Gas-Phase Multiply Charged Anions

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Singly charged negative ions in the gas phase have attracted considerable experimental and theoretical attention over the past decades. However, the existence of free doubly or multiply charged negative ions, in particular those of small systems, has remained a curiosity and a matter of some controversy. Recent experimental and quantum mechanical studies show that multiply charged negative ions of small molecules and clusters can exist as isolated entities.

Massey's book on negative ions in 1976 (*1*), along with his updated article in 1979 (*2*), summarized essentially everything that was known about singly charged anions at that time. This treatise has had an enormous impact in the field of negative-ion physics. Hotop and Lineberger (*3*) published an authorative review of recommended electron affinities (EAs) of all atoms, other than the rare earths, reported up until 1984. Bates (*4*) has completed the difficult task of reviewing the many advances in the understanding of the structure of negative ions up until 1990. This review also tabulates various estimates for the EAs of the lanthanides (La through Lu) and actinides (Ac through Lr). The mean value in each set is 0.1 eV. Compton (*5*) has reviewed the very recent theoretical and experimental developments in the field of atomic negative-ion physics up until 1994.

Most atoms and a considerable fraction of the known molecules can form stable, singly charged negative ions. Although singly charged negative ions have attracted considerable attention during the past 30 years, doubly charged negative ions have been viewed with curiosity and some experimental controversy. Only recently has their existence been firmly established. Doubly and higher multiply charged negative ions are commonly observed on surfaces, in solution, or as "building blocks" in condensed matter such as $[A^{n-}][B^{n+}]$ salts. In such chemical environments, the local electrostatic field constituted by the surrounding positively charged counterions helps stabilize the multiply charged anion with respect to fragmentation and to the detachment of one or more of the excess electrons. For a noninteracting $[A^{n-}]$ entity in the gas phase, however, the stabilizing local field is absent and the Coulomb repulsion between the excess charges can only be reduced by rearrangement of these charges over the small atomic or molecular region. In order to minimize the interelectron repulsion, many molecular anions adopt a gas-phase structure different from that in the condensed state. However, large residual interelectron repulsions cause multiply charged anions to be much more fragile to electron loss and fragmentation in the gas phase than in the condensed state. Thus, their formation and characterization is challenging, both experimentally and theoretically.

All of the evidence for long-lived gas-phase multiply charged negative ions has come from mass spectroscopy (MS). The experimental difficulties are great; in fact, none of the early observations of doubly charged atomic and diatomic anions have been corroborated, and many have been shown to be artifacts. A particularly poignant example is the early observation of the iodine dianion, I^{2-}. Bauman *et al.* (*6*) observed I^{2-} and I^- (10^{-4}:1 to 10^{-3}:1) using a Penning ion source with a 60° magnetic-sector magnetic mass spectrometer followed by an electric deflector for energy analysis. The energy analysis allowed them to rule out metastable decomposition of X_2^- as an artifact resulting in "X^{2-}" in the mass spectrum. This observation was questioned by Frees *et al.* (*7*), who used radioactive ^{131}I in their ion source. After collecting what they expected to be I^{2-} in the ion collector cup, no ^{131}I was detected, although ^{131}I was detected in the I^- cup, as expected. The Koski group concluded that the signal must have been caused by some impurity. Many experiments using MS techniques that do not directly count the negative ion particles—but rather detect their motion (frequency) in a combined electric and magnetic field—have been plagued by so-called harmonics, which appear at half-mass frequencies and give a false indication of doubly charged anions. Modern high-resolution mass spectrometers can circumvent many of these experimental difficulties, and there is now considerable experimental evidence for multiply charged polyatomic negative ions. However, there is no conclusive MS evidence for long-lived atomic or diatomic multiply charged negative ions.

Theoretically, isolated multiply charged molecular ions (A^{n+} or B^{n-}) generally are not stable because of the strong repulsion of their excess charges (electrons or positive holes) that may lead to molecular fragmentation (Coulomb explosion). Isolated anionic systems also may decay by emission (autodetachment) of an excess electron, which makes their theoretical investigation substantially more complex than that of cations. To obtain reliable results for the generally low binding energy of the outermost excess electron, one must have theoretically and computationally demanding methods that accurately account for the diffuse character of this electron and provide a balanced treatment of the electron correlation. Electron correlation has a major impact on their stability with respect to electron ejection for singly charged isolated anions and is generally expected to be even more crucial for multiply charged systems. Surprisingly, there are relevant exceptions where the presence of several excess charges suppresses the impact of electron correlation: Highly ionic systems constitute a special class where electron correlation is important but does not have a decisive influence on the absolute stability of a multiply charged anion to electron loss. Multiply charged anions also attract special interest because they belong to a class of systems that (i) always exist in the presence of excess charges and (ii) may dissociate if the number of extra charges is reduced. The electronic and nuclear symmetry used in the calculations must be carefully selected. For instance, from common chemical concepts the standard textbook dianion CO_3^{2-} is predicted to be a closed-shell species, but the use of a spin-restricted approach in calculations would make it impossible to describe reality, that is, the instability of CO_3^{2-} to dissociation into a free electron and the monoanion (open-shell system).

Interest in multiply charged anions began both as a scientific curiosity and from unfulfilled use in tandem accelerators. Doubly charged negative ions would effectively double the final ion kinetic energy without increasing the standoff voltage of the accelerator. Multiply charged anions are finding applications in biomedical MS and in the MS techniques related to the sequencing of the human genome.

Atomic Negative Ions

Almost all elements studied have stable ground-state negative-ion configurations, that is, positive EAs. Notable exceptions

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are nitrogen, beryllium, and magnesium; also, there is no evidence that mercury and zinc can form stable negative ions in their ground state. The first photodetachment experiment on a negative ion beam was performed by Branscomb and Fite (*8*) on the $1s^2\ ^1S_0$ ground state of the hydrogen negative ion, H^-. Lykke *et al.* (*9*) measured a highly accurate EA value of 0.75420(2) eV (number in parentheses is the standard error in the last digit) for hydrogen in a threshold photodetachment experiment using collinear laser and H^- beams. A very precise theoretical EA value for H^- was computed by Pekeris [0.754209(3) eV (*10*)]. During the past decade, many other atomic and molecular EAs have been accurately determined. Developments in ab initio quantum theoretical and computational techniques along with new experimental methods such as photodetachment threshold spectroscopy of the negative ion with tunable lasers have reduced the uncertainty of measured or predicted EA values to the range of 0.01 eV or less.

Experimental and theoretical studies show that alkaline earth atoms can in fact produce a stable negative ion (*4*). Because of their closed-shell electron configuration, rare gas atoms in their ground state routinely are considered as incapable of permanently binding an extra electron. However, this conclusion is strictly valid only for He and Ne because Ar, Kr, and Xe exhibit drastically different physical properties (such as chemical reactivity) from those of He and Ne and thus are considered "pseudo-closed" shell atoms. Conflicting experimental and theoretical data, however, leave open the possible existence of bound, or at least long-lived, rare gas negative ions. Haberland *et al.* have presented tentative experimental evidence for Xe^- bound states (*11*).

Molecular Negative Ions

Many experimentally and theoretically determined EAs for molecular (and atomic) systems have been tabulated by Bates (*4*) [see also (*3*, *12*, *13*)]. The EA values for atoms and small molecules (with up to five or six atoms) may be both negative and positive and generally range from about −2 up to ~4 eV (Fig. 1A). All of the atoms and most of the molecules with negative EAs generally are very short lived. A notable exception is CO_2^-, which exists in a quasi-bound state [lifetime of $(X^2A_1)CO_2^-$ ~ 90 ± 20 μs (*12*)] as a result of poor overlap of the nuclear wave function representing the bent and extended CO_2^- anion and that of linear CO_2. Note the abrupt changes of the EA values with the number of valence electrons (Fig. 1A). Negative ions with 8, 16, and 24 valence electrons are quite stable, reflecting the fact that greatest stability exists for closed shells.

Fluorides have attracted particular interest, partly because of their tendency to attach slow electrons and their subsequent use as gaseous dielectrics. Attention has also been devoted to fluorides because some have such a high first EA [>4 eV (*14*)] that they have been called "superhalogens." The hexafluorides, MF_6, where M is a *d*-shell transition metal atom, are prominent examples, having EA values of about 5 to 9 eV (Fig. 1, B and C) (*4*, *14*). Uranium hexafluoride, UF_6, an intermediate product in the reprocessing of nuclear fuel, is experimentally estimated to have an EA value of >5 eV (*15*). Fluorides of the atoms in the first rows of the periodic table generally have much lower EAs. Notable exceptions are the anions of the alkaline difluorides, MF_2^-, and alkaline earth trifluorides, MF_3^-. These ionic species bind the additional electron by 5 to 8 eV and thus fit into the category of "superhalogens" (Fig. 1D).

The large first EA of many MF_k-type fluorides and structurally related systems generally (*16*) can be attributed to (i) their nonbonding highest occupied molecular orbital (HOMO) (that is, this orbital consists mainly of atomic orbitals sited at the F atoms, which accommodate the extra electron); (ii) the high electronegativity of the F ligands, which effectively supports strong binding of an additional electron; (iii) the reasonably large number of F ligands, which makes the effective delocalization (distribution) of the excess charge density over the large ligand sphere amenable (thus, the smaller the extra portion of an electron to be accommodated by an atom is, the easier it is for an atom to hold this portion); and (iv) the high polarity (ionicity) of the $M^{\delta+}$-$F^{\delta-}$ bonds in MF_k fluorides (thus, binding of the extra electron is effectively supported by strong Coulomb attraction between this electron and the central, positively charged metal atom). For multiply charged negative molecular ions, largely ionic bonding character tends to stabilize the negatively charged species toward fragmentation and autodetachment of an extra electron.

Impressive progress, experimentally and theoretically, has also been made in the field of diatomic anions and carbon or metal cluster anions [see (*4*, *5*, *17*)]. The interest in negatively charged carbon clusters is partly attributed to the many possible structures they can adopt, including the closed-cage fullerenes [for example, EA(C_{60}) = 2.65 eV (*18*)]. Jin *et al.* (*19*) have predicted from charge-transfer "bracketing" reactions a large first EA of 4.06 ± 0.27 eV for the highly fluorinated fullerene molecule $C_{60}F_{48}$.

Atomic Dianions

Proceeding from the knowledge of stable singly charged negative ions in the gas phase, it is natural to ask if a free atom or

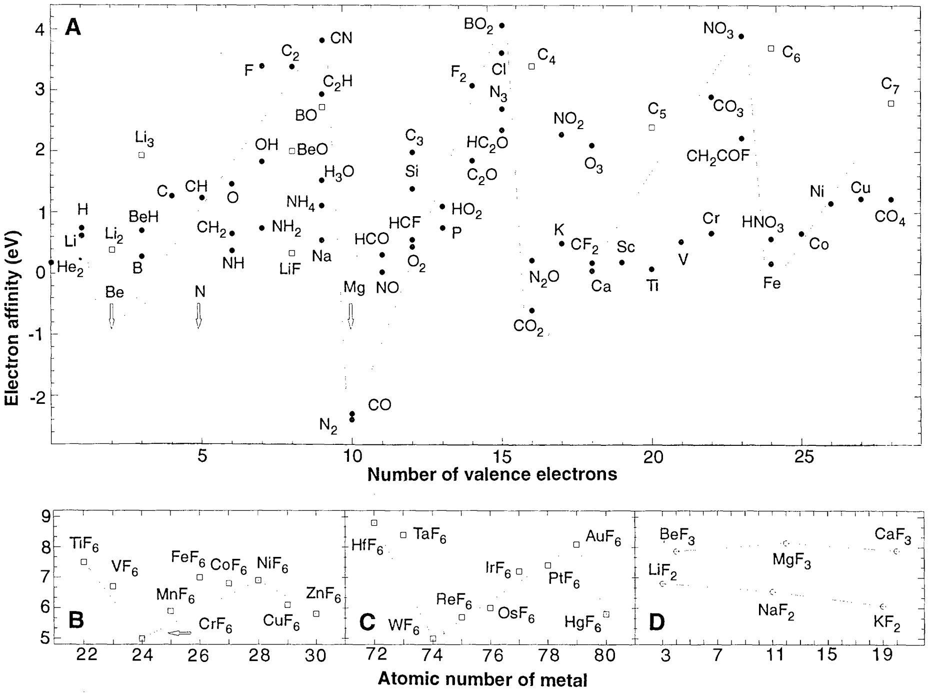

Fig. 1. (**A**) Experimentally measured (●) and calculated ab initio (□) EAs for some atoms and molecules made from elements of the first up to the fourth row of the periodic table. The EAs are plotted versus the number of valence electrons (excluding the two K shell electrons) of the neutral species. Calculated ab initio binding energies for the extra electron of (**B**) 3*d*-shell metal and (**C**) 5*d*-shell metal hexafluoride monoanions, together with those for (**D**) some singly charged negative alkaline difluorides and alkaline earth trifluorides.

molecule can become doubly negative charged. Milliken's oil-drop experiment shows that multiply charged negative droplets are stable, and classical electrostatics shows that an insulated conducting sphere charged with any number of electrons N can attract an additional electron provided it is close enough to the surface (at large distances, there is Coulomb repulsion). Classically, a conducting sphere can be infinitely charged (*20*). The potential acting on the extra electron naturally exhibits a Coulomb "barrier" that effectively increases the stability of the $(N + 1)$ electron system toward loss of the additional electron.

Quantum mechanically, however, it is not evident that a singly charged negative "sphere" such as an atom or molecule can accept a second extra charge. Early Bohr atom models (*21*) indicated that H^{2-} was unstable with respect to H and H^-. This is confirmed by a theorem of Lieb's (*22*). The instability of the isolated hydrogen dianion has been established also by many ab initio studies, which are too numerous to include [see, for example (*23*)]. Thus, at the quantal level we want to know how small a stable doubly negative charged system can be.

Theoretically, the overwhelming Coulomb repulsion between the two extra electrons confined to the small region of atomic dianions makes the occurrence of bound states highly improbable. Several studies have claimed experimental evidence for isolated long-lived dianions of some heavier atoms (*24, 25*), but most of these claims have been either retracted or shown to be flawed (*26*). Although some fragmentary evidence may exist for long-lived ($>10^{-6}$ s) atomic dianions, there is no conclusive evidence, experimental or theoretical, that either bound or long-lived atomic dianions exist in the gas phase.

Diatomic Molecular Dianions

In contrast to the case of atomic dianions, a molecular dianion (such as a diatomic) must be stable not only with respect to the ejection of an extra electron but also to fragmentation. A free dianion acquires stability as a result of electronic binding as well as a potential barrier to dissociation. Based on the most frequently encountered case of stable, singly charged negative dissociation fragments, the schematic picture in Fig. 2 illustrates this barrier with a hypothetical potential energy curve for a molecular dianion AB^{2-} (generally, A and B may not be atoms; they can be fragments of a larger system). The drawing shows the frequently encountered case of an avoided crossing (dotted lines) between two diabatic states (curves 1 and 2) of the same spin and symmetry representing the dissociation limits $A^{2-} + B$ and $A^- + B^-$. The attractive curve 1 correlates with the $A^- + e + B$ dissociation limit if neither A^{2-} nor B^{2-} exists as a bound state. In this case, the state is assumed to be a resonance with a complex potential-energy surface. The inclusion of a complex energy assures that the state decays (autodetaches). The shaded area indicates a possible broadening from the finite lifetime of the resonance state. Curve 2 represents a purely repulsive state being essentially Coulombic in character and correlates with $A^- + B^-$. The adiabatic potential-energy surface resulting from an avoided crossing with curve 1 exhibits a local minimum (ground-state structure, I) and a local maximum (transition-state structure, II). Thus, AB^{2-} is stable if its zero-point motion lies below the asymptotic limit of $A^- + B^-$. However, even if the lowest state, AB^{2-}, is above this asymptote, a long-lived AB^{2-} may exist if the precondition of a sufficiently deep minimum to support the zero-point vibration of the dianion is fulfilled. This state then can decay only by tunneling through the long-range Coulomb barrier. In this case, the height and width of the Coulomb barrier generally are the primary factors determining the lifetime of the metastable state. Compared to atomic dianions, the fragility to fragmentation greatly increases the complexity of both the experimental and theoretical investigation of molecular dianions. For any structurally stable or metastable dianion, the presence of a long-range electron-electron Coulomb repulsion assures that a (large) potential barrier to the addition or removal of the second extra electron generally will exist. This barrier can give rise to long-lived multiply charged negative ions that are adiabatically unbound (shape resonances) and provides additional dynamic stability to dianions that are adiabatically bound.

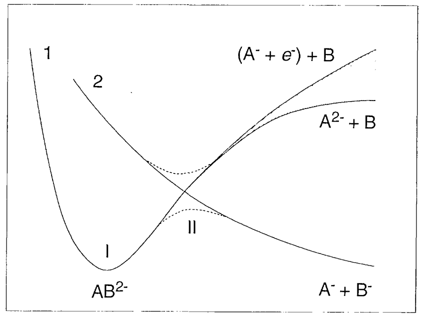

Fig. 2. Schematic drawing of potential energy curves illustrating the intersection of two diabatic states (solid lines). The avoided crossing between the corresponding adiabatic curves is indicated by the dotted lines. Both A and B can be molecules themselves. Notice that in the case of highly ionic molecular systems, the overall shape of the adiabatic potential energy surface also exhibits the characteristics shown in the figure, although the concept of an avoided crossing of two diabatic states might be debatable [the drawing stems from (*51*)].

In comparison with atomic dianions, one may envision that for diatomic dianions the repulsion between the two extra electrons can be reduced either by spatial separation of the excess charges or by their delocalization (smearing out) over the larger molecular structure. Two kinds of delocalization are generally possible: (i) the charges may be truly delocalized over a part or the whole molecular system, or (ii) the charges may be split into several parts, each of these localized on a different site (ligand). Spatial separation of two (localized) additional negative unit charges may be viewed as a special case of the latter. In this case, we can roughly guess the total binding energy per electron to be the EA of the accommodating entity minus the repulsion energy $V(r)$ of the distant electron pair; $V(r) = 14.4/r$ in electron volts for two electrons at a distance r in angstroms. A realistic estimate for diatomic dianions predicts an implausibly large minimal interatomic separation r of ~4 Å. Thus, the occurrence of bound or even long-lived diatomic dianions in the gas phase is highly improbable. In 1966, Stuckey and Kiser (*24*) claimed experimental evidence for strong signals of the long-lived free diatomic dianion CN^{2-}; their results, however, were not substantiated by other investigators and have been questioned because of the possibility of "harmonics" of CN^- in their omegatron MS experiment, although Kiser (*25*) has argued against this interpretation.

Molecular Dianions

The dianion of the dimer of benzo[*cd*]-pyrene-6-one, a large organic ketone, was the first long-lived doubly charged negative ion to be observed in the gas phase (*27*). Many observations have since been made of such large organic dinegative systems. One of them reports long-chain dicarboxylate dianions (*28*) that acquire stability through spatial separation of the two localized extra unit charges.

Interest in the dianions of fullerenes (*29*) has skyrocketed, with the C_{60} and C_{70} molecules eliciting the greatest attention. They were reported to form long-lived ($>10^{-3}$ s) gas-phase dianions (*30–32*). The observation of long-lived ${C_{60}}^{2-}$ would appear to be contradicted by existing calculations that yield a negative EA for ${C_{60}}^-$ (*33–36*). The addition of two electrons into the threefold degenerate t_{1u} empty orbital gives rise to a $^3T_{1g}$ ground state for ${C_{60}}^{2-}$. Ab initio restricted Hartree-Fock calculations show that ${C_{60}}^{2-}$ and ${C_{60}}^-$ are approximately equal in energy (*33*); a "jellium" description predicts that ${C_{60}}^{2-}$ is unbound (*34*); a semiempirical modified neglect of differential overlap (MNDO) calculation predicts that the second EA is negative by 0.4 eV (*35*); local density-functional calculations also give the second EA as −0.02 or −0.3 eV, with the latter expected to be more accurate (*36*). The metastability of C_{60}^{2-} is attributed to a shape resonance resulting from the long-range Coulomb repulsion combined with the shorter range electron-molecule binding, as pointed out previously (*30, 34*). The resulting Coulomb "barrier" is analogous to that which gives rise to α-particle decay from the nucleus. The Coulomb barrier restricting the motion of the two excess electrons in C_{60}^{2-} is shown in Fig. 3: The center of C_{60} is positioned at zero energy, and the two equivalent electrons (parallel spins) "waltz" around the C_{60}^{2-} at an energy corresponding to the estimated second EA (+0.3 eV). "Tunneling" through this Coulomb and angular momentum barrier ($\ell = 1$) is very improbable (*34*).

Jin *et al.* (*19*) recently studied dinegative ions of highly fluorinated derivatives of C_{60}, which provides further evidence of the importance of the Coulomb barrier. The dianion $C_{60}F_{48}^{2-}$ is produced by direct attachment of two electrons to gas-phase $C_{60}F_{48}$. The doubly charged anion exhibited unusual stability to the removal of either excess electron. This finding is attributed mainly to a positive second EA (~2 eV) and the presence of a large (1.5 eV) long-range Coulomb barrier, which is built from the bound state for the two extra electrons near the $C_{60}F_{48}^{2-}$ molecule and the Coulomb repulsion between these electrons at large interelectron separation. Note the analogy between this quantal finding of a Coulomb barrier near the molecular sphere and the classical electrostatic considerations regarding an insulated, conducting negatively charged sphere penetrated by an additional electron. The charge delocalization and strong binding of the extra electrons to the large number of F atoms may also support the electronic stability of $C_{60}F_{48}^{2-}$.

Regarding small molecular dianions, the observation of isolated doubly charged negative ions of van der Waals clusters of oxygen as small as $(O_2)_3^{2-}$ (*37*) is particularly interesting because this molecule does not appear large enough to reduce the interelectron repulsion sufficiently. More experimental or theoretical evidence, or both, is needed in this area. Recently, Schauer *et al.* (*38*) presented conclusive experimental evidence that long-lived ($>10^{-3}$ s) covalent carbon-cluster dianions, C_n^{2-}, as small as C_7^{2-} exist in the gas phase. A strong even-odd alternation of the abundance of these clusters was observed in MS experiments, with peaks for even-*n* clusters (closed-shell ground state) being much more intense than those for their odd-*n* neighbors (open-shell ground state). Assuming linear structures, as for the neutral and monoanionic precursors, theoretical studies [(*13, 39*); see also (*40*)] related this alternation pattern to the variation of the stability (that is, EAs) of the dinegative clusters (Fig. 4A). However, these studies predicted electronic instability (negative EA) for the smaller covalent clusters C_n^{2-} with $n < 10$ (Fig. 4A). Regarding C_7^{2-} and C_9^{2-}, the discrepancy between experiment and theory has been clarified in a recent theoretical study by Sommerfeld *et al.* (*39*). According to their results, the structurally and electronically stable (Fig. 4A) ground state of C_7^{2-} and C_9^{2-} is represented by the "center-ligand sphere" structure $[C(C_2)_3]^{2-}$ (D_{3h} symmetry) and $[(C_4)C(C_2)_2]^{2-}$ (C_{2v} symmetry) (*39*), respectively. The HOMO of both structures is nonbonding with respect to the central C-$C_{2,4}$ ligand interaction [EA(C_2) ~ 3.4 eV; EA(C_4) ~ 3.5 eV (*40*)]. In addition, if we assume a "center-ligand sphere" structure, the predominantly covalent dianions $[C(C_2)_3]^{2-}$ and $[(C_4)C(C_2)_2]^{2-}$ exhibit a markedly positive charged central C

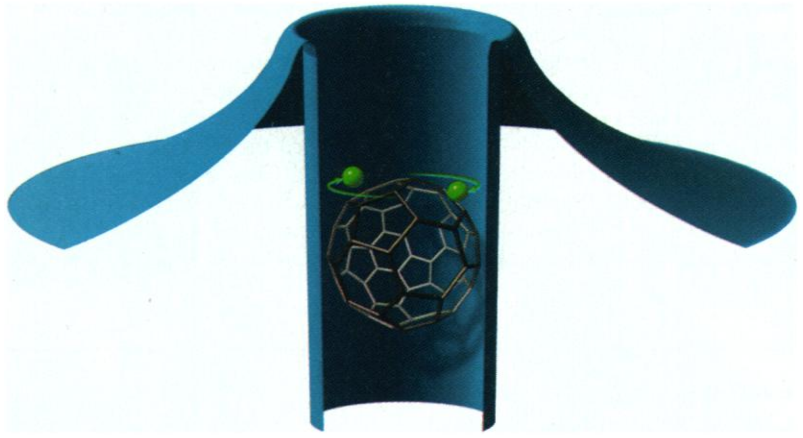

Fig. 3. The interaction potential of an electron at a distance from a singly charged negative sphere of radius *a* and dielectric constant *k*

$$V(r) = \frac{-e^2(k-1)a^3}{2(k+2)r^2(r^2-a^2)} + \frac{c^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2}$$

where ℓ is the angular momentum of the incident electron, m_e is the mass of the electron, and $\hbar$ is Planck's constant divided by 2π. The Coulomb barrier potential is that for $C_{60}^- + e$ ($k = 4.4$, $a = 3.5$ Å, and $\ell = 1$). The energy level occupied by the two "waltzing" electrons is +0.3 eV, in accord with recent EA calculations.

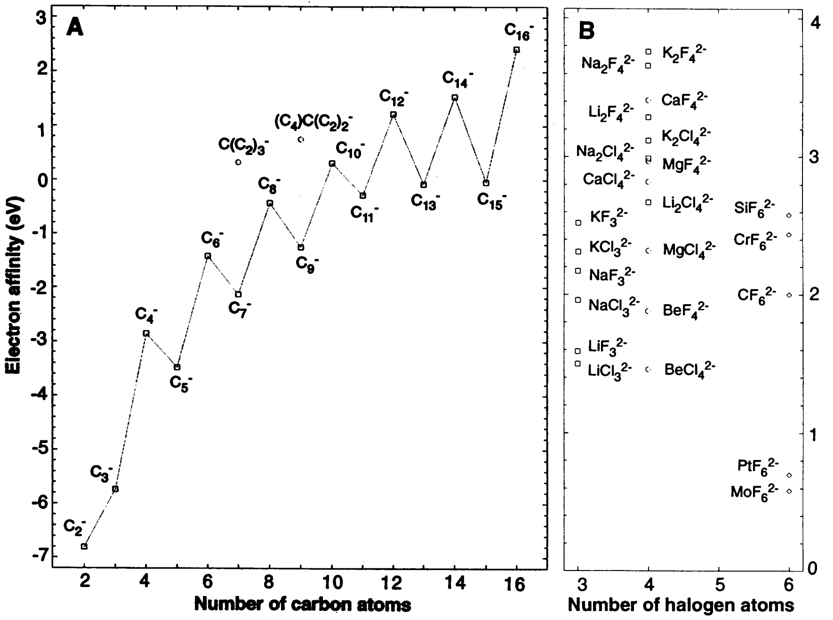

Fig. 4. (**A**) Calculated EAs for the carbon cluster monoanions C_n^- (*13, 37, 38*). (**B**) Calculated detachment energies for the (□) ionic doubly charged negative alkaline halides MX_3^{2-} (*46*) and $M_2X_4^{2+}$ (*52, 58*) and (○) alkaline earth halides MX_4^{2-} (*45, 51*), together with those for some (◇) dianionic hexafluorides (*12, 47–50*).

atom (~0.4) beside the "shell" of negatively charged C_2 and C_4 ligands. Note the close relation of this molecular constitution to that discussed above for the "superhalogens."

Several theoretical studies indicate that the separation of spatially localized extra charges at the ends of a chainlike structure generally do not represent a promising platform for the evolution of bound or long-lived negative ion states (*41*). The apparent instability of the linear clusters C_7^{2-} and C_9^{2-} amply demonstrates the validity of this general statement. However, there exists one recent theoretical study (*42*) that claims electronic stability of a linear dianion, that is, $Mg_2S_3^{2-}$. The vertical detachment energy calculated for this dianion is very small (0.2 eV). Also, the stability of $Mg_2S_3^{2-}$ to fragmentation has not yet been considered in more detail.

The possibility to adopt a "center-ligand sphere" structure should primarily be considered as a necessary but not at all sufficient prerequisite for electronic stability. Thus, even prominent textbook examples of dianionic covalent molecules that fit into this category such as CO_3^{2-} and SO_4^{2-} are predicted to decay by emission of an extra electron (*43–46*). In addition to autodetachment, a dianion adopting a "center-ligand sphere" structure may also be unstable toward fragmentation. This has been illustrated, for example, in the case of the gas-phase dianion HF_3^{2-} (*46*).

Several more recent theoretical studies (*47–50*) have also considered whether the attachment of a second electron to an MF_6^- monoanion provides a channel to the formation of electronically stable dianions (Fig. 4B). Miyoshi and co-workers (*47*) calculated a positive electron detachment energy of 4.85 and 1.76 eV for CrF_6^{2-} and MoF_6^{2-}, respectively. Korobov *et al.* (*48*) estimated the EA of PtF_6^- to be 3.9 ± 0.6 eV, and Gutsev (*49*) predicted a positive EA of 2.58 eV for SiF_6^-. No detailed studies of the structural stability of these dianionic transition-metal hexafluorides have been performed, which limits the meaning of their apparent stability to electron loss. Ewig and van Wazer (*50*) provided some theoretical evidence for CF_6^{2-} to be stable structurally (no dissociation) and electronically (no autodetachment).

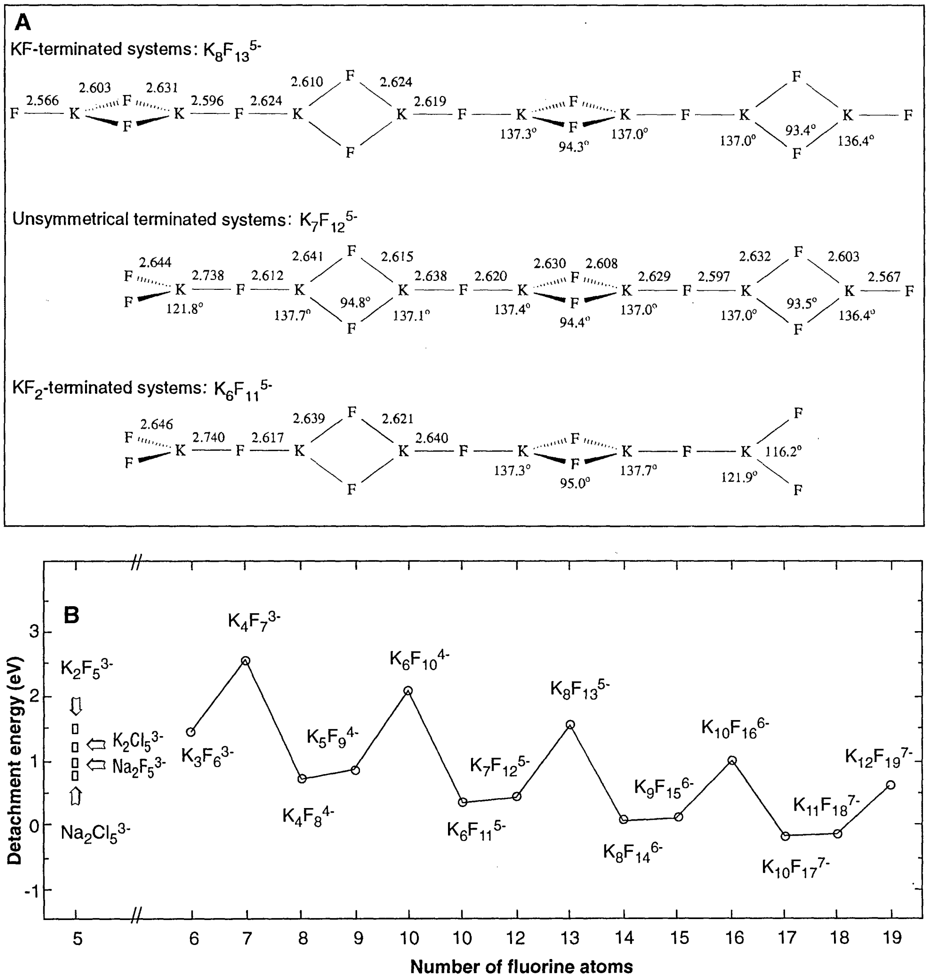

Fig. 5. (**A**) Calculated ionic model structural parameters for the metastable potassium fluoride pentaanions. (**B**) Calculated ionic model detachment energies for the smallest pseudo-linear potassium fluorides with three to seven extra charges. All systems are designed following the lines of a general construction principle (*52, 58*).

In the particular case of small free doubly charged negative molecular ions, the degree of each of the distinct types of molecular stability, which may be roughly categorized as electronic and structural, is determined directly by the strong electron-electron Coulomb repulsion of the two extra charges. Thus, we must probe each of these categories of molecular stability carefully with accurate quantum calculations in order to predict whether a given assemblage of atoms and electrons constitutes a novel family of species that may ultimately be prepared experimentally.

Thorough theoretical studies that considered these categories of molecular stability for small free doubly charged negative molecular ions by Cederbaum and co-workers (*45, 51*) and Scheller and Cederbaum (*46, 52*) have established that highly ionic small molecular dianions, including dinegative alkaline-earth tetrahalides MX_4^{2-} (M = Be, Mg, or Ca; X = F or Cl) (*45*) and highly ionic doubly charged negative alkaline halides MX_3^{2-} (M = Li, Na, or K; X = F or Cl) (*46*), should be stable. Both groups of systems are derived by expansion of the coordination sphere of the monoanion MX_3^- and MX_2^-, respectively, and not by simple addition of an electron to MX_4^- or MX_3^-. The latter monoanions do not exist themselves as stable species. Note, in particular, that LiF_3^{2-} presently is the smallest free molecular dianion conclusively predicted to exist in the gas phase as a stable dianion.

The small ionic dianions should have large binding energies for the extra electrons, a strong variation of the geometrical parameters, and a strong increase of the ionic character with respect to their neutral and monoanionic precursors. In particular, all of the dianions exhibit a nonbonding HOMO consisting predominantly of the halogen atomic orbitals. The small ionic dianions acquire stability to fragmentation and to loss of an extra electron by delocalization of the excess charge density over the large sphere of halogen ligands. The high electronegativity of the halogen ligands effectively supports strong binding of the extra electrons.

Detailed investigations with correlated levels of theory predict (kinetic) stability of the dianions MX_3^{2-} and MX_4^{2-} with respect to fragmentation (loss of a halogen ion). On the basis of the established stability of their singly charged negative fragmentation products (see, for example, Fig. 1), these small ionic dianions approach stability in a long-lived metastable state (resonance state) behind a long-range Coulomb potential barrier (see, for example, Fig. 2). Thus, only in the vicinity of the ground-state structure of the ionic MX_3^{2-} and MX_4^{2-} does the electrostatic attraction between the positively charged central metal atom and the negatively charged halogen ligands contribute markedly to the total binding energy and may locally be greater than the electron-electron Coulomb repulsion between the singly charged negative fragmentation products that dominate the course of the potential energy curve at larger distances (Fig. 2). Scheller and Cederbaum (*46*) used the Wentzel, Kramers, and Brillouin (WKB) quasi-classical formula to estimate the lifetime τ of the resonance state to be about 10^{11} years with respect to tunneling through the potential barrier. Aside from the presence of the broad Coulomb barrier (2 to 5 Å) for ionic dianions such as the MX_3^{2-} halides, the magnitude of τ also is related to the height (0.2 to 1 eV) of the barrier. Note that τ may decrease substantially because of thermal effects, that is, by occupation of thermally excited vibrational levels of the dianion.

The stability of the isolated dianions MX_3^{2-} and MX_4^{2-} to vertical and adiabatic electron loss (Fig. 4) has also been established with correlated levels of theory. The largely ionic character of the bonding leads to their large stability toward autodetachment of an extra electron. The large binding energy for the extra electrons is primarily attributed to the strong electrostatic attraction of these electrons by the central positively charged metal atom of the small ionic dianions. An ionic contribution to the bonding has general impact on the stability of small molecular dianions (*46*). The most vivid illustration of this effect is found in the electronic stability of the ionic carbon clusters $[C(C_2)_3]^{2-}$ and $[(C_4)C(C_2)]^{2-}$ with respect to their almost purely covalently bonded linear isomers.

Motivated by the highly ionic character of the MX_3^{2-} dianions, Scheller and Cederbaum (*46*) have introduced a conceptually simple electrostatic model (the ionic model) that can reliably predict properties of largely ionic multiply charged negative molecular ions with little computational effort. This model borrows from concepts of ionic solids and assumes unit charges sited at the atomic locations of the molecules, that is, the bonds are treated as completely ionic. The ionic model has been used for geometry optimization, frequency analysis, transition-state searches, calculation of the binding energy of the extra electrons, and searching for larger highly ionic molecular dianions and even multiply charged negative systems. The ionic-model data generally agree very well with available ab initio results (within a threshold of about 3% for the MF_3^{2-} systems). This close agreement amply demonstrates that the stability of highly ionic isolated molecular dianions with respect to both fragmentation and autodetachment of an extra electron can be explained in terms of simple classical electrostatic considerations.

Highly Multiply Charged Molecular Anions

Highly multiply charged anions of very large molecules such as proteins, oligonucleotides, and peptides are commonly observed in applied MS with electrospray and ion-spray techniques. Fenn and colleagues (*53*) developed the electrospray ionization method in which liquids are ejected into a drying gas that passes through a capillary. Charging of the ions in the electrospray occurs in a region between the capillary and a skimmer held at a high potential difference. The potential of liquid ionization techniques such as electrospray and ion spray or the ion vaporization technique is illustrated in a recent study by Covey *et al.* (*54*), who show the removal of up to 11 protons from a synthetic DNA molecule (mass = 4261 daltons) corresponding to 11 excess electrons on the resulting anion. Compton (*26*) has briefly reviewed this subject.

Henion and co-workers (*55*) have detected the dianion of 17B-estradiole disulfate using the ion-spray technique. This experimental method is now also routinely used to detect the illegal use of anabolic steroids in sporting events. Other sulfonates have been detected by Lai and Evans (*56*) using the electrohydrodynamic or ion evaporization technique. Multiply charged anion MS is also playing a role in the effort to sequence the human genome.

The encouraging theoretical evidence for the existence of isolated highly ionic molecular dianions, however, points to the need to identify small and medium-sized triply and higher charged negative systems that fit into the category of high ionicity of the bonding. Some qualitative arguments on the stability of multiply charged negative metal fluorides have been given earlier (*57*). However, a first promising attempt in this area based on the ionic model has been reported. A construction principle, which starts from a suitable structural base unit such as the dianionic MX_3^{2-} or MX_4^{2-} halides, enables the systematic design of stable highly multiply charged negative molecular ions in the gas phase (*52*). The atomic configuration of the particular base unit must be maintained because for small multiply charged molecular anions, the occurrence of stability to dissociation or to electron autodetachment or both strongly depends on how the composing atoms or groups of atoms are arranged.

This constraint effectively transfers the stabilizing effects fundamental to a particular atomic configuration (such as a dianion) to its multiply charged negative successors. In particular, proceeding from the bound dianionic alkali halides MX_3^{2-} as the structural base unit, the smallest pseudo-linear alkali halides that may support three, four, or more extra electrons in a long-lived negative ion state have been investigated (*52*, *58*). Detailed theoretical studies at the ab initio level of theory show that the highly ionic members from the series of smallest trianions that emerge from the construction principle, $M_2X_5^{3-}$, are stable with respect to fragmentation (Coulomb barrier height and width of ~0.1 eV and 2 to 5 Å, respectively) and loss of an extra electron (*58*) (Fig. 5). The $M_2X_5^{3-}$ ($\equiv[X_2M\text{–}X\text{–}MX_2]^{2-}$) ions in their ground state exhibit three spatially separated halogen "layers." Each of these layers can accomodate one of the extra electrons, effectively reducing their mutual repulsion. The occurrence of long-lived states for the trianions $M_2X_5^{3-}$ is primarily attributed to this spatial distribution of the extra charges and to available Coulomb attraction.

It is predicted (*58*) that for the higher negative charged successors of $M_2X_5^{3-}$ designed according to this construction principle, the sequence of metal and halogen layers as well as the highly ionic bonding character is preserved (Fig. 5A). The termination of the pseudolinear molecular chain strongly influences the stability of the multiply charged negative alkali halides to both fragmentation and electron autodetachment. In particular, symmetrically KF-terminated potassium fluorides may support up to seven extra electrons (*58*) (Fig. 5B). The smallest hepta-anion predicted to be stable with respect to fragmentation and electron autodetachment, $K_{12}F_{19}^{7-}$, includes 13 halogen layers. However, in the sequence of smallest unsymmetrically or KF_2-terminated chains, the structurally stable penta-anions represent the borderline with respect to instability toward electron loss (Fig. 5). Beyond pseudolinear multiply charged negative alkali halides, the construction principle (*52*) is predicted to allow the design of small, stable, truly two- and three-dimensional highly charged negative structures.

Conclusions

The field of multiply charged negative ions has blossomed. The existence of stable and metastable doubly charged negative clusters or small molecules, or highly multiply charged negative DNA molecules or metal-halogen clusters, is firmly established. The modern experimental and theoretical techniques available, along with the discovery of new molecular systems, makes doubly and highly multiply charged anions a promising area of research. The connection of gas-phase multiply charged anions to those known to exist in the condensed state likewise offers an exciting challenge for future research.

New developments in high-resolution laser photodetachment spectroscopy should allow accurate measurement of atomic and molecular EAs. Likewise, the explosive technical progress as well as the price reduction in the field of supercomputing hardware devices now routinely makes amenable accurate large-scale computations of the EA for rather large molecular systems by elaborate theoretical techniques. In many critical cases, the recent progress already has allowed experiment and theory to converge to commonly accepted (final) results.

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RESEARCH ARTICLES

Reconstitution of I_{KATP}: An Inward Rectifier Subunit Plus the Sulfonylurea Receptor

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A member of the inwardly rectifying potassium channel family was cloned here. The channel, called BIR (Kir6.2), was expressed in large amounts in rat pancreatic islets and glucose-responsive insulin-secreting cell lines. Coexpression with the sulfonylurea receptor SUR reconstituted an inwardly rectifying potassium conductance of 76 picosiemens that was sensitive to adenosine triphosphate (ATP) (I_{KATP}) and was inhibited by sulfonylureas and activated by diazoxide. The data indicate that these pancreatic β cell potassium channels are a complex composed of at least two subunits—BIR, a member of the inward rectifier potassium channel family, and SUR, a member of the ATP-binding cassette superfamily. Gene mapping data show that these two potassium channel subunit genes are clustered on human chromosome 11 at position 11p15.1.

ATP-sensitive potassium currents, I_{KATP}, were discovered in cardiac muscle (*1*) and later found in pancreatic β cells, pituitary tissue, skeletal muscle, brain, and vascular and nonvascular smooth muscle (*2*). I_{KATP} functions in secretion and muscle contraction by coupling metabolic activity to membrane potential. In pancreatic β cells, ATP-sensitive potassium channels (K_{ATP} channels) are crucial for the regulation of glucose-induced insulin secretion (*2, 3*) and are the target for the sulfonylureas, oral hypoglycemic agents widely used in the treatment of noninsulin-dependent diabetes mellitus (NIDDM) (*4*), and for diazoxide, a potassium channel opener. The sulfonylurea receptor (SUR) is a member of the ATP-binding cassette superfamily (*5*) with multiple transmembrane-spanning domains and two potential nucleotide-binding folds. Truncations of SUR that remove the second nucleotide-binding fold cause familial persistent hyperinsulinemic hypoglycemia of infancy (PHHI), a rare disorder of