis sets up to (7s6p3d2f2g), which have been devised to yield highest possible correlation energy for a given size. The dynamical correlation energy was obtained by a sequence of MRCI+Q calculations with an increasing number of reference configurations. According to the suggestions of Noro and Yoshimine[87] the reference configurations were selected in the manner that their corresponding weights in the MRCI wave functions of the neutral and the anion were highly comparable. Their best EA estimate is 0.39 eV, which is still 0.06 eV off from the best experimental value of 0.451 eV.[93]

An earlier attempt on the EA of fluorine has been made by Adamowicz and Bartlett[94] using numerical orbitals within the framework of many-body pertur-

bation theory (MBPT) as well as coupled cluster (CC) theory. Although an MBPT result is found 0.2 eV in excess of the experimental EA, their most sophisticated CC result is 3.373 eV, in close agreement with the recommended value of 3.399 eV. Scuseria[95] used a slightly different CC variant to arrive at an F^- stability of 3.36 eV. Strout and Scuseria[96] employed a (23s26p10d5f3g) Gaussian basis set and the CC approach to evaluate an EA of 1.415 eV for the O atom. They argue that at most 0.02 eV of the remaining deviation (0.04 eV) is due to errors in the differential correlation energy, whereas the lack in higher angular momentum basis functions is more severe.

Hughes and Kaldor[97] employed the Fock space-coupled cluster theory with single and double excitations for the evaluation of electron affinities. They considered valence and core correlations as well as relativistic effects and find an average error of 0.04 eV in the EA values of F, Cl, Br, and I, which can be qualified as highly accurate. It is worth noting that the inclusion of triple substitutions deteriorates the results. This seems to be a special feature for Fock space-coupled cluster theory, since no peculiarities with triple substitutions have been observed with conventional coupled clusters approaches.

Sundholm and Olsen[98] performed a high precision study on the electron affinity of B, using a finite-element MCSCF approach, which allows very long CI expansions. On account of the numeric approach, the basis set truncation error is negligibly small and the main computational problem reduces to the calculation of the differential correlation energy. For this purpose they studied the convergence of the EA with the increasing sizes of the active spaces and their highest level result yields 0.2678 eV. The relativistic contributions are very small, as expected for first row elements, and reduce this value by 1 meV, so that they arrive at a final EA of 0.2668 eV. The deviation from the 0.277 eV given by Hotop and Lineberger[20] amounts to only 30% of the experimental error bar whence the authors conclude that the remaining disagreement is due to experimental uncertainties.

A way to circumvent the basis set as well as the correlation energy problem can be found by using the quantum Monte Carlo (QMC) method for EA calculations. Urban et al.[99] collected QMC electron affinities from the recent literature and compared them with their own values obtained from basis set techniques. Despite several practical problems especially for atoms with higher nuclear charges, they could compute very accurate electron affinities for various atoms of the first and second period. Their juxtaposition reveals that the QMC EAs are mostly even better than the corresponding coupled cluster CCSD-(T) values. In a few cases like C and F, however, the QMC results are found to overshoot the experimental data a little bit.

The basis set problem could in principle also be circumvented in a certain way by using the momentum space[100] instead of the conventional position space for describing the electronic wave function. Both descriptions convey the same information, since they are connected via a Fourier transform, but emphasize quite different aspects. The basis set

problem for anions in position space results from the diffuse electrons with low kinetic energy, which need spatially highly extended basis functions. The momentum space representation especially accounts for the valence electronic structure,[101] since extended position space functions map unto regions close to the origin in momentum space. While this feature has principally no effect on exact wave functions, it can be employed for approximate approaches to obtain a better description of (extended) valence shell regions, such as in anions. The first computational approaches on Li^- and F^- seem very promising,[102] but much further experience is needed.

Alternative to the methods and results discussed above, EA's can also be obtained directly by using electron propagator theories, which all rely on the one particle Green's function.[103] By solving the Dyson equation for an N electron system, which is called the initial state, simultaneous solutions to the $(N-1)$ cation and $(N+1)$ anion final states can be obtained within the framework of perturbation theory. Consequently, two quantities for anions can in principle be calculated directly within this approach, namely VIP, when the anion is chosen as initial state, and VAE, when the neutral molecule is chosen as the reference system. The traditional implementations work well when the nondynamical correlation in the reference system plays only a minor role, and thus, a single configuration suffices as a reference wave function. Failures have to be envisaged, however, when this condition is not met. Golab and Yeager[104] proposed the multiconfiguration spin tensor electron propagator (MCSTEP) method, which is a more versatile solution to the one particle Green's function, based on an MCSCF initial state and explicit inclusion of angular momentum coupling methods for the spin. The MCSTEP ionization potentials for Li^-, Na^-, and K^- as calculated by Graham et al.[105] are among the most precise theoretical data for alkali anions hitherto. Yeager et al.[106] employed the same computational approach to calculate the EA of the C atom and obtain 1.2904 eV, which slightly overshoots the experimental value of 1.268 eV. This little failure could be attributable to a certain imbalance in their chosen basis set, but even a slight methodological bias cannot be excluded, since the MRCI and MRCI+Q data are 1.2213 and 1.2607 eV, respectively, calculated with the same basis set.

A further serious problem appears for molecular systems. Neutral molecules have in general more compact electronic wave functions than their corresponding negatively charged ions, the electron distributions of which are quite diffuse. The weakly occupied orbitals in the neutral ground state MCSCF wave function are spatially close to their strongly occupied counterparts, which they actually correlate, instead of being diffuse as needed for the anion wave function. In order to keep the calculations tractable and cost effective, the anion has to be taken as the initial state. Therefore, only vertical ionization potentials of the anion can be evaluated, and finally the MCSCF energy changes due to changes in geometry have to be applied as adiabatic corrections. Yeager et al.[107] treated OH^-, NH_2^-, BO^-, and CN^- in this way and arrived at adiabatic electron affinities of 1.867 and 0.69 eV for OH and NH_2, respectively,

compared to the corresponding experimental values of 1.83 and 0.78 eV. Less satisfactory values are obtained for BO (2.772 eV) and CN (4.126 eV), for which the experiments yield 3.1 and 3.82 eV, respectively. It might be criticized that this procedure frequently overshoots the correct EA's when the extra electron resides in a doubly occupied orbital. In this case the single electron in the neutral system remains in an orbital which might be more diffuse than optimum for the corresponding ground state, since the orbitals of the initial and the final state are of similar size. BO^- and CN^- both have a $^1\Sigma^+$ anion ground state, which upon ionization turns to the $^2\Sigma^+$ ground state of the neutral species.

Mosley and Pickup[108] studied electron attachment energies of first and second row homonuclear diatomics using the electron propagator method with moderately sized contracted basis sets. They find their results in good agreement with other ab initio studies, and furthermore, they provide an analysis of the orbital relaxation and correlation effects, which occur upon electron attachment to the neutral systems.

Although the cited examples in this section make clear that high accuracy in the EA's of very small systems can in principle be achieved when sophisticated theoretical approaches are employed, it is hard to imagine at present that such accurate results might also be obtained for molecules larger than diatomics, even if ANO basis sets are employed.

It seems appropriate to recall at this point that all truncated MRCI approaches have a drawback, which is commonly apostrophed as *size extensivity* or *size consistency* error,[109,110] which means that the electronic energy does not scale properly with the number of electrons. Especially, when a supersystem (molecule) is broken apart (two or more subsystems, each with much less electrons) D_e values and other calculated quantities may become insignificant. EA calculations, on the other hand, involve the comparison of an N and an $N+1$ electron system, which do not differ significantly in the "electronic sizes". This reasoning can, however, be misleading when the excess electron interacts strongly with just one or very few electrons, as might be expected for hydrogen-like atoms. The experience with actual calculations, as presented above, tells that the size extensivity error does not seem to be a severe problem, provided that proper CAS reference wave functions are employed for the respective singles and doubles CI procedures and Davidson-like corrections for the unlinked diagrams are applied,[111] as in the MRCI+Q approaches. Basis set deficiencies and other probably unconsidered errors (e.g. relativistic effects) may in many cases cause more severe errors than the lack of size extensivity. In order to be safe with respect to this error, it would be desirable to employ size-consistent theoretical tools (e.g. the CEPA method in all its variants or the versatile coupled cluster approach; for the performance of the latter compare the section above), but most of the existing implementations of these "methods of choice" for EA computations can handle only one reference configuration, and this can turn out as a drawback in some difficult cases.

In short we like to mention an alternative theoretical methodology, called the density functional theory (DFT) approach, which has mostly been employed in solid state physics, but has also become a versatile tool in molecular physics during the last years. There are several variants, local and nonlocal approaches, which have been excellently reviewed by Ziegler.[11] The most sophisticated DFT approaches, including electron correlation and nonlocal corrections, can often compete with other high quality ab initio methodologies. Computed EA's for CN, BO, NO_2, and some other molecules compare well with corresponding data from CI calculations with large basis sets.[11] The local spin density functional (LSD) approach was used to compute the EA's of many atoms of the periodic table and good agreement between calculated and experimental values is found.[38,112] Despite this success the positive ground state EA's, which are obtained for the noble gas atoms have to be considered as unphysical (compare section III.B) and, moreover, are at variance with all other high level ab initio methods. It is especially this fact which led Nicolaides and Aspromallis[39] to the conclusion that the LSD approach should be contemplated.

A very recent LSD study[113] on the dissociation energy of F_3^- yielded geometries and harmonic vibrational frequencies in good agreement with corresponding CI data, but the binding energies tend to be overestimated.

From the existing data the performance of the method with respect to EA's cannot yet be fully appreciated, but there is no doubt that further developments will make it a powerful tool in particular for polyatomic anions.

A final source of errors in calculated EA's, which has not been addressed yet, originate from relativistic effects. It is known, that these corrections will become more and more important with increasing nuclear charges of the involved atoms (compare sections III.C and III.D), but a general statement on their actual magnitudes is virtually impossible. One reason for this difficulty is the fact that relativistic effects are mostly estimated from the comparison of conventional SCF or higher level approximations to the corresponding relativistic spinor calculations. The impossibility of disentangling relativistic from correlation corrections further complicates the discussion of a global trend in relativistic effects on electron affinities (section III.D). Ilyabaev and Kaldor[114] used the same Gaussian spinor basis for their relativistic as well as nonrelativistic calculations, considering the electron correlation by the CC singles–doubles approximation. They obtain a relativistic contribution of 0.5 meV for the EA of Li and only 0.25 meV for the EA of Na, although the total relativistic energy changes amount to 0.023 eV for the former and 5.96 eV for the latter anion. The relativistic corrections to the nonrelativistic EA's of O and F are −7.7 meV and −0.029 eV, respectively. Notwithstanding the fact that their final EA of the F atom is 0.5 eV too small in comparison with experiment, so that especially in this case the reported relativistic contribution might be not very reliable with respect to a high precision result, these investigations indicate that such corrections cannot be ignored even for some first period elements, if one sets out for highly precise theoretical EA data.

Table 3. Experimental Electron Affinities (EA) of Homonuclear and Mixed Alkali Diatomics and the Coinage Metal Diatomics

dimer	EA (eV)^a	dimer	EA (eV)^a	dimer	EA (eV)^b
Na$_2$	0.430	NaK	0.465	Cu$_2$	0.836
K$_2$	0.497	KRb	0.486	Ag$_2$	1.938
Rb$_2$	0.498	KCs	0.471	Au$_2$	1.938
Cs$_2$	0.469				

^{a} Reference 117. ^{b} Reference 119.

VI. Molecular Anions

A. Diatomics

1. Anions of Groups 1 and 11 Elements

The alkali dimer molecules A$_2$ are in the valence shell isoelectronic with H$_2$ and can also be associated a bond order of 1. The bonding in the neutral and the negatively charged diatomics of the higher group 1 homologues are, however, quite different from that in the hydrogen molecule. While the anion H$_2^-$ is unstable with respect to H$_2$ and a free electron, theoretical investigations find considerable EA's of 0.46, 0.546, and 0.501 eV for Li$_2$, Na$_2$, and K$_2$, respectively.[115] The reason for the different bonding roots in the atomic polarizabilities, which are much larger for the metal atoms than for hydrogen. Due to this the A$_2^+$ cations exhibit comparable or even larger dissociation energy, (D_e), values than the neutral systems, contrary to H$_2$. Attaching an extra electron to the neutral diatomics leads to the $^2\Sigma_u^+$ ground states of the A$_2^-$ ions, and one would suppose that the HOMO is made up of the s valence orbitals and, therefore, antibonding in character. The analysis of Partridge and Bauschlicher[116] on Na$_2^-$ and K$_2^-$ revealed that the antibonding σ_u HOMO is largely polarized out of the bonding region and that the large stabilization, which is associated with this polarization, causes the dissociation energies of the anions to be very similar to those of the corresponding neutral dimers.

In order to account for this polarization effect, the authors point out that p and d polarization functions are of special importance in the valence region. Comparative calculations with and without such polarization basis functions clearly demonstrated that the EA and D$_e$ values decrease, whereas the equilibrium distances r_e significantly increase when unpolarized basis sets are used. The effect on D_e and r_e is, however, even more pronounced for the cations and the neutral than for the negatively charged systems.

The mixed alkali diatomics exhibit quite uniform EA values; they differ by only 0.02 eV and are mostly found between the values of the corresponding homonuclear molecules (Table 3). Despite these small EA differences it is rather easy to rationalize the general trend in terms of atomic polarizabilities. When α is taken as the polarizability of the highest electropositive element and r as the bond distance, a clear linear relation between EA and $α/r^2$ is obtained, which confirms the ionic character in the mixed diatomics.[117] This parallels the findings for alkali halide anions, where the excess electron is localized at the metal atom.[118]

The bonding situation in the coinage metal dimer Cu$_2$ and its anion is very similar to that just dis-

cussed for the homonuclear alkali diatomics. The 4s electron in the Cu atom is, however, more tightly bound than in an alkali metal and for this reason the polarizability of the copper atom is considerably smaller than for Na or K. Consequently, $Δr_e$ between Cu$_2$ and Cu$_2^-$ is much smaller than the corresponding values for the alkali dimers, while the D_e and the adiabatic EA turn out to be much larger.[116]

Photodetachment spectra for coinage metal negative ion clusters, including dimers, have been recorded by Ho et al.,[119] Leopold et al.,[120] Pettiette et al.,[121] Ganteför et al.,[122] Taylor et al.,[123] and Cha et al.[124]

Akin to Cu$_2^-$, the extra electron in Ag$_2^-$ resides in a σ_u^+ orbital, which is strongly polarized away from the central bond, as has been found by Zhang and Balasubramanian[125] in large-scale MRCI calculations. Bauschlicher et al.[126] used ANO basis sets in the MRCI approach in connection with a relativistic pseudopotential and obtained EAs of 0.75 (Ag$_2$) and 1.59 eV (Au$_2$), which are 0.28 and 0.41 eV smaller than the corresponding experimental values of 1.028 and 1.939 eV.[119] They prefer, however, to scale their theoretical data with a factor of 1.3, which has been determined from atomic data, and the such obtained EAs, 0.97 (Ag$_2$) and 2.06 eV (Au$_2$) are rather close to the experiment.

Very recently, Bonačić-Koutecký et al.[127] made a theoretical attempt on the structures and photodetachment spectra of silver cluster anions, employing large-scale CI methods for the valence electrons and describing the atomic cores (including 3d) with a relativistic one electron pseudopotential, which also accounts for core–valence correlation effects. EA of Ag$_2$ and VDE of Ag$_2^-$ are computed as 1.06 and 1.126 eV, respectively, in very good agreement with the experimental data.[119] There is, however, an intriguing fact that the optimized bond distances of Ag$_2$ (2.776 Å) and Ag$_2^-$ (2.780 Å) are very similar, in contrast to the Cu and also the Au dimers. This also contrasts the findings of Bauschlicher et al.,[126] who determined Ag$_2$ and Ag$_2^-$ to have bond lengths of 2.658 and 2.719 Å; they concede, however, that their estimates for the silver dimers are expected to have the largest errors.

Au$_2$ has the largest EA of the coinage metal diatomics, which is confirmed by experimental[119] as well as theoretical[126] investigations. The low photon flux photodetachment cross section studies on Au$_2^-$ reveal that, apart from the strongly bound ground state, there is also a resonance slightly above threshold.[122] The nature of this resonance is not yet clear but the tentative assignment is a $\sigma \rightarrow \sigma^*$ excited Feshbach resonant state, which decays via electronic autodetachment.

The theoretical study on the mixed group 11 diatomics[126] shows that the D_e values of neutral CuAg and AgAu and their anions are larger than for the corresponding homonuclear diatomics. This enhanced bonding is attributed to an ionic contribution arising from the large EA of the Au atom, and does not occur for CuAg, since the atomic EAs of Cu and Ag are similar. The binding of the excess electron in CuAu$^-$ is quite interesting, since the electron resides largely in the s orbital on Cu, since the Au atom withdraws a certain portion of charge from the

Table 4. Spectroscopic Constants^a for the $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$ States of MO$^-$ and the $^2\Sigma^+$ and $^2\Pi$ States of MO at the MRCI+Q Level^b (Reprinted from Ref 129. Copyright 1993 American Institute of Physics)

state	r_e (a_0)	w_e (cm^{-1})	T_e (cm^{-1})
LiO($^2\Pi$)	3.194 (3.190)	808 (813)	0
LiO($^2\Sigma^+$)	3.006	862	2496 (2516)
LiO$^-$($^3\Pi$)	3.300	698	−3211
LiO$^-$($^1\Pi$)	3.300	700	−3104
LiO$^-$($^1\Sigma^+$)	3.178	750	−2052
LiO$^-$($^3\Sigma^+$)	3.135	721	−516
NaO($^2\Pi$)	3.866 (3.877)	488 (492)	0
NaO($^2\Sigma^+$)	3.667	520	2061 (2018)
NaO$^-$($^3\Pi$)	4.011	409	−4217
NaO$^-$($^1\Pi$)	4.008	410	−4046
NaO$^-$($^1\Sigma^+$)	3.826	444	−3878
NaO$^-$($^3\Sigma^+$)	3.835	423	−2402
KO($^2\Pi$)	4.440	404	0
KO($^2\Sigma^+$)	4.147	446	−184
KO$^-$($^1\Sigma^+$)	4.302	365	−3847
KO$^-$($^3\Pi$)	4.595	330	−3455
KO$^-$($^3\Sigma^+$)	4.298	361	−3401

^{a} The spectroscopic constants are computed with a quadratic fit to $1/r$. ^{b} The experimental T_0 values have been converted to T_e values using the theoretical results for w_e. The experimental results [(a) Yamada, C.; Fujitake, M.; Hirota, E. E. *J. Chem. Phys.* **1989**, *90*, 3033. (b) Yamada, C.; Fujitake, M.; Hirota, E. E. *J. Chem. Phys.* **1989**, *91*, 137] are given in parentheses. The experimental T_0 values have been converted to T_e values using the theoretical results for w_e.

Table 5. Experimental Electron Affinities (EA) of Some Heavy Metal Diatomics

dimer	EA (eV)	dimer	EA (eV)
Fe$_2$	0.902^a	Sn$_2$	1.962^c
Co$_2$	1.110^a	SnPb	1.569^c
Ni$_2$	0.926^b	Pb$_2$	1.366^c
Pd$_2$	1.685^b	Sb$_2$	1.282^d
Pt$_2$	1.898^b	Bi$_2$	1.271^e (0.62)^f

^{a} Reference 131. ^{b} Reference 132. ^{c} Reference 133. ^{d} Reference 134. ^{e} Reference 135. ^{f} Reference 136.

Almost nothing is known about the closely related CuO$^-$ ion. The EA is determined as 1.777 eV from photodetachment spectra,[130] but it is unclear whether the ground state is $^1\Sigma^+$ or not, although isoelectronic considerations with ZnO suggest that this might be the case.

3. Some Heavy Metal Diatomics Anions

These species have been the subject of several recent experimental studies.[131–136] Although their electron affinity values are known experimentally from photodetachment spectra (see Table 5), not even the ground state symmetries of the anions can be assigned unambiguously in several cases. Especially those diatomics composed of atoms with d holes are notoriously difficult. The Ni atom has a 3d^{8}4s^2 ground state configuration and a plethora of closely spaced electronic states, ranging from $\sigma\sigma$ to $\delta\delta$, result upon dimerization, which renders enormous complications for the analysis of the anion. According to the experimental findings the Ni$_2^-$ ground state is characterized by $(3d^{18}\delta\delta)(4s\sigma_g^+)^2(4s\sigma_u^+)$, whereas $(4d^{19}\sigma_u^+)(5s\sigma_g^+)^2$ and $(5d^{18})(6s\sigma_g^+)^2(6s\sigma_u^+)$ pertain to the ground states of Pd$_2^-$ and Pt$_2^-$, respectively. These significant differences within the group 10 dimer anions result from their different corresponding atomic ground states. The Pd atom is quite unique, since it has a $(4d^{10})(5s^0)$ ground state configuration, which demands promotion of a 4d electron to 5s in at least one Pd atom to allow for covalent bonding in Pd$_2$, the ground state of which is X$^2\Sigma_u^+$. According to the $(4d^{19}\sigma_u^+)(5s\sigma_g^+)$ occupation scheme, Pd$_2$ is not expected to be strongly bound in its ground state ($D_0 \approx 1$ eV). In their photoelectron studies Ho et al.[137] find an EA of 1.687 ± 0.008 eV, which is quite large. On account of the $(5s\sigma_g^+)^2$ occupation in the $^2\Sigma_u^+$ ground state of Pd$_2^-$, the bond distance is shorter than in the neutral dimer and the D_0 is twice as high.

Fe$_2^-$ and Co$_2^-$ were expected to be very complicated, since ab initio CI calculations of Shim and Gingerich[138] predicted very high state densities of 112 for Fe$_2$ and 84 for Co$_2$ within an energy range of 0.5 eV above the corresponding ground states. Leopold and Lineberger[131] examined the low-lying electronic states of Fe$_2$ and Co$_2$ in the energy range of 1 eV above the ground states by negative ion photodetachment spectroscopy and obtained surprisingly simple spectra with only two transitions for each state. The spectral analysis reveals that electron detachment from Fe$_2^-$ and Co$_2^-$ does not induce significant changes in the bond lengths, which contradicts the assumption that the excess electron resides in an antibonding σ orbital. Since the theoretical studies

Cu atom in the neutral molecule. A more refined analysis exhibits that only 40% of the extra charge is located at the Au atoms.[126]

2. Alkali Oxides and a Related System (CuO)

As oxides of group 1 metals, all these molecules are highly ionic species, which can be envisaged as M$^+$O$^-$, a closed shell metal cation and an open shell O$^-$, where the single electron can occupy either a σ or a π orbital. This leads to a set of two low-lying electronic states, $^2\Pi$ and $^2\Sigma^+$, respectively. The ground states of LiO and NaO are $^2\Pi$, while in the higher analogs RbO and CsO the $^2\Sigma^+$ state is lower in energy. The KO molecule is in between both groups and thus very difficult, since the purported $^2\Sigma^+$ ground state and the $^2\Pi$ excited state are as close as 200 cm^{-1} in energy.[128] According to these neutral ground states, the lowest anion states can be $^3\Pi$, as for LiO$^-$ and NaO$^-$, or $^1\Sigma^+$ as for KO$^-$. The spectroscopic data as computed by Bauschlicher, Partridge, and Pettersson[129] are compiled in Table 4.

All these values were obtained at the MRCI+Q level of theory, using rather involved atomic natural orbitals (ANO) basis sets, including a core polarization potential, which proved to be important for the ordering of the electronic states. The anions are best considered as M^{0}O$^-$ species, but the $^1\Sigma^+$ states also contain some contributions from M$^+$O^{2-}. The $^3\Pi$ and $^3\Sigma^+$ states arise by adding the excess electron to the $^2\Pi$ or $^2\Sigma^+$ states of the neutral oxides, and the HOMO is polarized away from O$^-$ in order to minimize the Coulomb repulsion. On account of this electronic structure it is not unexpected that the r_e, w_e, and the energy differences between the lowest states of the neutrals and the anion states are rather similar. The properties of $^3\Pi$ and $^1\Pi$ are highly comparable, since they differ only in their spin couplings, which is rather small on account of the fact that the open shell orbitals are largely localized on either center.

Table 6. Adiabatic Electron Affinities (EA) of a Few Small the Neutral C_n Clusters and Vertical Detachment Energies (VDE) of C_n^- Clusters (All Data in eV)

cluster	EA_{exp}	EA_{theor}	VDE_{exp}	VDE_{theor}
C_3^-	2.00^a	2.02^b	1.95^c	$1.89,^b 1.81^d$
C_4^-		3.65^e	3.88^a	3.94^e
C_5^-	2.84^a		2.57^f	
C_6^-	4.18^g		4.10^c	4.08^h

^{a} Reference 148. ^{b} Fueno, H.; Ikuta, S. *Chem. Phys. Lett.* **1993**, *204*, 320. ^{c} Reference 142b. ^{d} Ortiz, J. V. *J. Chem. Phys.* **1992**, *97*, 7531. ^{e} Reference 144b. ^{f} Adamowicz, L. *Chem. Phys. Lett.* **1991**, *180*, 466. ^{g} Reference 149. ^{h} Reference 145.

show that the 3d shells are nonbonding and strongly localized at the atoms, it could be argued that the anion accomodates the surplus electron in such a nonbonding orbital. This assumption could explain the small geometric changes but would be in disagreement with the sparcity of states within the observed energetic range. Alternatively it could be reasoned that the 3d shells exhibit in fact a somewhat more bonding than localized character, as suggested by the theoretical calculations.

Apart from such inconsistencies between theory and experiment, which happen to occur for such complicated systems, reliable assignments can in most cases only be obtained using theoretical guidelines. A certain disparity between theory and experiment has to be accepted sometimes, since the calculated electron affinities are often significantly smaller than the measured values.[136] On the one hand this is due to basis set problems, on the other hand relativistic effects such as spin—orbit coupling and moreover electron correlation effects both have marked influences on the results.

B. A Few Small Clusters

1. C_n^- and Si_n^-

The carbon clusters have been reviewed by Weltner and van Zee[139] in 1989 and they have also considered some negatively charged systems. Therefore, we will give only a short sketch of present theoretical as well as experimental knowledge and progress. Until recently it was believed that only linear C_n^- species exist for $n \leq 10$. This belief was based on the fact that there are two significantly different EA progressions associated with the n-odd and n-even clusters, since the former have a closed shell $^1\Sigma_g^+$ ground state and the latter an open shell $^3\Sigma_g^-$ ground state. This causes smaller electron binding in n-odd (1.95 eV up to 3.70 eV for $n = 1, ..., 9$) than in clusters with even n (3.27 up to 4.42 eV for $n = 2, ..., 8$).[139-141] The most reliable data exist for the very small clusters and our *knowledge decreases exponentially with n*.[139] Some of the recent data on a few small C_n^- cluster ions are collected in Table 6. These data pertain to linear molecules, since the favored anions, as derived from photodetachment studies, always seem to corresponds to a linear nuclear arrangement.

Even for the simple C_2^-, there is no general consent on the "exact" electron affinity, since 3.3 or 3.37–3.408 eV are possible according to the experiments.[142] The most recent value of 3.269 ± 0.006 eV, which is somewhat smaller, has been measured by Ervin and Lineberger,[140] and it might be taken as the most

reliable EA presently available for the carbon dimer. Watts and Bartlett[143] employed the coupled cluster approach to investigate EA, vertical EA, and VDE for the carbon dimer. Since $(^2\Sigma_g^+)C_2^-$ is much better described by a single configuration than the $^1\Sigma_g^+$ state of the neutral molecule, the singles doubles (CCSD) results exhibit a bias toward the anion and consequently overshoot the experimental EA quite considerably by up to 0.28 eV, when an UHF reference wave function is used, and 0.26 eV in case of an RHF reference wave function.[143b] Inclusion of the triple excitations CCSD(T) reverts the bias somewhat to the neutral system and leads to a calculated EA of 3.198[143a] and 3.23 eV[143b] when a PVQZ+ basis set is employed. But even this last value differs by at least 0.04 eV from the experiment. These rather careful calculations demonstrate once again the cumbersome theoretical access to good EA's.

The larger n-even C_n^- species are expected to have π_g^3 or π_u^3 ground state configurations, and in fact theoretical studies predict $C_4^-(^2\Pi_g)$[144] and $C_6^-(^2\Pi_u)$[145] to be the lowest states. Calculations by Adamowicz[146] suggested that $^4\Sigma$ (with broken inversion symmetry) might be the ground state for C_8^-, but a more recent study by Watts and Bartlett,[147] who took care of the correct inversion symmetry, clearly revealed that the $^4\Sigma$ ground state as postulated by Adamowicz is wrong, and consequently, his calculated first EA is completely unphysical, since the $^4\Sigma_u^-$ and $^4\Sigma_g^-$ anion states, which would correspond to the symmetry broken solution for $^4\Sigma$, are 7.47 and 8.15 eV higher in energy than the $^2\Pi_g$ ground state. Their CCSD(T) VDE calculated with respect to the $^2\Pi_g$ state is 4.39 eV, and thus quite close to the experimental values of 4.38[142b] and 4.42 eV.[148] This seemingly very high computational precision could, however, be somewhat fortuitous, since single reference wave functions have been used for all electronic states, which might disturb the full $D_{\infty h}$ rotational symmetry and consequently yield a somewhat lower energy for $(^2\Pi_g)C_8^-$. On account of the CCSD(T) approach, which allows one to recover a large portion of the correlation energy, this error cannot be expected to be very serious. Imposing the correct inversion symmetry appears to be of utmost importance and shows that disregarding this requirement may lead to wrong "ground states" and unreasonably high EA's, as obtained in ref 146.

According to Watts and Bartlett[147] the general trends in the linear C_n^- ions can be summarized as follows: (1) The n-even systems have either π_g^3 or π_u^3 ground state configurations, yielding $C_4^-(^2\Pi_g)$, $C_6^-(^2\Pi_u)$, $C_8^-(^2\Pi_g)$, and $C_{10}^-(^2\Pi_u)$. (2) The n-odd anions exhibit either π_g^1 or π_u^1 occupation schemes, and this also leads to $^2\Pi_g$ or $^2\Pi_u$ ground states, such as in $C_3^-(^2\Pi_g)$ and $C_5^-(^2\Pi_u)$, but their properties should be very different from those of the n-even series.

The C_6^- cluster exhibits a very unique feature within this series, since the photodetachment spectra reveal the existence of an excited state[149] with a stability of 43 cm^{-1} and a geometry very similar to that of neutral C_6. Since the theoretical study on the vertical excited valence states[145] provides no hint for such a weakly bound electronic state near the ioniza-

Table 7. Calculated Vertical (VEA) and Adiabatic (EA) Electron Affinities and Experimental Data for Small Si_n Clusters^a (Adapted from Ref 164)

cluster	VEA^b	EA^b	exp^c
Si_3 C_{2v} $^1A_1$	1.824 ($^2A_1$)	2.166 (C_{2v} $^2A_1$)	2.0
Si_4 D_{2h} ^1A_g	1.870 ($^2B_{2g}$)	1.929 (D_{2h} $^2B_{2g}$)	1.8
	0.566 ($^2B_{3g}$)	1.515 (C_{2v} $^2B_2$)	
Si_5 D_{3h} $^1A_1'$	0.628 ($^2A_2''$)	2.293 (D_{2h} $^2A_2''$)	2.5
	1.321 ($^2E'$)	2.154 (C_{2v} $^2A_1$)	
Si_6 C_{2v} $^1A_1$	0.985 ($^2B_2$)	2.033 (D_{2h} $^2A_{2u}$)	1.8
Si_7 D_{5h} $^1A_1'$	1.303 ($^2A_2''$)	1.765 ($^2A_2''$)	1.7
Si_8 C_{2h} ^1A_g	1.817 (^2A_u)	2.438 (C_{3v} $^2A_2$)	2.3
	1.474 (^2B_u)	2.007 (C_{2h} ^2B_u)	
Si_9 C_s $^1A'$	2.309 ($^2A'$)	2.737 (C_s $^2A'$)	2.4
Si_{10} C_{3v} $^1A_1$	1.810 ($^2A_1$)	2.066 (C_{3v} $^2A_1$)	2.2

^{a} All Data are given in eV. ^{b} Reference 164. ^{c} Reference 154.

tion threshold, it is believed to be one of the very rare examples of a "dipole-induced" stable state. The stability criterion would be a sufficient polarizability of the π-electrons in the C_6 molecule, in order to stabilize an excess electron with very small kinetic energy. Further in-depth theoretical investigations are necessary to elucidate the nature of such electronic states.

Several theoretical investigations predict stable cyclic cluster anions,[144,150] especially for the n-even series. Although the cyclic C_n^- ions have significantly lower electron detachment energies than the corresponding linear structures, they should be stable enough to be experimentally accessible. The experimental evidence for nonlinear carbon cluster anions is, however, quite rare.[148,151] The reason that cyclic anions are reluctant to show up in photodetachment experiments has recently been attributed to the fact that not only the lower energy of the linear anions favors the linear structures, but the presence of various low-frequency vibrational modes, especially in the noncyclic clusters, consequently leads also to an entropic advantage of the linear over the cyclic anions.[152] Until now, only for C_4^- a nonlinear isomer could be unambiguously identified by Coulomb explosion imaging,[151] yielding an electron affinity of 2.1 eV. This finding is in good agreement with the theoretical values of 2.13 eV calculated by Watts et al.[144] and 2.17 eV as obtained by Ortiz[153] for the $^2B_{2g}$ state of a lozenge (D_{2h}) structure of C_4^-. Watts et al.[144] determined the cyclic anion the be 1.3 eV higher in energy than linear C_4^-.

The Si_n^- clusters (Table 7) differ significantly from the corresponding C_n^- species, since there is no evidence for linear structures. The experimental[154–156] as well the theoretical[157–164] investigations make sure that even the small cluster ions up to $n = 10$, even though they are often highly symmetric, represent 2- or 3-dimensional structures. The adiabatic as well as the vertical electron affinities of the Si_n clusters are significantly smaller than for the C_n systems, and there are no characteristic alterations with the cluster size. The measurements on the Si_n^- ($n = 3–10$) ions showed[154] that all EA's are between 1.7 (Si_7^-) and 2.5 eV (Si_5^-). Thus there are no dramatic changes as a function of n, as may be seen in Table 7, which compiles the experimental EA's together with the theoretical data, calculated by von Niessen and Zakrzewski[164] using rather large atomic natural orbital (ANO) basis sets and employing the Green's

function approach. Bearing in mind the substantial number of valence electrons for the larger systems, these calculated data can be considered to be in good agreement with the measurements. Several Si_n^- clusters such as Si_4^-($^2B_{2g}$), both states of Si_5^-, and the lowest lying states of Si_6^-, Si_7^-, and Si_8^-, exhibit enormous adiabatic changes (up to a factor of 4 with respect to VEA and EA) upon electron attachment, which has been extensively studied by Raghavachari and McMichael Rohlfing.[157]

Despite the rather modest EA's of some 2 eV for the various Si_n clusters most of them have one or several bound excited anion states. It is found[164] that Si_3 (C_{2v}), Si_4 (D_{2d}), Si_5 (D_{3h}), Si_6 (C_{2v}), Si_7 (D_{5h}), Si_8 (C_{2h}), Si_9 (C_s), and Si_{10} (C_{3v}), have three, four, two, three, two, five, four, and two stable vertical electron affinity states, respectively, apart from their corresponding ground states.

2. Various Cluster Anions

On account of the vast abundance of literature on huge varieties of different clusters, which prevents any in-depth presentation, we just allude to the most recent reviews and articles, which cover many aspects of cluster anions too. In these studies many problems connected with cluster size effects, excess electron states such as charge localization and surface states, electron attachment to and solvated electrons in clusters, and many other aspects, associated with polar or unpolar cluster constituents, are broadly surveyed experimentally as well as theoretically.[165] These studies cover results on small- to medium-sized negatively charged clusters of He, Ar, noble metals, alkaline metals, O_2, NaCl, H_2O, NH_3, and various other polar and unpolar molecules, and moreover a broad spectrum of mixed cluster anions.

For a special reading there are quite a few papers on special topics of coinage metal cluster ions such as resonance states in photodetachment spectra of Au_2^-,[166] image-charge-bound states in Au_6^-,[167] photoelectron spectra of Cu_n^-,[120,121,124] and Cu_n^-, Ag_n^-, Au_n^-;[119,123] theoretical investigations on the structures and EA's of Cu_n, Ag_n, and Au_n ($n = 3$)[126] and ($n = 4,5$);[168] and a recent effective core potential study on Ag_n^- ($n = 2–9$).[127] A study on small group 13 and group 15 cluster anions such as $GaAs^-$, $GaAs_2^-$, and others has been done by Meier et al.[169] Some photodetachment studies on small clusters anions should be noted, such as group 14 dimers,[133] Sb_n^- ($n = 2–4$),[134] and Bi_n^- ($n = 2–4$).[135] Photofragmentation and photodetachment studies on larger semiconductor anion clusters such as Si_n^-, Ge_n^-, and $Ga_xAs_y^-$ have been performed by the group of Smalley.[170]

C. Hypervalent Anions (MH_m^- and Some Related Species)

This class of ions, denoted by MX_m^-, has the very simple building principle that M is normally a main group element, X designates a monovalent atom, and m exceeds the maximum valency of M exactly by one. One important subset of these species are the hypervalent hydrides, MH_m^-. None of the free anions except SiH_5^- has been detected[171] yet in the gas phase, but the isolated neutral molecules $LiBH_4$, $NaBH_4$, and KBH_4, which are better described as

BH_4^- with a counterion, could be identified.[172] Various ab initio investigations[173-180] revealed that many of these complex anions are geometrically as well as thermodynamically stable. The most prominent features resulting from these studies are the very high vertical ionization potentials (VIP),[179,180] which even exceed those of the halogen ions. Boldyrev and von Niessen[179] attribute this strong binding of the extra electron to the fact that it resides in a bonding HOMO, which is spatially delocalized over all m hydrogen atoms. The alkali complex anions exhibit linear $D_{\infty h}$ minimum geometries and the corresponding electronic valence configurations are $(\sigma_g^+)^2(\sigma_u^+)^2$. LiH_2^- and NaH_2^- are lower in energy with respect to the reaction asymptote $MH + H^-$ by 54 and 47 kcal/mol, respectively, but the dissociations energies $MH_2^- \rightarrow M^- + H_2$ are found as 5.3 [173] (M = Li), and -12 kcal/mol[180] (M = Na), so that NaH_2^- is thermodynamically unstable. A barrier could be expected, however, for this latter reaction, since $NaH_2^-(^1\Sigma_g^+)$ and $Na^-(^1S) + H_2(^1\Sigma_g^+)$ do not correlate (at least not in C_{2v}). The computed VIP's cluster around 3 eV, which corresponds to the lowest detachment energy $LiH_2^-(^1\Sigma_g^+) \rightarrow LiH_2(^2\Sigma_g^+) + e^-$. Removal of an electron from the σ_g^+ orbital leads to $(\sigma_u^+)^2(\sigma_g^+)$ $LiH_2(^2\Sigma_g^+)$ and the corresponding ionization potential is only some 0.3 eV higher. The adiabatic correction to the former ionization energy amounts to 2.32 eV,[180] due to the geometric and thermodynamic instability of $LiH_2(^2\Sigma_u^+)$, leaving an adiabatic EA of only 0.74 eV. This is not true for the higher VIP, since $LiH_2(^2\Sigma_g^+)$ is structurally very similar to the linear anion, so that the adiabatic correction is very small.

All the complex anions with alkali metal centers heavier than Li should be thermodynamically unstable.[130]

BeH_3^- and MgH_3^- both are stable species with D_{3h} symmetry and the first vertical ionization energies are found as 3.86 and 3.74 eV, respectively, leading to the ^2E neutral states. Both of these neutral radicals are unstable in D_{3h} on account of Jahn–Teller distortion, which yields stable C_{2v} structures. The adiabatic corrections are approximately 1 eV, so that EA's of 2.86 and 2.89 eV,[180] respectively, are obtained. The highest VIP's are theoretically predicted for BH_4^- (4.54 eV) and AlH_4^- (4.75 eV) species in tetrahedral symmetry, but the adiabatic values are significantly lower. The adiabatic EA is 3.12 eV for the BH_4^- complex ion with respect to C_{2v} ($^2B_2$)BH_4 and 3.11 eV for ALH_4^- with respect to $AlH_2^- + H_2$, since there is no C_{2v} minimum for the neutral Al complex.[180]

Despite their isoelectronic valence electronic structure, SiH_5^- and CH_5^- behave quite differently, since in D_{3h} the former is a minimum ($^1A_1$), whereas the latter represents a saddle point. SiH_5^- is thermodynamically stable with respect to $SiH_4 + H^-$, but unstable[180,181] versus $SiH_3^- + H_2$, although the corresponding reaction barrier must be rather high due to its observability.[171] Boldyrev and von Niessen[179] performed additional calculations on the hypervalent transition metal hydride anions, comprising CuH_2^-, ZnH_3^-, TiH_5^-, and VH_6^-, and even the bicentric complexes $B_2H_7^-$ and $Al_2H_7^-$, with the pertinent result that their VIP's are surprisingly high. For $Al_2H_7^-$ the value is 6.1 eV, which is the maximum found hitherto for hydride complex anions.

Despite the geometric as well as thermodynamic stabilities and the unexpectedly high VIP's of several hypervalent complex anions, it is quite difficult to assess adiabatic electron affinities. For highly unstable neutral complexes such as AlH_4, these may be of very little relevance for experimental studies.

The related hydrogen bihalide anions FHF^-, $ClHCl^-$, and $BrHBr^-$ are calculated to have VIP's of 6.23, 5.07, and 4.60 eV, respectively, which are all significantly higher than those for the halogen atom anions, but decrease with the increasing size of the terminal atoms.[179] Their dissociation energies with respect to the lowest asymptote $XHX^- \rightarrow XH + X^-$ are only 1.67, 1.00, and 0.91 eV and thus considerably smaller. A very thorough study on the mixed bihalide anion $FHCl^-$ and many pertaining data to homonuclear and mixed bihalide anions have been published by Klepeis et al.[182]

D. "Solvated" H^-

The stability of a hydride ion solvated by a molecular M is governed by charge–dipole, charge–induced dipole, or charge–quadrupole interactions. It was common sense until recently that the solvent must be either polar or at least highly polarizable in order to form a thermodynamically stable complex. Stärck and Meyer[183] performed high-level calculations to find H_3^-, i.e. $H^-(H_2)$, to be stable. The van der Waals minimum is located for a linear structure with $r = 1.416$ a_0 and $R = 6.182$ a_0, the depth of the electronic minimum well is 1.1 kcal/mol. There are four vibrational levels and the D_0 dissociation energy is 0.2 kcal/mol. Isotope effects are quite significant and $D_0 = 0.31$ kcal/mol for $H^-(D_2)$. Belyaev et al.[184] found by means of the diatomics-in-molecule (DIM) method that the first excited state correlates to H + $H_2^-(^2\Sigma_u^+)$ and that it has two shallow valleys and a rather deep well of 2.4 eV below dissociation at $r_{ab} = r_{bc} = 2.1$ a_0.

The H_5^-, i.e. $H^-(H_2)_2$, should be V-shaped[185,186] but thermodynamically unstable with respect to $H_3^- + H_2$. $H^-(D_2)_2$ and $H^-(HD)_2$ should exist according to the theoretical predictions. Electron correlation has a vital influence on the structures as well as on the stabilities of the anions, since these contributions account for some 50% of the stabilities with respect to the corresponding monomers.[185] Due to the instability of H_5^-, $H^-(H_2)_n$ complexes with $n > 2$ are not expected to form in the gas phase.

H_3O^- and NH_4^- both have been detected in the Fourier transform ion cyclotron mass spectrometer.[187] The calculated structures[188] corroborate the interpretation of a solvated ion. The minima show the hydride ion in an unsymmetrical position almost collinear with one O–H or N–H bond with a slight bias toward the center. This type of charge–dipole interaction is quite general and is also met in S_N2 reactions.[189] The stabilities of the hydride complexes with H_2O and NH_3 as solvents are due to the fact that the O–H and N–H bonds are comparable in their strengths to H_2. When higher homologues, such as H_2S, are chosen as solvent, proton abstraction occurs without any barrier[174] and yields $HS^-(H_2)$, since the S–H bond is much weaker and SH^- is

significantly more stable than OH^-. Thus the stabilities of these complexes critically depend on a fine balance of bond strengths and electron affinities. It was recognized by Gutowski et al.[190] that NH_4^- (T_d) and H_3O^- (C_{3v}) are members of the so-called double-Rydberg anion family. They are all composed of a cationic core and a pair of strongly correlated electrons in diffuse orbitals, so their structures are reminiscent of the corresponding cations. Only NH_4^- and H_3O^- are geometrically (but not thermodynamically) stable, whereas the other species like CH_5^- and FH_2^- undergo fragmentation. The special features of double-Rydberg anions have been deeply discussed by Simons and Gutowski.[3]

E. Carbon and Silicon Hydrides

1. Saturated Systems

Tersely stated none of the small alkanes or silanes forms a stable anion in the gas phase, which structurally resembles the neutral ground state. For alkanes there are only resonances (compare section VIII.B), which are mostly caused by σ^* orbitals and typically 6–8 eV in energy above the neutral ground state. Electron impact studies on methane[191] and ethane[192] revealed very diffuse bands with maxima in this region. According to the high energies involved, these resonances are in general very short-lived and consequently the associated bands in the electron transmission spectra (ETS) are often as broad as several electronvolts, which sometimes even thwarts the localization of the band center. Further complications can arise in certain cases, when the band center is shifted owing to an overlap of two or more resonance states, as has been verified for chloromethane.[193] The lifetimes of such resonances depend strongly on the respective molecule, i.e. on the resonance position and further details, but they are typically in the range of 10^{-12}–10^{-15} s with respect to autodetachment. Another decay mechanism especially for higher-lying resonances is the dissociative attachment, which is frequently observed in low-energy electron–molecule collisions.[165h] For the larger n-alkanes the most important process is H^- elimination,[194] according to $(C_nH_{2n+2})^- \rightarrow C_nH^\bullet_{2n+1}$ $+ H^-$. This process is the favored product channel, since the EA of the hydrogen atom amounts to 0.75 eV, whereas the alkyl radicals exhibit no propensity to attach an extra electron.[195] The experimental onset of such dissociative electron attachment occur at incident energies of 8–9 eV, which by far exceeds the C–C and C–H bond strengths. Sanche and Schulz[196] concluded therefore that such high-lying electronic states can only be reconciled with core-excited shape resonances, where a valence electron is promoted to a Rydberg or mixed-Rydberg valence 3s- or 3p-type orbital and the incident electron enters an excited orbital of the positive ion core. The autoionization lifetime of such a resonance has to be in excess of 10^{-14} s, which corresponds to the time scale of vibrational motions, since this temporary electronic state has to survive at least one vibrational cycle to let dissociation take place. The 1.7 eV decrease[194] in the dissociative attachment maxima observed with the increasing chain length for the first four gas phase n-alkanes is attributed to the increasing polarizabilities of the corresponding neutral

parents. Sanche and Parenteau[197] and Rowntree et al.[198] found by electron-stimulated desorption technique that there is no such decrease for physisorbed alkanes (methane through nonane), and explain this finding by the prominent importance of the bulk polarizability, which does not depend significantly on the molecular dimensions.

Even more interesting are cyclic hydrocarbons with low-lying resonances, such as cyclopropane or [1.1.1]-propellane,[199] which have been studied by ETS. Electron impact experiments on cyclopropane revealed that this anion is much more stable in the gas phase than generally believed, but the resonance is still some 2.6 eV higher in energy than the neutral system.[200] An exceptionally low attachment energy of 2.06 eV is observed for [1.1.1]propellane,[199a] which corresponds to an electron capture in the $3a_2''$ LUMO. The lifetime broadening is only in the order of a vibrational spacing, which is much smaller than observed for typical σ^* resonances in alkanes. There are, however, also high-lying σ^* resonances with maxima at 6.3 and 6.8 eV.

Besides the temporary anions, which structurally resemble the corresponding neutral parent molecules, several theoretical investigations do predict stable $C_nH_{2n+2}^-$ anions, which are dissimilar to the neutral hydrocarbon molecules. They are either clusters of the form $(C_nH_{2n+1})H^-$ or $C_nH_{2n-2}^-$ ions clustered with H_2.[174,180]

Calculations of Tada and Yoshimura[201] on species with silicon and germanium backbones suggest that systems like disilane and digermane with an attached electron might be kinetically stable by a positive vertical electron detachment, but are certainly thermodynamically unstable with respect to autoionization. The optimized anion geometries are found not too far from the corresponding neutral structures. The sequence of stability is found as H_3-Si–SiH_3^- < H_3Si–GeH_3^- < H_3Ge–GeH_3^-, which parallels the decreasing diffuseness of the singly occupied MO (SOMO) orbital. These findings have to be taken with care, however, since the basis sets used for these investigations were too small to render decisive information on the stabilities of such saturated gas phase anions. The VIP's are found as 0.16, 0.46, and 0.71 eV for disilane, silylgermane, and digermane, respectively, and the adiabatic EA's are −1.22, −1.00, and −0.78 eV. So the stability of such species is questionable and there is no experimental evidence of their existence in the gas phase hitherto. It has to be noted that anions of larger silicon ring systems, such as the dodecamethylcyclohexasilane $[(CH_3)_2Si]_6^-$, are stable. Grev and Schafer[202] performed a theoretical analysis of the anion's SOMO and pointed out that these species resemble in a way traditional aromatic systems.

2. Unsaturated Systems

There is no knowledge of stable anion states of simple isolated alkenes. If the electron attachment energies are taken as the negative vertical electron affinities, the latter values are −1.74 and −0.68 eV for ethene[203] and 1,3-butadiene,[204] respectively. It is ascertained that the electron affinities of linear polyenes (with respect to the π_{-1}^* SOMO) increase with increasing length. The pairing theorem for

linear polyenes states that the sum of the ionization potential and the electron affinity is constant, i.e. IP + EA = constant, for a specific π_n, π^*_{-n} orbital pair.[205] Despite the fact that this theorem only holds for alternate olefins within the Hückel and PPP approaches and not for the all-electron Hamiltonian, it can be employed as a guideline for the search of the crossover region between resonant and bound π^*_{-1} anion states. The recent analysis of Staley and Strnad[206] showed that this stability threshold lies between 1,3,5-hexatriene and 1,3,5,7-octatetraene, since they find π^*_{-1} electron affinities of -0.22 and 0.06 eV, respectively, and there is no significant difference between the Z and E conformers. This implies that the linear polyenes must have at least four double bonds to bind an additional electron. Cyclic olefins are, however, less reluctant to electron attachment, especially when they are puckered, which raises the EA on account of the energy lowering of the LUMO.[207] Chou and Kass[208] detected a $C_4H_4^-$ radical in reactions of O^- with bicyclo[1.1.0]-butane and assigned this species to the bicyclo[1.1.0]-but-1(3)-ene anion. This putative assignment is corroborated by recent theoretical studies,[206] which yield an EA of 0.17 eV for this species. The also conceivable cyclobutadiene anion forms a π^*_{-1} resonance rather than a stable state, but this resonance is only 0.08 eV above threshold. The even smaller cyclopropene ring exhibits an EA of -1.45 eV,[203] which is not very far from that of ethene, and alkyl substitution does not alter this feature markedly.[209]

There is a very interesting new and little studied group of anions, which are called "distonic" on account of their spatially separated charge and radical sites. Most of the experimentally as well as theoretically studied examples, however, are cations.[210] Guo and Grabowski[211] used the flowing afterglow technique to investigated gas phase reactions of the benzyne radical anion. They observe that CO_2 is readily added to give a distonic species consisting of a phenyl radical and a carboxylate anion. This radical anion is characterized by a rather unreactive charge site. Van Doren et al.[212] exploited the C^- transfer capability of OCC^- in a gas phase reaction with $O=CF_2$ and observed the formation of $C_2F_2O^-$. The structure of this product ion is not yet clear; it could be CCF_2O^- or $CF=CFO^-$, both of which are expected to be distonic anions.

A very interesting member of the distonic anion family is the tetramethyleneethane radical anion, which is believed to have been seen very recently in the gas phase.[213] Its inreactivity is quite unique, since there is neither $I^\bullet$ or $tBuO^\bullet$ transfer to the radical site nor does $CH_3S^\bullet$ transfer takes place as is observed for many distonic cations. Therefrom it is concluded that this distonic radical *is unique and cannot be treated as a conventional radical species or even as its cationic counterpart*.[213] This class of anions is quite new, and their behavior is not yet understood, so there is a special demand for reliable theoretical contributions.

In accordance with the considerable negative electron affinity ascribed to closed shell systems such as acetylene, small alkyne radical anions could not yet be detected in the gas phase. And, until recently, even in matrix studies no smaller species than the

Table 8. Calculated Adiabatic Electron Affinities (EA) of the Closed Shell Si_2H_n Systems (Data Taken from Ref 218)

system	symmetry	anion state	EA (eV)[a]
$H_2Si=SiH_2(^1A_g)$	C_{2h}	^2A_g	1.03
$HSi=SiH(^1A_g)$	C_{2h}	^2A_g	1.76
	C_{2h}	^2B_g	1.23
$Si(H_2)Si(^1A_1)$	C_{2v}		<0
$Si=SiH_2(^1A_1)$	C_{2v}	$^2B_2$	1.73
	C_s	$^4A''$	0.66

metastable hexyne anion could be observed and identified unambiguously.[214] It was rather surprising, therefore, that Matsuura and Muto[215] succeeded in discovering the $C_2H_2^-$ anion in low-temperature alkane matrices. The hyperfine coupling constants extracted from the ESR spectra cannot be reconciled with a π-type but only with a trans-bent (C_{2h}) σ-type radical anion, which would parallel the findings for $Si_2H_2^-$ as shortly discussed in the sequel. Nothing is known yet about the electron attachment energy for $C_2H_2^-$, but from the time constants of an ESR experiment it can be inferred that this anion should be much more stable than assumed hitherto. This very new aspect in alkyne anion chemistry will certainly provoke a fresh impetus to theoretical studies.

The open shell alkynes, in contrast to the closed shell species, exhibit very large electron affinities. The linear $^2\Sigma^+$ ground state of C_2H is found to have an EA of approximately 3 eV with respect to the also linear $^1\Sigma^+$ state of the C_2H^- ion.[216] The transition state for the intramolecular hydrogen migration has C_s symmetry rather than C_{2v}, since the symmetrically bridged structure is a shallow minimum, approximately 0.9 eV higher in energy than the global minimum.[216b,c]

The unsaturated closed shell silicon hydrides differ significantly from their carbon homologues, since the computed electron affinities of these molecules are quite large,[217,218] and they should form rather stable anions in the gas phase. Table 8 provides a short collection of adiabatic EA's for stable negatively charged states. Most interestingly, the disilene anion has a stable ^2A_g state with an EA of 1.03 eV. It is surprising that the extra electron does not localize, and the molecule retains its C_{2h} symmetry upon electron attachment. The adiabatic correction, however, is some 0.7 eV and thus quite large, since the stabilization is accomplished by a strong pyramidalization at the SiH_2 moieties, which mimicks a silyl anion configuration at each silicon center. The additional electron resides in an a_g orbital, which is polarized away from the bond center and, thus, has largely abandoned its antibonding character. The Si_2H_4 system is very peculiar, since the neutral molecule and the anion exhibit a complementarity in their internal rigidities. The uncharged molecule is fluxional with respect to planarization and has a torsional barrier of about 1 eV,[219] whereas the anion exhibits a barrier of almost 1 eV to planarization[217] but the torsional barrier shrinks to 0.38 eV and the transition state for this motion is characterized by a strong localization of the surplus electron.[220]

The C_{2h} $Si_2H_2^-$ conformer exhibits a very stable ^2A_g ground state, where the extra electron occupies a strongly polarized a_g orbital. The ^2B_g excited state
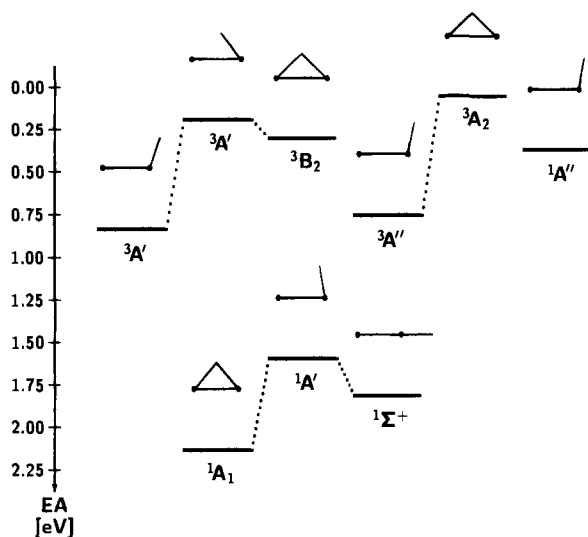
Figure 2. Stationary points located on the singlet and triplet potential energy surfaces of Si_2H^- (the bullets denote the Si atoms). The scale (eV) gives the stability with respect to the Si_2H ground state. $^1A'$, $^3A_2$, and the highest $^3A'$ states correspond to saddle points, all remaining structures are minima. (Data are taken from ref 221.)

is also stable by more than 1.2 eV and shows no propensity for a three dimensional bridged structure but retains C_{2h} symmetry. It is noteworthy that the bridged conformers are reluctant to form stable anions and, thus, the most stable Si_2H_2 species, namely the double bridged (C_{2v}) $Si(H_2)Si$ disilyne, has no bound anion state. This behavior can be rationalized by the fact that the vacant orbitals in the bridged neutral systems are destabilized due to the rather short Si—Si distances, and the structural relaxation upon electron attachment is insufficient to yield a stable negative ion.

Calculations on the Si_2H radical exhibit a rather large ground state electron affinity of 2.14 eV. The anion shows a wealth of stationary points, most of which are nonlinear, on the singlet and triplet potential energy surfaces.[221] Figure 2 illustrates the relative stabilities of the stationary points for the various stable electronic states of Si_2H^-. On the singlet ground state PES the symmetrically bridged $^1A_1$ (C_{2v}) as well as the linear $^1\Sigma^+$ ($C_{\infty v}$) are minima, and the former is the global minimum. This finding is complementary to C_2H^- which has $C_{\infty v}$ symmetry.[140,216]

The theoretical investigations elucidate that the unsaturated silicon hydrides should form rather stable gas phase anions, but hardly any experimental data on their stabilities were available until now.

3. On the Verge of Stability: CH_3^-

Most of the neutral radicals, like carbon and silicon hydride radicals, exhibits positive electron affinities and form rather stable anions.[222] The methyl radical is quite unique in this respect. In their photoelectron spectra Ellison et al.[223] observed a long progression of the $v_2'' = 0^\pm$, 1^+ levels of the anion to the $v_2 = 0, ...,$ 10 vibrational levels of CH_3, and they derived a very small adiabatic electron affinity of 0.08 ± 0.03 eV. These spectroscopic and mass spectrometric observations[224] suggest that the lifetimes of the lowest vibronic anion states $0^\pm$ and 1^+ should be of the order

of $10^{-6}-10^{-7}$ s. This means that these autodetaching vibronic states have lifetimes, which exceed those of typical resonances by at least 6 orders of magnitude. The very low stability of CH_3^- has remained a challenge for theory over many years, and all theoretical attempts prior and subsequent to its first observation were unsuccessful.[225] In 1991 Kraemer et al.[226] were the first to succeed to calculate a positive EA of 0.09 eV in close agreement with experiment, using large basis sets augmented by diffuse functions in the MRCI approach. The anion exhibits a pyramidal C_{3v} structure with C—H bond distances of 1.096 Å and bond angles of 109.5°. The study of the inversion potential at the MRCI level of theory reveals that the wave functions contain significant contributions from configurations in which one of the lone-pair electrons resides in low-lying Rydberg-like orbitals. Due to its weakly bound nature the valence ground state of the anion is close in energy to this series of Rydberg states, which even becomes continuum states upon planarization. This intricate interaction of a weakly bound with various unbound states invalidates the Born—Oppenheimer approximation, and therefore, a diabatic description has to be invoked.[226] The photoelectron spectrum calculated with this approach is in good agreement with the experimental spectrum, the calculated inversion barrier is obtained as 820 cm^{-1} and the tunneling splitting of the $0^\pm$ levels is 14 cm^{-1}.

Salzner and Schleyer[227] maintain that the methyl anion is even stable without accounting for zero point corrections, but their reported stability of 0.01 eV is too small to be of any significance.

F. Some Aspects of Dipole-Supported States

In a series of important theoretical considerations[228] it could be worked out that the critical dipole moment for a fixed dipole to bind an electron is 1.625 D, and that there is an infinite number of stable states. These predictions promoted theoretical investigations, especially on alkali hydrides and halides. There are several important specific papers on alkali halide EA's[229] and a broad collection of EA data on halides and hydrides has been presented by Bates.[12] Various groups succeeded in calculating positive EA's for polar diatomics,[230] and Carlsten et al.[231] could detect $LiCl^-$ in the gas phase. Garrett[232] demonstrated that the simple Born—Oppenheimer (BO) approximation is inappropriate for such anions, since the critical dipole moment decreases with the momentum of inertia, and increases with the dipole length. The finite momenta of inertia (∞ would correspond to the BO situation), which are encountered in practice, increase the limiting dipole moment, especially for excited states, and consequently only a finite number of bound states may exist. Adamowicz and McCullough[233] used the Koopmans' theorem approach to compute the stabilities of several excited states of LiH^-, LiF^-, $LiCl^-$, NaF^-, and MgO^-. Even the first excited states are only bound by approximately 10 meV, and at most five excited states (MgO^-) have been obtained. These highest excited states are, however, artifacts of the BO approximation. High quality coupled cluster calculations by Adamowicz and Bartlett[234] yielded excited states EA's of 2.8 and 23.4 meV for LiH and BeO, respectively.

The first really convincing experimental verification that dipole-bound negative ion states do exist has been provided by Zimmerman and Brauman[235] and Jackson et al.,[236] who studied substituted acetophenone enolate anions. Subsequent high resolution (<0.01 cm^{-1}) photodetachment studies on various anions, where the neutral systems have dipole moments in excess of 3 D, gave definitive evidence on the existence of dipole supported states along with information on rotationally resolved autodetachment resonances from short-lived dipole-bound states. We mention only a few spectroscopic studies on anions like CH_2CHO^-,[237] CH_2CFO^-,[238] CH_2CN^-,[239] CH_3CN^- (acetonitrile),[240] $C_6H_5O^-$ (phenoxide),[241] and FeO^-.[242] Coupled cluster calculations by Adamowicz[243] on nitromethane revealed that at least one dipole-bound state with a stability of 3.5 meV should be supported on account of the 3.46 D dipole moment in CH_3NO_2. According to the theoretical as well as experimental results, there is no doubt that highly polar molecules such as those discussed above can form at least one or, depending on the magnitudes of the dipole moment and the rotational constants, several dipole supported states.

There is a good deal of literature on cluster negative ion states, many of them on $(H_2O)_n^-$, $(NH_3)_n^-$, with $n \gg 1$, and also alkali halide cluster anions, which are beyond the scope of our review, thus it should suffice to mention just a few references.[244]

While large and medium-sized clusters are well known from gas phase experiments, little knowledge exists on very small systems, which may also support dipole-bound states. These small systems are well suited for a cooperative activity of theory and experiment. Although $(H_2O)_2$ is known to have a dipole moment of 2.6 D, which is significantly larger than the critical value, the existence of a bound anion state has been doubted for quite a long time on account of lacking experimental evidence. It is quite certain now, however, that at least one dipole-supported state has been detected, and its binding energy is estimated as 17 meV from field detachment experiments[245] or ≈ 30 meV from photodetachment spectroscopy.[244b] Quantum simulations on $(H_2O)_2^-$ revealed that the water dimer has positive electron affinities for geometric arrangements with medium and high dipole moments.[246] The ammonia dimer, $(NH_3)_2$, has a dipole moment smaller than 1 D and, therefore, the $(NH_3)_2^-$ ion is not expected to form in the gas phase.

Very recently Desfrançois et al.[247] succeeded to produce the "mixed" $(NH_3H_2O)^-$ ion by very slow electron attachment from Xe**(nf) Rydberg atoms and could observe this anion in the mass spectra. They infer that the binding of the excess electron is very small but no EA or VDE estimates are given.

In an excellent photodetachment experiment Taylor et al.[167] could ascertain the existence of excited anion states in Au_6^-, which correspond to image–charge dipole bound states. Since the neutral molecule exhibits D_{6h} symmetry and consequently has no permanent dipole moment, the binding in this case is supported by the polarization interaction of the electron with the charge image in the highly polarizable target molecule. The binding is very weak (in the order of a few millielectronvolts) as has been found by preliminary calculations. The observability of these states is attributed to the fact that Au_6 is a closed shell ground state molecule with a very large HOMO–LUMO gap of 2.5 eV. This very special situation prevents facile electronic excitations in the neutral cluster, which would strongly promote the decay of these loosely bound anion states.

VII. Doubly and Higher Charged Anions

A. Theory versus Experiment

In 1960 Stuckey and Kiser[248] performed electron bombardment of halogenated hydrocarbons and reported that the dianions of the fluorine and chlorine atoms, respectively, are much more abundant than the monoanions. While Baumann et al.[249] reported an increase in the doubly negative atomic ion production with increasing masses, Ahnell and Koski[250] disproved the results for chlorine. Relying on investigations of Peart and Dolder,[251] Schnitzer and Anbar[252] reinvestigated the H^{2-} system and claimed to have indirectly observed a relatively long-lived H^{2-} state with a half-life of some 23 ns to yield H^- and a free electron. They believed that the H^{2-} formation occurs via electron attachment to a highly excited H^{-*} precursor. Spence et al.[253] tried to reconfirm the results of Baumann et al. with an essentially improved spectrometer, but were unable to find evidence for group 17 atomic dianions. Further negative results on I^{2-} and O^{2-} were reported by Frees et al.[254] and Hird and Ali.[255] This situation remained completely controversial until 1984, when Brownstein[256] succeeded to derive a rigorous result for the maximum number of electrons N_m that can form a *bound state* which is associated with a normalizable wave function of the Hamiltonian. His result provided an inequality on N_m and the nuclear charge Z of an atom in the form $N_m < F(N_m) * Z + 1$, where $F(N_m) = 4$ for small and $F(N_m) = 2$ for large N_m. This result is even valid in the case that the N_m electron system is embedded in the continuum of the N_{m-1} system, so that $E_{N_m} > E_{N_m-1}$. This boundary, however, conveys no useful information for chemists who are interested in molecules with $Z \gg 1$. In a pioneering work Lieb[257] could provide a much more rigorous limit on N_m in a bound state of a system consisting of K pointlike nuclei with total charge Z. He established the relation that such a system can never bind more than $N_m < 2Z + K$ electrons, a result which holds for bound states ($E_{N_m} < E_{N_m-1} < 0$) and, moreover, is independent of any statistics. Despite the weakness of this limit on the maximum number of electrons in a stationary state, which allows no appraisal of most of the experimental results, it gives a definite answer for the simplest system with $Z = 1$ and thus rules out the existence of a bound state for H^{2-}. Most recent theoretical investigations of Robicheaux et al.[258] yield a very sound basis that not even resonances can exist for the hydrogen dianion. Since these theoretical inequalities provide no useful information on systems with $Z > 1$, the question on the existence of atomic dianions has not yet been settled and remains a matter of steady interest.

More recently Chang et al.[259] attempted a very careful search for long-lived ($\geq 10^{-5}$ s) doubly charged atomic ions of group 8 and group 9 elements as well

as hydrogen and could not get any evidence notwithstanding the fact that their upper limits of the ratios of the doubly to the singly charged anions were 2–8 orders of magnitude better than those of Spence et al.[253] and Kutschera et al.[260] Kalcher[261] employed MCSCF-CI techniques for the mono- and dianions of the third period elements Si, P, S, and Cl. Despite the fact that the doubly charged ions are found significantly lower in energy than the corresponding neutral atoms, there are no hints for bound states. Several conceivable high-spin states have been considered but can be termed neither stable nor metastable, since all those electronic states of the respective monoanions, to which they are dipolarly connected, are found to have lower energies.

If the nonexistence of monocentric dianions could be established, it would not be too much of a surprise, since the electron affinities of the free atoms are quite small and stable excited states of anions are the exception rather than the rule. These are not promising prerequisites for the formation of atomic dianions, and therefore one would conjecture that atoms never attach more than one excess electron. That N_m should never exceed $Z+2$ had already been conjectured from the above-mentioned inequality for fermion systems, and this has been further corroborated by an investigation of Benguria and Lieb,[262] who have given an upper bound for the maximum number of electrons in a stable state within the framework of the classical Thomas–Fermi–von Weizsäcker (TFW) theory. They found that within TFW $N_m \leq Z + 1$ holds for atoms and $N_m \leq Z + K$ for systems with K nuclei. Relying on these results one could infer that atomic dianions do not exist (which is in perfect agreement with the facts known about atoms hitherto) but molecular dianions (especially for $K \gg 1$) are conceivable, provided the neutral system meets some special conditions. On the one hand we could imagine molecules or complexes consisting of as many highly electronegative elements as possible, on the other hand we could suspect that either long-chained linear or other large molecules might be appropriate candidates, if they can accomodate the excess electrons at regions which are very distant from each other in order to minimize the Coulomb repulsion energy.

B. Some Known Dianions

There have only been a very few examples of multiply charged stable anions until now. After the observation of C_{60}^-, C_{60}^{2-}, and C_{60}^{3-} in solution,[263,264] Limbach et al.[265] succeeded to detect the C_{60}^{2-} ion in the gas phase and could assure with that discovery that such fullerenes are appropriate molecules to form stable dianions. Stimulated by these experiments Chang et al.[266] performed a restricted Hartree-Fock study on various C_{60}^- ions including C_{60}^{2-} and C_{60}^{3-}, adopting the C_{60} geometry also for all the investigated ionic states. Since the two extra electrons reside in the $7t_{1u}$ orbitals they find the ground state of the dianion to be the $^3T_{1g}$. Due to the HF approach they do not get direct evidence of a bound doubly charged anion, but they arrive at an energy which is 1.05 eV higher than for the neutral fullerene. They argue, however, that C_{60}^{2-} should be stable since they find an error of 1.8 eV in the binding

energy for C_{60}^-, and if this error is estimated to be twice as much for C_{60}^{2-} its energy turns out to be 2.5 eV lower than for C_{60} and remains only 0.2 eV above the lowest C_{60}^- energy. Despite these virtually appealing arguments their calculated data render no convincing evidence that C_{60}^{2-} should really be stable on theoretical reasons, because on the one hand even their estimated energy is at best equal to that of C_{60}^- and on the other hand it is rather doubtful that the HF error for the dianion is in fact additive. Hutter and Lüthi[267] performed restricted Hartree–Fock calculations on C_{60}^{m-} for $0 \leq m \leq 6$, optimizing all structures. They find a first EA of 1 eV, but the lowest $^1T_{1g}$ state of the dianion is already unstable by 0.75 eV.

Since the experiments unambiguously revealed a stable C_{60}^{2-}, this demonstrates nicely that the first EA, which is some 2.7 eV for C_{60}, needs not be very large to yield a positive second EA, provided the size of the molecule is sufficiently large that both extra electrons can avoid each other. In such cases, when the attached electrons are separated by considerable distances within a molecule, one can speak of *local electron affinity domains*. Benzo[cd]pyren-6-one[268] and estradiol glucuronide sulfate[269] are known from experiments to form stable dianions in the gas phase. More recently, Schauer et al.[270] discovered carbon cluster ions with double negative charge in the gas phase using a double-focusing mass spectrometer and reported ions as small as C_7^{2-}. For the doubly charged clusters they observed an alternating intensity pattern opposite to that of the singly charged species, since the even-n C_n^{2-} dianions appear more intensely than the odd-n components; C_8^{2-} and C_{10}^{2-} are found most intense of all. Following these experimental findings Adamowicz[146] has performed an ab initio study on the linear $D_{\infty h}$ C_8^{2-}, employing symmetry-broken orbitals and an UHF based first-order correlation orbital (FOCO) technique. Watts and Bartlett[147] performed a very concise theoretical study using the coupled cluster approach on C_7^{2-} through C_{10}^{2-}, taking account of the correct symmetries, and they were able to show that the results of ref 146 are in error, since not only the ground state symmetry was wrong but also the first EA was completely unphysical. They got no evidence for a stable C_7^{2-}, whereas C_9^{2-} turned out to be bound at the SCF level of theory, but not when electron correlation was included. They point out that, according to their detailed investigations, electron correlation destabilizes the n-odd and stabilizes the n-even species, and they get positive EA's for C_8^- and C_{10}^-. The geometry optimizations of the mono- and dianions reveal that there are strong changes upon electron addition to the corresponding neutral C_n clusters. Attachment of two excess electron induces pronounced bond alternations especially for the n-even dianions, which are more acetylenic than cumulenic in character.[147]

These findings are in full agreement with the theoretical studies of Sommerfeld et al.,[271] who reconfirmed that all linear or quasilinear C_7^{2-} isomers are unstable with respect to C_7^- and a free electron. The D_{3h} isomer $C(C_2)_3^{2-}$, however, is found to represent a minimum on the $^1A'_1$ PES, and this dianion is vertically (0.45 eV) as well as adiabatically

(0.32 eV) stable with respect to the lowest electronic state of the D_{3h} monoanion $C(C_2)_3^-$ ($^2A'_2$). The latter is energetically higher than the linear ($D_{\infty h}$) C_7^- anion. Calculations on the stability of the odd-numbered C_9^{2-} dianion[271] yielded results similar to those for C_7^{2-}, in that the $D_{\infty h}$ iosomer is even unstable with respect to vertical electron detachment, whereas the $(C_4)C(C_2)_2^{2-}$ C_{2v} structure exhibits a positive VIP. The authors conclude that such *triangular structures of the type* $[C(C_n)(C_m)(C_k)]^{2-}$, *where n, m, and k are even integers, may emerge as a general building scheme for odd-numbered carbon cluster dianions*.[271] The HOMO's in these species contain no bonding interaction between the central carbon and the attached C_n units. The population analysis confirms a positively charged central carbon atom in the dianion, so that ionic contributions strengthen the covalent bonding. This is reminiscent of the bonding principle in the D_{3h} MX_3^{2-} alkali halide dianions, addressed in section VII.C.

Further likely candidates for metastable gas phase dianions are the doubly charged ions of the so-called superhalogens or superhalides, MX_n^{2-} (M stands for a group 2, 4, or 6 element or a transition metal and X is a halogen), since their first EA's are in general very high.

The tetrahalide dianion BF_4^{2-} was investigated by Weikert et al.[272] using the Green's function method. They evaluate a VDE of 1.88 eV and find the tetrahedral structure to be a minimum. Weikert and Cederbaum[273] extended these studies to the homologue Mg and Ca fluorides and chlorides. The Green's function and CI data confirm that all these MX_4^{2-} (M = Be, Mg, Ca; X = F, Cl) systems are metastable minima with remarkably large VDE's between 1.8 and 3.4 eV and the corresponding Coulomb barriers to $MX_3^- + X^-$ dissociation seem to be high and broad enough to prevent instantaneous vibrational or tunneling dissociation.

Model potential calculations on group 6 hexahalides by Miyoshi and Sakai[274] and Miyoshi et al.[275] yielded positive EAs for CrF_6^- and MoF_6^-, whereas WF_6^{2-} should be unstable. A recent ab initio reinvestigation of the CrF_6 mono- and dianion performed by Hendrickx et al.[276] resulted in an EA of 1.31 eV for CrF_6^- and, even more interesting, there is quite a large barrier of some 1.73 eV for the dissociation reaction $CrF_6^{2-} \rightarrow CrF_6^- + F^-$. Due to these findings the authors reason that CrF_6^{2-} could be a stable gas phase dianion.

Theoretical investigations of Klobukowski[277] showed that $SeCl_6^{2-}$ and $TeCl_6^{2-}$ are octahedral minima at the MP2 level of theory. $SeCl_6^{2-}$ and $TeCl_6^{2-}$ are found to be 6.29 and 5.67 eV, respectively, more stable than the corresponding neutral hexachlorides, but no VDE's are reported. Boldyrev and Simons[278] studied the octafluorides SeF_8^{2-} and TeF_8^{2-}. They find the (D_{4h}) square antiprism structures to be minima and energetically lower than the cubic structures, which exhibit imaginary harmonic vibrational frequencies. They estimate a Koopmans' VDE of approximately 5 eV for TeF_8^{2-}, which is the largest value found hitherto for a dianion. For a further reading on related topics we suggest the review of Compton.[13b]

C. Which Is the Smallest Stable Dianion?

For small molecules with rather high electron affinities, such as HSO_4 the EA of which is 4.5 eV, there are no hints, neither experimental nor theoretical, that HSO_4^{2-} or SO_4^{2-} could be stable in the gas phase.[279] Bowie and Stapleton[280] maintain to have detected NO_2^{2-}, which is even smaller than the sulfate ion, but theory as well as subsequent experiments have been unsuccessful until now in obtaining a positive electron affinity for NO_2^-.

Since the experimental result are not reliable to date, the question of the smallest stable dianion could not be answered until the beginning of 1993, when two theoretical groups, Boldyrev and Simons[281] and Scheller and Cederbaum[282,283] made an effort in this direction. Both set out for small systems, which allow two excess electrons to separate spatially in order to minimize the mutual Coulomb repulsion. The aspect of spatial separation of two surplus electrons is associated with two strategies: (a) choose a linear system, which facilitates the localization at the (symmetry equivalent) terminal atoms; (b) choose a highly symmetric (nonlinear) system, which facilitates an even distribution of both electrons.

Boldyrev and Simons[281] followed strategy a and investigated linear tri-, tetra-, and pentaatomic molecules, with electronegative terminals, which are necessary, when the dianion should be shorter than C_7^{2-}. Their investigation comprised NCN^{2-}, $OBeO^{2-}$, $OCCO^{2-}$, $SCCS^{2-}$, $Be_2O_3^{2-}$, $Be_2S_3^{2-}$, $Mg_2O_3^{2-}$, and $Mg_2S_3^{2-}$. Split valence basis sets, augmented by diffuse s and p functions, were employed at the MP4 level of theory to calculate the stabilities of the above-mentioned dianion series. They arrive at the conclusion that solely $Mg_2S_3^{2-}$ has a positive ionization potential of 0.2 eV, whereas all remaining doubly charged systems are unstable with respect to autoionization. They infer that the latter species might be the smallest (linear) stable dianion.

Strategy b was chosen by Scheller and Cederbaum[283] who studied a series of MX_3^{2-} ions (M = Li, Na, K; X = F, Cl) employing Hartree-Fock as well as Green's function techniques. These doubly negative ions have D_{3h} symmetry and are metastable minima on the PES. The electronic ground states are found as closed shell structures and both excess electrons reside in a π-type out-of-plane orbital, which is made up almost exclusively from the p components on the halogen atoms. The HOMO is, therefore, nonbonding with respect to the central metal atom and allows for an even distribution of both electrons over all three symmetry equivalent ligands. These are exactly the features necessary for an $MX^{(n-1)-}$ (M electropositive, X electronegative) system to attain its maximum EA with respect to M^{n-} for a given k.[284] The Mulliken population analysis (which might not be too significant for such polar species) indicates that the gross populations on the X atoms in MX_3^{2-} are larger and the M–X overlap populations are smaller than in the corresponding MX molecule. Ions of this type have highly heteropolar metal–ligand bonds and it has been shown by Scheller and Cederbaum[282] that a rather simple ionic model, based on point charges and a characteristic force, which counteracts the Coulomb attraction, can be employed to estimate their stabilities quite satisfactorily. The

first vertical ionization energies for the MF_3^{2-} systems are 1.59, 2.17, and 2.52 eV for M = Li, Na, and K, respectively. The corresponding IP's of the MCl_3^{2-} series are 1.50, 1.96, and 2.31 eV. It is observed that the first VIP increases with the size of M^+ and decreases with the size of X^-. This can be explained by assuming M^+ and X^- as hard spheres with the corresponding radii ϱ_{M^+} and ϱ_{X^-}. It is $\varrho_{Li^+} < \varrho_{Na^+} < \varrho_{K^+}$, and $\varrho_{F^-} < \varrho_{Cl^-}$ and for any M we get $\varrho_{M^+}/\varrho_{F^-} > \varrho_{M^+}/\varrho_{Cl^-}$. This implies that for a given central cation the mutual repulsion between the anionic ligands X^- grows with increasing ϱ_{X^-} and, therefore, reduces the binding of the second excess electron.

The lowest reaction channel of these metastable D_{3h} dianions is the fragmentation reaction $MX_3^{2-} \rightarrow MX_2^- + X^-$, and this breaking up takes place on a PES, which is repulsive like $1/r$ for interfragment distances far beyond those at the corresponding C_{2v} transition states. The barriers to fragmentation are found between 0.18 eV (LiF_3^{2-}) and 0.25 eV (NaF_3^{2-}) at the CI level of theory.[283] This means that such dianions are shallow minima on strongly repulsive potential surfaces, and it is hard to see how they could be produced in the gas phase. Accessibility via the "inverse fragmentation" reaction is highly unlikely because of the shallowness of the minimum well. Alternatively, electron attachment $MX_3^- + e^- \rightarrow MX_3^{2-}$ seems to be problematic, since the corresponding monoanions are either unstable or have structures that are completely different from those of the doubly negative ions. In the same way as MX_3^- must not be imagined as the monoanion of MX_3, MX_3^{2-} should be considered neither as dianion of MX_3 nor as monoanion of MX_3^-. For this very reason only vertical ionization energies instead of adiabatic electron affinities can be evaluated. The conclusion at present is that LiF_3^{2-} is the smallest metastable dianion from the theoretical but probably not from an experimental point of view. The even smaller HF_3^{2-} cluster, though stable with respect to autodetachment at the stationary D_{3h} geometry, is not a minimum but unstable to fragmentation.[283]

D. Y-Shaped Anions

The interest in this special type of compounds—not only mono- and dianions but also cations—dates back into 1972, when Gund[285] introduced the concepts of "Y-delocalization" and "Y-aromaticity". Ever since that time the trimethylenemethane dianion (TMM^{2-}), the prototype acyclic 6π-electron system, has challenged many theoreticians over the years to attempt to elucidate its purported stability over the (E)- or (Z)-butadiene dianion isomer and to speculate whether this additional stability can be attributed to Y-aromaticity and/or charge alternation.[286] A new controversy was provoked by Agranat et al.,[287] who concluded that no significant preference for the Y-topology of the dianions would be detectable at higher levels of theory. Subsequent investigations revealed that TMM^{2-} is nonplanar in that the CH_2-groups are strongly pyramidal at its minimum geometry[288] and that the relief of planarity brings the relative stabilities of the Y- and the (Z)- or (E)-butadiene form closer together. Such a pyramidalization on an sp^2 negatively charged carbon center is, despite of the accompanying decrease in energy,

of no special significance, since the Hartree–Fock orbitals impose a severe spatial confinement on the extra electron, which then prefers sp^3 hybridization. The propensity to such nonplanarity with respect to the flexibility of the employed basis set as well as the level of electron correlation calculation has been studied on CH_3^- some years ago[289] (compare section VI.E.3). It is reiterated,[290] however, that a certain preference for the Y-shaped dianion persists due to a favorable charge distribution. From a rigorous theoretical point of view, all these results are questionable, since the investigated dianion is unstable with respect to autoionization and, thus, any theoretical result at a higher level of sophistication should yield TMM^- and a free electron. Nevertheless these theoretical considerations are quite useful, since they demonstrate once more the general building principle of doubly charged anions, in that the center is positive and all the excess charge resides at the molecular perimeter, as discussed in the previous section. This corroborates the assumption that such dianions, if they happen to be stable, are stabilized on account of charge alteration rather that Y-aromaticity.

Much more rigorous evidence of Y-aromaticity has been obtained for the tricyano- (TCM^-) and trinitromethanide (TNM^-) anions. The comparison of the electron densities in cyanoform and nitroform with those of TCN^- and TNM^- reveal that the electron densities in the C–C bond points[291] of the former and the C–N bond points of the latter increase upon deprotonation, whereas the corresponding C–N and N–O bond points are characterized by an electron density decrease.[292] This is in accordance with the expected changes due to conjugative effects. While in the TCM^- ion all atoms are in one plane, in TNM^- only the C and the N atoms are coplanar, whereas the nitro groups are twisted with respect to this plane. This anion shows a peculiar electronic structure, because in addition to the "expected" bond points there are, apart from the three ring points, three further bond points between the adjacent oxygen atoms of neighboring NO_2 groups.[292] This finding is indicative of a completely new type of bonding interactions in such anions, which provide a new challenge especially for theory.

E. Multiply Charged Systems

Reinhardt and Compton[8] have recorded a negative ion of mass 103 $\pm$ 2 amu when heating gold in fluorine gas or thermally decomposing $(AuF_5)_n$ clusters, and their reasoning is that it should be AuF_6^{3-}, a triply negative species, since this complex needs just three electrons to "complete a shell". Their conjecture, however, is not quite convincing, since the authors hold the opinion that the electronic structure of AuF_6^{3-}, if it really exists in the gas phase, should look like a giant resonance rather than a conventional anion, and, therefore, the aufbau principle cannot be invoked as a guideline. This is, however, the only trianion hitherto, which is at least suspected to exist in the gas phase, but there have been no theoretical investigations until now that could corroborate this assumption.

Pyykkö and Zhao[293] screened many linear A=B=C systems with various numbers of valence electrons,

comprising mono- up to tetranegative ions. In order to avoid problems with continuum states they used conventional basis sets of double-ζ + polarization quality. Although several SCF orbital energies are positive and would tend to zero energy upon admixture of continuum functions,[294] the calculated geometries are in good agreement with experimental data obtained from salts, which corroborated the assumption that the crystal field has a vital influence on the stabilities but not on the interatomic distances. Notwithstanding the fact that the isolated polyanionic species are thermodynamically unstable, the calculated relative stabilities of those isomers involving atoms with different electronegativities may provide insight in the general bonding principles of possibly stable oligonegative ions. Assuming increasing electronegativities from A to C it is found that for a valence electron system B=A=C the one with the most electropositive element in the molecular center is most stable of the three possible isomers, irrespective of positive, negative, or zero total charge. The energetic orderings $FBC^{2-} < FCB^{2-}$, $OBN^{2-} < BNO^{2-}$, $NCC^{3-} < CNC^{3-}$, $OBC^{3-} < OCB^{3-}$, etc. can serve as paradigms.[293] Via the electronegativity perturbation theory it can be shown[295] that the valence π-electrons determine the stabilities of the 14−16 valence electrons systems. Since the "nonbonding" MO, which has either zero or only a small contribution on the central atom, plays the most important role for the stability, it is quite easy to rationalize that the most stable isomer B=A=C should have the electropositive atom in the middle.

On the basis of the findings on the MX_3^{2-} alkali halide dianions (section VII.C) Scheller and Cederbaum[296] proposed a construction principle for $K_mF_n^{x-}$ (up to $m = 12$, $n = 19$, $x = 7$) ions, which could be stable against autodetachment as well as dissociation. Starting from KF_3^{2-}, KF and KF_2^- units are added according to the rule that all metal centers should retain 3-fold coordination. This recipe demands a systematic extension of the basic unit by KF and/or KF_2^- moieties such that one or two F atoms constitute cross-links between the alkali centers. The result is a "layered" structure, where all fluorine layers are separated by alkali atoms, which seems to be the key design for possibly stable multiply charged alkali halides. It is found that $K_2F_4^{2-}$ has a $F-K(F_2)K-F$ (D_{2h}) structure, the excess electrons are bound by 4.8 and 3.76 eV, and the barrier to the dissociation $K_2F_4^{2-} \rightarrow 2KF_2^-$ is 0.46 eV. The extra electrons reside completely on the terminal F atoms, which minimizes the Coulomb repulsion. $K_2F_5^{3-}$ adopts a $F_2K-F-KF_2$ (D_{2d}) structure, where one electron accomodates in each fluorine layer. The VDE is obtained as 2.49 eV and there is a small (0.11 eV) barrier in the fragmentation channel $K_2F_5^{3-} \rightarrow KF_2^- + KF_3^{2-}$. $K_4F_7^{3-}$ can be envisaged as $K_2F_5^{3-} + 2KF$, introducing two terminal KF units. The VDE of 4.05 eV strongly exceeds that of $K_2F_5^{3-}$. Using this building principle the authors predict systems up to $K_{12}F_{19}^{7-}$ to be stable against autodetachment, although these polyanions need to be studied in more detail in order to find out whether or not they are stable with respect to dissociation.

This seems to be the first systematic approach to small polyanions, which may possibly be stable in the gas phase. According to the construction principle a linear spatial extension seems to be inevitable for accomodating an increasing number of excess electrons, since this is the only way to relieve the mutual Coulomb repulsion. This should be a more promising way toward multiply charged anions than amassing halide ligands around a single center like in the superhalogens, since from steric reasons it appears highly unlikely that the latter can attach more than two excess electrons (compare section VII.B).

VIII. General Related Problems

This chapter is intended to provide some short allusions to questions for which there are only qualitative reasonings but no sound quantitative answers available (section VIII.A), and to address in short some fields of research, which are only loosely related to the present topics.

A. What is the Largest EA?

The question, which molecule M might have the largest EA is intimately related to the ionization potential IP of M. The IP of M (which is assumed to be also stable as M^+ and M^-) always has to exceed the EA, since otherwise it is easy to see that the electronic state of M, with respect to which IP and EA are defined, cannot be the ground state of the neutral molecule M. It is a prerequisite of M, therefore, to have a large IP in order to be able to bind an excess electron very strongly. Atomic systems can be excluded from this consideration, since all known atomic EA's are significantly smaller than the corresponding atomic IP's. There are quite a few molecules, especially fluorides like CF_4, SiF_4, SF_6, etc., which exhibits IP's in the range of 15−17 eV, and for that reason it was initially believed that this should constitute an upper bound[297] to EA_{max}, but neither experimental nor theoretical evidence could be provided for such high values. Even though some superhalogens like IrF_6, PtF_6, or AuF_6 have EA's of some 8−10 eV,[8,13] which may be termed as very large in comparison to commonly encountered values, it became apparent that the even higher earlier upper bound had to be revised. Gutsev and Boldyrev[284] reconsidered the maximum EA problem in the framework of LDF theory. Their analysis is based on the F superhalogens MF_6, which are ideally suited for high EA's. The reason for this is that the excess electron resides in a nonbonding orbital, which is delocalized over all F ligands. This rationalizes the observation that the EA's of these MF_6 systems do not dramatically depend on the nature of the transition metal center, but are much more dominated by the F_k ligand framework. This motivated the authors to ignore the centers and instead to consider solely the ligands. They work out qualitatively (estimated errors are ±1 eV) that EA_{max} ($k=2$) = 5.5 eV and EA_{max} ($k=6$) = 6.5 eV. The limiting value for $k \rightarrow \infty$ is obtained as 11 eV, whence EA_{max} ($k = \infty$) = 10−12 eV can be estimated. None of the known (reliable) EA's hitherto is beyond this ultimate theoretical limit. The largest theoretical VDE values have been derived for TeF_7^- and SeF_7^-, the Koopmans value of which amount to 11.9 and 11.2 eV, respectively.[278]

B. Some Remarks on Resonances (Temporary Anions)

All negative ion states that are energetically above the ground state of the corresponding neutral molecule are termed as resonances. There are, however, two categories of resonances, which differ significantly in their behaviors.

(a) When an electronic anion state (resonance) M^{*-} is bound with respect to $M^* \rightarrow e^-$, this electronic structure is normally called a Feshbach resonance. The excited state M^* of the neutral molecule is higher in energy than the corresponding M^{*-} state of the anion.

(b) Shape resonances are characterized by the attachment of an electron in a "virtual orbital", which is associated with an angular momentum barrier. The electron "tunnels into the resonance state", where it persists for a certain time, which is normally longer than the characteristic cycle times of the outer electrons, before it escapes (autodetachment) again by tunneling out. The characteristics of such resonances strongly depend on the shapes of the potential barriers, and consequently, orbitals which do not cause an angular momentum barrier, do not give rise to a resonance. The study of temporary anions complements our knowledge of electronic states gained from stationary (bound) negative ions. Jordan and Burrow[7] even state more fundamentally that *measurements of temporary anion formation provide a means to probe the normally unoccupied orbitals of neutral molecules.*

There are quite a few electron-scattering techniques, which have been employed for the study of temporary anions, and electron transmission spectroscopy (ETS) has emerged as versatile tool in the study of many polyatomic molecules.[7]

From a theoretical point of view type a resonances in most cases do not raise more serious problems than bound anion states, since they can (at least in principle) be studied with standard variational techniques. In contrast to that a different theoretical approach is needed for shape resonances. Since this type of negative ion states is only briefly touched on and is not a basic topic of our review, a short allusion of the basic problems should be sufficient. It is the basic idea, as stated succinctly in ref 7, that the virtual molecular orbitals (VO), which do not "feel" a Fermi correlation with the bound electrons, may represent extra electrons not really belonging to the respective molecule. So various of the VO's, which result from basis set calculations, may be envisaged as potential "resonance candidates". Since resonances are often associated with a highly diffuse extra electron, it is the expectation that extended basis sets are needed to account for this feature. VO's are, however, variationally unstable in the sense that their eigenvalues tend to zero upon successive basis set extensions, and consequently, any VO of a given angular momentum l, obtained as a by product of a variational calculation with a "very complete" basis set up to l, cannot describe anything else but a neutral molecule and a "free" electron and thus fails to yield an idea of the respective characteristics of the resonance. Various theoretical attempts have been presented to circumvent this problem and to "stabilize" such resonances. Important contributions came from Hazi and Taylor,[298] the group of Jordan,[299] and Chen and Gallup.[300] An overview of the application of various methods to molecular problems has been presented by Collins and Schneider.[301]

C. General Stability Principles of Charged Systems

In all the previous sections we have considered anions only from the conventional point of view as being composed of a set of positively charged nuclei with total charge Z and $Z + 1$ or probably even $Z + 2$ electrons. The last decade provoked an increasing interest in more exotic systems, where an electron is replaced by a muon μ^-. Many experiments have provided information ranging from nuclear chemistry, such as muon-catalyzed fusion, to purely chemical applications, such as ESR spectra of muon spin labels to elucidate the features of muon hydrogen bonds. So we would like to digress very briefly to such exotic ions in order to systematize the basic requirements for the stabilities of charged systems from a more global point of view, for such considerations could render also rules which hold for the conventional anions. Although there are apparent regularities with respect to replacing one particle by another, the theoretical foundations are still at the beginnings. If we consider the most simple systems, consisting of two particles with masses m^+ and m^- and charges $+1$ and -1, respectively, bound by the Coulomb interaction, the total energy scales with the reduced mass $\varrho = m^+m^-/(m^+ + m^-)$. For the systems e^+e^-, $e^+\mu^-$, H (pe^-), $\mu^+\mu^-$, $p\mu^-$, we immediately get stabilities of -0.25, -0.497654, -0.499786, -51.76, and -93.02, respectively, in atomic units. Since ϱ gets never close to zero, such systems are always stable, irrespective of the components.

A completely new dimension opens when we proceed to ions made up of three particles with masses m_1, m_2, and m_3. Known protagonists from this family are the hydrogen cation H_2^+ (e^-pp), the hydride ion H^- (pe^-e^-), and surprisingly even the positronium anion Ps^- ($e^+e^-e^-$),[302] which are all perfectly stable. H^{μ^-} ($p\mu^-e^-$) is unstable and there are good arguments[303] that e^-pe^+ is unbound too. The heuristic rule, derived from these experiences, says that *like charges should be associated with like masses* to achieve stability. All the above-mentioned systems obey this rule and the instability of H^{μ^-} can easily be understood: the total energies are directly and the radii of the 1s orbitals are indirectly proportional to ϱ and, therefore, the $p\mu^-$ system is very stable and tightly bound so that an additional electron cannot be attached in a stationary state any more.

Martin et al.[304] attempted to derive general rules of stabilities from the universality of the binding mechanism. They recognized the difficulty in quantifying "like masses", since H_2^+, HD^+, and HT^+ are *cum grano salis* equally stable, notwithstanding the fact that $|m_2 - m_3|/(m_2 + m_3)$ is far from being small in the latter. They proposed a rescaling of the masses to get the more convenient variables $\alpha_i = m_i^{-1}/(m_1^{-1} + m_2^{-1} + m_3^{-1})$ with $\alpha_1 + \alpha_2 + \alpha_3 = 1$. In these variables the meaning of "like masses" can be associated with $|m_2 - m_3|$ close to zero. Some of the such obtained results are listed in Table 9. All these ionic triads are bound, since Hill[305] could show that all

Table 9. Inverse Masses (See Text), Threshold Energies $E(m_1 + m_2)$ for the Two-Particle, and Total Energies $E(m_1 + m_2 + m_3)$ for the Three-Particle Systems^a (The Data Are Collected from Ref 304)

$(m_1 + m_2 + m_3)$	$\alpha_1{}^b$	$E(m_1 + m_2)$	$E(m_1 + m_2 + m_3)$
$e^+e^-e^-$ (Ps$^-$)	0.33333	−0.25000	−0.26200
$\mu^+e^-e^-$	0.00241	−0.49759	−0.52506
pe^-e^- (H$^-$)	0.00027	−0.49973	−0.52735
$p_\infty e^-e^-$	0.00000	−0.50000	−0.52775
e^-pp (H$_2^+$)	0.99891	−0.49973	−0.59715
μ^-pp	0.81620	−92.925	−102.24

^{a} All values are in atomic units and given to five decimal places. ^{b} $\alpha_2 = \alpha_3 = (1 - \alpha_1)/2$.

symmetrical species with $m_2 = m_3$ are bound, i.e. their energies are below the corresponding thresholds. So the system $p_\infty e^-e^-$ is stable and even "asymmetric" ions $p_\infty e'e$ are calculated to have stationary states, provided m_2 does not exceed 1.57 m_e. The most rigorous limits for the regions of stabilities can be denoted by a bipartite crucial inequality:

$$\frac{m_1 m_2}{m_3(m_1 + m_2)} < 1.57 \qquad m_3 > \frac{3}{4}m_2\left(\frac{m_1}{m_1 + m_2}\right)^2$$

and all those systems that have been identified as stable obey this relation. The miscellaneous species e^-pe^+ or $e^-\mu^-e^+$, which violate at least one of the inequalities, are not bound. Therefrom it may be conjectured that H$^-$ is the only anion within the conventional "chemically interesting" family the stability of which has been rigorously proved from first principles.

Even though no stringent information exists for molecular ions, it is conceivable that these inequalities might be used as guidelines for intrinsically ionic species. It is interesting to see that the symmetric anions LiH$_2^-$ and LiF$_2^-$, which fulfill both inequalities, form stationary states (section VI.C), whereas the "asymmetric" species LiFH$^-$ or NaFH$^-$, violating at least one of the inequalities, could not be observed yet. Despite the appealing correspondence, this simple application to such complicated molecular systems is no more than a prenotion of further stability theorems which are still waiting for discovery.

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