

Multiply Charged Anions in the Gas Phase

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I. Introduction

The understanding of ions in classical chemistry is based on the experiences of chemists working with solids and solutions. When properties of ions are addressed, one often implies a surrounding environment that interacts with the respective ion. For example, the counterions are always present in crystals, and in solution the ions interact with the molecules of the solvent. Most of the experimental data on ions has been collected in experiments performed in the presence of counterions and solvent molecules. It is thus natural to ask how the ions are influenced by the surrounding environment and how their characteristics may change in its absence. To address these questions one has to examine the ions in the gas phase without influence of counterions or solvent molecules.

Obviously, isolated monocations possess an infinite lifetime in the gas phase, since they can only lose their positive charge and become neutral by catching an electron or a negatively charged particle. This general characteristic of monocations is exploited by mass spectrometry, which is a standard tool for analyzing organic and inorganic chemical compounds. Molecular multiply charged cations can also

exist but typically stabilize themselves by fragmentation into several monocationic parts, the so-called Coulomb explosion, which happens due to the strong electrostatic repulsion between the positive charges.¹

For monoanions, the situation is different. In contrast to cations, anions can stabilize themselves by spontaneous emission of an electron, the so-called autodetachment. Thus, it is not a priori clear whether anions exist in the gas phase as stable entities, i.e., whether a nucleus of charge N can bind $N + 1$ electrons. Today it is well-established that most of the elements form bound atomic negative ions,^{2,3} and there are only a few exceptions, for example, helium, nitrogen, beryllium, and magnesium. Most of the molecular monoanions known from condensed phases represent stable gas-phase systems as well, and only a few electronically unbound molecular anions are known, e.g. CO^- or N_2^- .⁴

Turning to multiply charged anions (MCAs), several MCAs exist in condensed phases, which are commonly observed on surfaces or as “building blocks” in solids such as $[A^{n-}][B^{n+}]$ salts. The most prominent examples for such MCAs are the “textbook” dianions and trianions CO_3^{2-} , SO_4^{2-} , or PO_4^{3-} , and even atomic dianions are postulated to exist, e.g., O^{2-} and S^{2-} (see, for example, refs 5 and 6). Although these species exist in condensed phases, it is rather unlikely that they represent stable gas-phase MCAs due to the strong electrostatic repulsion of the excess electrons. The Coulomb repulsion strongly favors the emission of one electron and supports the dissociation of the molecular framework into two monoanionic fragments. Indeed, this is the reason most of the small dianions spontaneously emit one electron when they are brought into the gas phase without stabilizing effects of counterions or solvent molecules.

Today, the nonexistence of bound atomic dianions is a well-established fact, but only little is known about metastable or resonance states of atomic dianions. Thorough quantum chemical treatment of the atomic dianions O^{2-} , S^{2-} , B^{2-} , and Al^{2-} has proven that the lifetimes of these species are on the order of several femtoseconds (ref 7 and references herein). No stable isolated diatomic or triatomic gas-phase dianions are known. As for atomic systems, some experimental and theoretical studies have been performed to examine the resonance states of such small dianions such as C_2^{2-} ,^{8–10} B_2^{2-} ,⁹ BN^{2-} ,¹¹ NO_2^{2-} ,¹² and CN_2^{2-} .¹³ Even the prominent MCAs known from condensed-phase chemistry are now well-established

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Andreas Dreuw was born in 1972 in Neuss, Germany. He received his undergraduate education in chemistry at the universities of Düsseldorf and Heidelberg. In 1996, he joined the research group of Prof. Cederbaum at the University of Heidelberg for his diploma as well as Ph.D. thesis. He received his Ph.D. in theoretical chemistry in May 2001 for the thesis "Unusual Anionic Systems Stabilized by Their Electrostatics and Spin". He is now part of the research group of Prof. Head-Gordon at the University of California at Berkeley as an "Emmy-Noether" fellow of the Deutsche Forschungsgemeinschaft. His research interests are singly and multiply charged anions in the gas phase and electronically excited states of small and large molecules.

to be unstable with respect to electron emission, such as CO_3^{2-} ,^{13–15} SO_4^{2-} ,^{14–18} or PO_4^{3-} .¹⁶ On the basis of these findings, it is natural to ask whether there exist small gas-phase MCAs at all, and if they do, what are the reasons for their existence in contrast to the "textbook" systems? To answer these questions, the experimental and theoretical search for small, stable MCAs in the gas phase and the examination of their geometric and electronic properties have quickly become the topic of a nowadays rapidly developing research field.

Today several reviews and feature articles dealing with MCAs in the gas phase are available in the

literature,^{19–21} which summarize the situation until 1995. Three feature articles focus on experimental techniques to examine multiply charged anions in the gas phase.^{1,22,23} In this review, we intend to give a complete overview of the research field of stable and long-lived multiply charged anions in the gas phase until today. In this context, long-lived means observable in a mass spectrometer. Most of the long-lived MCAs discussed in this review exhibit such astronomically huge lifetimes that they can in principle be considered as stable. Special emphasis is put on some of the most important and most recent developments in the research field. We stress the general differences between neutral systems and multiply charged anions, and the sometimes very unusual chemistry of multiply charged anions.

The review is organized as follows. In section II, we will give a concise overview of the research field of MCAs in the gas phase. In section III, we will present several recent developments in detail, and we first concentrate on MCAs for which both experimental and theoretical data are available. This is the case for the alkaline earth tetrahalides (section III.B), mixed silicon–carbon dianions (section III.A), and mixed beryllium–carbon dianions (section III.C). Then we turn to a recent theoretical examination on oxygen–carbon dianions, which have been shown to form dianions with a tetrahedrally coordinated oxygen atom in a mainly covalent bonding situation (section III.D). In section III.E, the question is addressed whether it is possible to stabilize the electronically unstable *closo*-hexaborate dianion $\text{B}_6\text{H}_6^{2-}$ by substitution of the hydrogen atoms through appropriate ligands. The most important experimental progress in the research field was the application of photodetachment photoelectron spectroscopy to MCAs, which will be outlined in section III.H. The repulsive Coulomb barrier, which is a general phenomenon in MCAs and closely connected to photoelectron spectroscopy, has recently been studied theoretically as well as experimentally. The main results are described in section III.G. In section III.H, we present the small molecular trianion $\text{N}(\text{BF}_3)_4^{3-}$, which has been found by theory to be a long-lived gas-phase MCA. Finally, we summarize some experimental and theoretical works that aim at the investigation of the influence of solvent molecules and counterions on the properties of MCAs (section III.I). These studies bridge the gap between gas phase and condensed phases. The review will be concluded by a brief outlook onto future perspectives in this blossoming research field (section IV).

II. Overview

Due to the strong Coulomb repulsion between the additional electrons of multiply charged anions (MCAs), *small* MCAs are unlikely to represent electronically stable entities. As already mentioned in the Introduction, most of the small di- and trianions known from condensed phases are unstable with respect to electron emission and thus emit spontaneously one electron, when they are brought into the gas phase. Obviously, the electrostatic repulsion decreases when the spatial size of the system in-

creases, and for this reason, it is not surprising that some time ago large dianionic molecules have been found to form stable isolated dianions. For example, the dianion of the dimer of benzo[*cd*]pyren-6-one, a large organic ketone, was the first long-lived doubly charged negative ion to be observed in the gas phase.²⁴ Since then many observations of such large organic dianionic systems have been reported. One of them is the observation of long-chain aliphatic dicarboxylate dianions,²⁵ which obviously acquire their electronic stability through charge localization at the ends of the chain in separate electron affine carboxylate groups. The dianions of phthalic, isophthalic, and terephthalic acid as well as the dianions of 2,3- and 2,6-naphthalenedicarboxylic acid have very recently found application in the selective generation of the corresponding distonic radical anions of benzene and naphthalene and allowed the derivation of thermochemical data for these anions.²⁶

Fullerene dianions, first of all C_{60}^{2-} and C_{70}^{2-} , have attracted the interest of experimental and theoretical groups. The dianions were observed in mass spectrometric experiments, implying a minimum lifetime of at least 10^{-3} s.^{27–30} The experimental observation of C_{60}^{2-} seems to contradict the theoretical prediction that C_{60}^{2-} possesses a negative electron detachment energy, i.e., it cannot bind a second extra electron.^{31–34} It is astonishing that a molecule as large as C_{60} cannot form a stable gas-phase dianion! Electronic stability of the dianion can be reached when the C_{60} cage is fluorinated to give $C_{60}F_{48}^{2-}$, which has been experimentally found to possess a positive electron detachment energy of about 2 eV.³⁵

The experimental observation of C_{60}^{2-} could finally be explained by the existence of a repulsive Coulomb barrier. This barrier hinders the emission of one of the excess electrons and is invoked by the combination of the long-range repulsion and the short-range electron–molecule binding that the emitted electron experiences.^{27,34} Therefore, an emitted electron must tunnel through this barrier to leave the molecule, which can be a very unlikely process giving rise to a finite but relatively long lifetime of the metastable species. We will return to the repulsive Coulomb barrier in section III.G and discuss its nature in more detail.

The research field of multiply charged negative ions in the gas phase received great impetus by the experimental observation of small carbon cluster dianions by Schauer et al. in 1990.³⁶ This observation may even be seen as the actual starting point of the research field. The dianions were produced by sputtering graphite and measured with a double-focusing mass spectrometer. Conclusive experimental evidence was presented that long-lived covalent C_n^{2-} ($n = 7–28$) clusters exist in the gas phase. Meanwhile, the findings of Schauer et al. have been confirmed by other experimental groups^{37–39} as well as theory.^{40–46} Thorough theoretical examination of these C_n^{2-} dianions has confirmed the onset of stability with the seven atomic cluster C_7^{2-} , which is up to now the smallest known covalent free stable dianion.⁴² While even n isomers of the C_n^{2-} dianions possess primarily linear geometries,⁴¹ the odd n

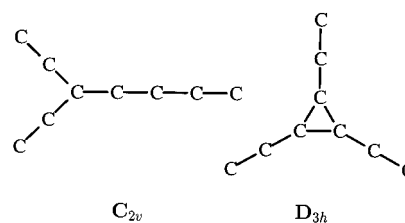


Figure 1. Geometrical structures of the only C_9^{2-} isomers that are stable with respect to electron autodetachment.⁴³

isomers, above all C_7^{2-} and C_9^{2-} , possess only branched geometrical isomers, which can bind their two excess electrons.^{42,43} The stable isomers of C_9^{2-} are displayed in Figure 1.

The only electronically stable isomer of the smallest pure carbon dianion C_7^{2-} is a D_{3h} symmetric system, which possesses a so-called “center-ligand sphere” structure, i.e., it consists of one central C atom to which three electron affine C_2 units are bound.⁴² This dianion is better referred to as $C(C_2)_3^{2-}$ and is closely related to the C_{2v} symmetric C_9^{2-} isomer.

A “center-ligand sphere” structure seems to be favorable to stabilize two excess electrons and to support the formation of bound dianionic and possibly higher negatively charged states. Indeed, many multiply negatively charged complexes of central metal atoms surrounded by several halide ligands are known in chemistry of condensed phases, e.g. MnF_5^{2-} or $FeCl_6^{3-}$.⁵ Several early theoretical studies deal with the electronic stabilities of dianionic metal hexafluoride complexes such as AuF_6^{2-} ,⁴⁷ CrF_6^{2-} and MoF_6^{2-} ,⁴⁸ PtF_6^{2-} ,⁴⁹ SiF_6^{2-} ,⁵⁰ and ZrF_6^{2-} ,⁵¹ but the structural stability of these systems is not addressed. Ewig and van Wazer provided theoretical evidence for the chemically unusual CF_6^{2-} to be stable with respect to electron autodetachment as well as with respect to fragmentation.⁵²

Recently, ZrF_6^{2-} has been observed experimentally in a mass spectrometer and its EDE has been proven by photodetachment photoelectron spectroscopy to be 3 eV.⁵³ An extensive experimental study of the electronic stability of the hexahalide complexes MX_6^{2-} ($M = Re, Os, Ir$ or Pt ; $L = Cl$ or Br) has revealed that all these species represent stable gas-phase dianions.⁵⁴ In line with these experiments, also $Re_2Cl_8^{2-}$ has been studied by photodetachment photoelectron spectroscopy.⁵⁵ The electronic stability of $Re_2Cl_8^{2-}$ has been proven, and evidence for the existence of a Re–Re quadruple bond is given.

Theoretical investigation of the octafluoride complexes SeF_8^{2-} , TeF_8^{2-} , and $TlCl_5^{2-}$ has demonstrated their longevity with respect to loss of a fluorine anion and their stability with respect to electron autodetachment.⁵⁶ TeF_8^{2-} exhibits a remarkably large electron detachment energy of about 5 eV.⁵⁶ Also the triply charged closed-shell anions MF_6^{3-} ($M = Sc, Y$, or La) have been examined,^{57,51} but none of these trianions has been found to be clearly stable with respect to electron emission or fragmentation.

The *smallest* known long-lived dianions so far are the alkaline trihalides AX_3^{2-} ($A = Li, Na$, or K ; $X = F$ or Cl), whose existence has been predicted theoretically by Scheller and Cederbaum,^{15,58} but which could so far not be observed experimentally, and their

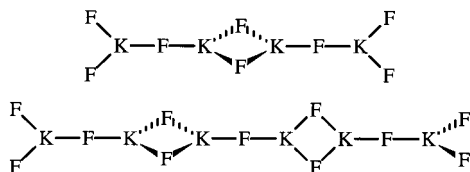


Figure 2. Chainlike structures of the highly ionic alkali halide MCAs $K_4F_8^{4-}$ (top) and $K_6F_{11}^{5-}$ (bottom). Both the tetraanion and the pentaanion have been found to be stable with respect to electron emission as well as fragmentation.⁶⁶

detection remains a challenge to experiment. It has been shown that the temperature plays a relevant role for the dissociation lifetime of these dianions.⁵⁹ In contrast, the dianionic earth alkaline tetrahalides EX_4^{2-} ($E = \text{Be, Mg, or Ca}$; $X = \text{F or Cl}$) have been predicted as early as 1991^{60,61} and could recently be observed in a mass spectrometric experiment⁶² (see also section III.A). Both classes of dianions are derived by expansion of the coordination sphere of the monoanions AX_2^- and EX_3^- , respectively, and not by addition of an electron to the monoanions AX_3^- and EX_4^- , neither of which exist as stable entities themselves. The electronic and structural stability of the dianions AX_3^{2-} and EX_4^{2-} is due to the high ionicity of the systems and can be understood in the framework of an “ionic model”.^{15,58} The smallest AX_3^{2-} systems possess starlike D_{3h} symmetric structures, in which three singly negatively charged halide ligands are bound to a central alkali metal cation. This structural arrangement guarantees that the electrostatic attraction between halide anions and the alkali metal cation always exceeds the repulsion between the ligands by a factor of $\sqrt{3}$. This polarization pattern is also found in the above-mentioned stable covalent carbon cluster dianions C_7^{2-} and C_9^{2-} ^{42,43} and seems to be a requirement for their electronic stability.

On the basis of the results for the purely ionic AX_3^{2-} dianion, a general construction principle could be derived to generate highly multiply charged negative molecular ions in the gas phase.⁶³ Following this construction scheme, long-lived dianions of general formula $A_2X_4^{2-}$ ($A = \text{Li, Na or K}$; $X = \text{F or Cl}$) have been predicted⁶⁴ and long-lived trianions as small as $A_2X_5^{3-}$ have been found.⁶⁵ Even highly charged quasi-linear alkali halide chains have been reported to represent stable entities in the gas phase,⁶⁶ e.g. $K_4F_8^{4-}$ or $K_6F_{11}^{5-}$ (Figure 2).

Experimentally, large alkali halide cluster dianions with general formula $A_nX_{n+2}^{2-}$ ($n \geq 5$) have been recently observed using an electrospray time-of-flight mass spectrometer.⁶⁷ These cluster dianions were assigned to three-dimensional crystal-like structures by density-functional theory calculations.⁶⁷

Small linear doubly charged anions, e.g., $SMgS^{2-}$, $SCCS^{2-}$, and $OBeOBeO^{2-}$, have been extensively studied theoretically by Boldyrev and Simons.⁶⁸ On the basis of their results, they excluded the existence of linear dianionic species with less than five constituting atoms. They have found the linear dianion $SMgSMgS^{2-}$ to possess a vertical electron detachment energy of about 0.2 eV, but neither stability with respect to dynamical electron loss nor

stability with respect to fragmentations have been considered.

Several theoretical and experimental studies deal with the stability of sulfur and sulfoxy dianions S_n^{2-} and $S_nO_m^{2-}$, respectively. Early theoretical studies have shown that the sulfate dianion SO_4^{2-} does not represent a stable dianion in the gas phase^{14,16} but needs at least three water molecules to stabilize its excess negative charges.^{18,69} So far, the smallest observed sulfoxy dianions have been dithionate $S_2O_6^{2-}$ and peroxydisulfate $S_2O_8^{2-}$,^{18,70} which are well-known from the chemistry of condensed phases. The experimental findings have been confirmed by thorough quantum chemical treatment.¹⁷ Chainlike sulfur dianions S_n^{2-} , as they exist in polysulfide solutions, are predicted to be stable with respect to electron autodetachment when the chain possesses at least seven atoms; i.e., S_7^{2-} is the smallest free stable sulfur dianion.⁷¹

Another class of long-lived gas-phase dianions represent the silicon–oxygen clusters $Si_mO_n^{2-}$ studied by Sommerfeld et al., who could not clearly assign electronic stability to the $Si_2O_4^{2-}$ dianion⁷² but found two long-lived isomers of $Si_2O_5^{2-}$.⁷³

Searching for new stable dianions in the gas phase with ab initio methods,^{74,75} has revealed mixed silicon–carbon dianions $Si_mC_n^{2-}$ (see also section III.B). The smallest theoretically predicted stable dianion of this class is a D_{3h} symmetric, starlike SiC_6^{2-} dianion, which is closely related to the smallest carbon dianion C_7^{2-} . Furthermore, also stable chainlike SiC_8^{2-} and $Si_2C_6^{2-}$ dianions have been found to be free, stable dianions. Recently, the existence of the silicon–carbon dianions has been confirmed experimentally by Gnaser, who produced the dianions by sputtering a SiC specimen and detected SiC_6^{2-} in a mass spectrometer.⁷⁶

Similar to the generation of mixed-silicon carbon dianions, Klein and Middleton produced mixed beryllium–carbon dianions BeC_{2n}^{2-} ($n = 2-7$) by sputtering a mixture of graphite and Be metal and identified the dianions with accelerator mass spectrometry and Coulomb explosion imaging⁷⁷ (see also section III.C). Meanwhile the existence of the BeC_n^{2-} dianions has been confirmed experimentally by Berkovits et al., who further analyzed BeC_6^{2-} by photodissociation studies.⁷⁸ Theoretical examination of the mixed beryllium–carbon dianions has revealed that the smallest observed species BeC_4^{2-} is probably unstable with respect to electron loss but exhibits a long lifetime due to its repulsive Coulomb barrier,⁷⁹ which is displayed in section III.G in Figure 17. The first clearly stable dianion is BeC_6^{2-} . In contrast to the smallest free stable carbon dianions or mixed silicon–carbon dianions, the BeC_n^{2-} dianions exhibit strictly linear structures.⁷⁹

Analogously, oxocarbon dianions have been examined theoretically with ab initio methods (see also section III.D⁸⁰⁻⁸²), and a D_{3h} symmetric starlike isomer of OC_6^{2-} , better referred to as $O(C_2)_3^{2-}$, has been found to be the smallest stable dianion of this class of dianionic systems.^{80,82} The larger OC_8^{2-} dianion possesses several isomers representing stable gas-phase dianions.⁸² Among them there is the

remarkable isomer $O(C_2)_4^{2-}$, which possesses a tetrahedrally coordinated central oxygen atom. This dianion is to our best knowledge the first single molecule that has a tetrahedrally coordinated oxygen atom in a mainly covalent bonding situation. Substituting the C_2 units of the $O(C_2)_3^{2-}$ and $O(C_2)_4^{2-}$ cluster dianions with isoelectronic BN units has yielded similar results. A free stable starlike $O(BN)_3^{2-}$ dianion has been found, and the existence of a tetrahedral $O(BN)_4^{2-}$ isomer has been confirmed.

Monocyclic oxocarbon dianions $C_nO_n^{2-}$ ($n = 3-6$) have been investigated with respect to their aromaticity.⁸³ The structure of these dianions consists of an n membered carbon ring, and a carbonyl or enolic oxygen is attached to each carbon atom. It has been shown that these systems are clearly aromatic with decreasing aromaticity toward the larger systems. Although these dianions are well-known in the chemistry of condensed phases, they are not stable with respect to electron emission in the gas phase. Exchange of the oxygen atoms with acetylide C_2 groups leads to related pure carbon dianions. The smallest member of these monocyclic systems is the previously discussed D_{3h} symmetric isomer of C_9^{2-} shown in Figure 1. A recent theoretical study addresses the question whether this electronically stable dianion and its higher homologues, e.g. a four-membered carbon ring with a C_2 unit on each carbon, possess also aromatic character.⁸⁴

Extensive theoretical effort has been made to investigate dianionic *closo*-borate clusters, which are now known to be unstable with respect to electron emission up to a size of 12 boron atoms.^{85,86} $B_{12}H_{12}^{2-}$ is the smallest stable gas-phase dianion of this class. $B_{13}H_{13}^{2-}$ is again unstable, but from that size on all larger *closo*-borates represent electronically stable systems. The aromaticity of the *closo*-borates as well as their relative stabilities has been studied in several theoretical works.^{87,86} In a recent theoretical investigation the question is addressed whether it is possible to stabilize the electronically unstable systems $B_5H_5^{2-}$ and $B_6H_6^{2-}$ by substitution of the hydrogen atoms through appropriate ligands (see section III.E).⁸⁸ It has been shown that CN and BO ligands strongly stabilize the excess negative charges, such that dianions such as $B_5(CN)_5^{2-}$, $B_5(BO)_5^{2-}$, $B_6H_2(CN)_4^{2-}$ and $B_6(CN)_6^{2-}$, or $B_6(BO)_6^{2-}$ represent stable gas-phase dianions and should thus be observable in mass spectrometric experiments. Note, that while *closo*-hexaborate systems have already been synthesized in condensed phases, *closo*-pentaborate derivatives have until now evaded preparation.⁸⁹

Multiply charged metal cluster anions, so-called Zintl anions M_m^{n-} , have been objects of experimental and theoretical studies. As early as 1993 theoretical examinations of multiply charged metal clusters have been performed by Yannouleas and Landman, who investigated multiply charged sodium cluster anions using shell-corrected versions of the uniform jellium background model and the local density approximation.^{90,91} On the basis of their results, spherical symmetric Na_{43}^{2-} , Na_{205}^{3-} , and Na_{255}^{4-} are predicted to be the first stable sodium cluster dianions, trianions, and tetraanions, respectively, but smaller

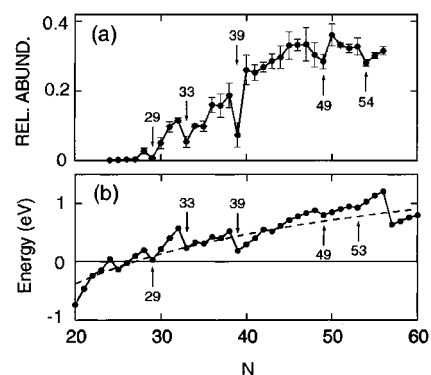


Figure 3. Experimental yields of silver cluster dianions Ag_n^{2-} plotted versus cluster size (upper part (a)) are compared with calculated electron detachment energies of the dianions at $T = 300$ K (lower part (b)). The experimental and theoretical data are in excellent agreement. Adapted from ref 96. Copyright 2001 American Physical Society.

MCA, such as Na_{35}^{2-} , may be observable due to the repulsive Coulomb barrier, which hinders the emission of one of the excess electrons (see section III.G).

Recently, the experimental observation of small gold cluster dianions Au_n^{2-} ($n = 12-28$) in a time-of-flight mass spectrometer has been reported after their production by laser vaporization of gold metal, storage of Au_n^- in a Penning trap, mass selection, and electron attachment.^{92,93} These observations have been confirmed theoretically, indicating that Au_{12}^{2-} is the smallest system that possesses a positive electron detachment energy.⁹⁴ These authors also predict the existence of a stable Ag_{24}^{2-} cluster dianion.⁹⁴

Using the same experimental setup as for the gold clusters, multiply charged titanium cluster anions Ti_n^{m-} ($m = 1, 2, 3$) have been produced and Ti_{55}^{2-} further analyzed by photodetachment.⁹⁵

A combined theoretical and experimental study of dianionic silver and trianionic gold clusters reassured the onset of stability of silver cluster dianions Ag_n^{2-} with $n \geq 27$ and gives conclusive evidence for the existence of Au_n^{3-} ($n \geq 54$).⁹⁶ The calculated electron detachment energies for the silver cluster dianions Ag_n^{2-} are in excellent agreement with the experimental yields of clusters (Figure 3). Laser ablation of metal surfaces is a simpler approach to yield multiply charged anions in the gas phase. Application of this technique to gold and lead made the observation of doubly charged gold and lead cluster anions Au_n^{2-} ($n \geq 29$) and Pb_n^{2-} ($n \geq 35$), respectively, possible. Also triply charged lead cluster anions Pb_n^{3-} ($n \geq 76$) have been observed.⁹⁷

Besides the metal cluster trianions described in the last paragraph and the already mentioned highly ionic $Li_2F_5^{3-}$ trianion, higher than doubly charged spatially small species are scarce. The theoretical search for a small molecular trianion, which possesses mainly covalent bonds, culminated in the discovery of a long-lived $N(BF_3)_4^{3-}$ system (see section III.H).⁹⁸ Although this trianion is neither stable with respect to electron emission nor thermodynamically stable with respect to fragmentation into $N(BF_3)_3(BF_2)^{2-}$ and F^- , the system is found to be long-lived with respect to both. The emission of one of the excess

electrons is hindered by the repulsive Coulomb barrier, and the splitting off of a fluorine anion is analogously hindered by a very broad potential barrier, implying a long lifetime for the trianionic $\text{N}(\text{BF}_3)_4^{3-}$ molecule. On the basis of these results, the $\text{N}(\text{BF}_3)_4^{3-}$ trianion has been predicted to be observable in a mass spectrometric experiment.

Recently, very important progress in the experimental examination of MCAs in the gas phase has been made by Wang et al., who managed to obtain photodetachment photoelectron spectra of multiply charged negative ions. They combined an electro-spray ionization source which has been proven to be a useful tool to generate free MCAs, for example, $\text{Cr}_2\text{O}_7^{2-}$ ⁹⁹ or $\text{Mo}_8\text{O}_{26}^{4-}$,¹⁰⁰ with a magnetic-bottle time-of-flight photoelectron spectrometer.¹⁰¹ In 1998, Wang et al. reported the first photodetachment photoelectron spectrum of a multiply charged anion, the spectrum of the citric acid dianion.¹⁰² Since then, several dianions have been studied with this new apparatus: linear aliphatic dicarboxylate dianions,^{103–105} benzene dicarboxylate dianions,¹⁰⁶ acetylene dicarboxylate and succinate,¹⁰⁷ SO_4^{2-} ⁶⁹ and $\text{S}_2\text{O}_8^{2-}$,⁷⁰ MX_6^{2-} ($\text{M} = \text{Re}, \text{Os}, \text{Ir}, \text{or Pt}; \text{X} = \text{Cl or Br}$)⁵⁴ and $\text{Re}_2\text{Cl}_8^{2-}$,⁵⁵ MX_4^{2-} ($\text{M} = \text{Pt or Pd}; \text{X} = \text{Cl or Br}$),^{23,108} ZrF_6^{2-} ,⁵³ and the tetraanion of copper phthalocyanine tetrasulfonate^{109,110} (see also section III.F).

Investigating the photodetachment photoelectron spectra of the linear aliphatic dicarboxylate dianions $^-\text{OOC}(\text{CH}_2)_n\text{COO}^-$ ($n = 3–10$)^{103–105} has revealed photon energy dependent features, indicating the presence of tunneling processes. This observation is a direct experimental proof of the existence of the repulsive Coulomb barrier (RCB) in multiply charged anions. Along with these experimental studies, a theoretical examination of the electronic stability of the dianionic dicarboxylates oxalate, malonate, and succinate appeared in the literature supporting their instability.¹¹¹

The existence of the RCB was further corroborated by the observation of a negative electron binding energy in MCAs, when Wang et al. recorded the spectra of the copper phthalocyanine tetrasulfonate tetraanion.^{109,110} Although the highest occupied molecular orbital of the tetraanion is unbound, the electrons are held back from being emitted by the RCB. A similar observation has been made for the PtCl_4^{2-} and PtBr_4^{2-} systems, both of which have been found to possess adiabatic electron detachment energies of -0.25 and -0.05 eV, respectively,^{108,112} indicating that the dianions are unstable with respect to electron autodetachment. Similarly, Weis et al. have studied the stability of the MX_4^{2-} ($\text{M} = \text{Pt or Pd}; \text{X} = \text{Cl or Br}$) systems using a penning trap.¹¹³ They could confirm the electronic metastability of PtCl_4^{2-} , which undergoes electron emission on a seconds time scale, while all other systems did not show any decay. In line with these experiments, platinum–cyanide complexes $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_6^{2-}$ have been investigated using collision-induced dissociation techniques.¹¹⁴ It has clearly been shown that $\text{Pt}(\text{CN})_4^{2-}$ is the smallest stable dianion of this class and $\text{Pt}(\text{CN})_3^{2-}$ possesses a lifetime of less than 4 μs .

As already mentioned above, the RCB is a general phenomenon in MCAs and hinders the emission of one of the excess electrons. Thus, the existence of the RCB is the reason for the observability of electronically unbound states of MCAs in mass spectrometric experiments. Its existence can simply be explained by the electrostatic forces present, since the emitted electron experiences a short-range binding and a long-range repulsion, which both combine to a repulsive barrier potential. The RCB has been invoked for the first time by Compton and others when discussing the observability of electronically unstable fullerene dianions (see above)^{30–35} and has been estimated theoretically for sodium clusters.^{90,91} Although the electrostatic forces dominate the appearance of the RCB in compact dianions,^{103,115} the RCB is a complicated nonlocal and energy-dependent potential that is not straightforward to compute.¹¹⁶ A formally exact theory for the RCB exists that is based on Green's function formalism of scattering.¹¹⁶ Approximation schemes to determine local RCB potentials are also available. It has been shown that the local potentials are meaningful approximations for the true RCB, when the system under investigation is spatially extended.¹¹⁶ The application of the local approximation schemes to several systems, e.g., Ag_n^{2-} ,⁹⁶ BeC_4^{2-} ,⁷⁹ PtCl_4^{2-} ,¹¹³ or C_8^{2-} ,¹¹⁶ and calculation of the lifetime within semiclassical WKB theory has given reasonable estimates for the respective lifetimes of the MCAs.

An electrostatic dipole potential with a dipole moment greater than 1.625 D possesses an infinite number of bound anionic states within the Born–Oppenheimer approximation.¹¹⁷ Recently, Sarasola et al. have investigated the critical dipole strength that supports bound dianionic states¹¹⁸ and have found a value of about 2.6 D. Skurski et al. have shown that the critical dipole strength for binding two electrons strongly depends on the charges of the dipole. For small charges the critical dipole strength tends to infinity, while for large charges the critical dipole moment seems to approach a limit below 2 D.¹¹⁹

Along this line of thought, investigations for real molecules that can bind two excess charges by their dipole moment have been performed. Skurski et al. reported that the linear anionic molecule $[\text{LiCN}\cdots\text{LiCN}\cdots\text{LiCC-PF}_5]^-$ possesses a huge dipole moment of ca. 36.5 D, which can bind a second extra electron by its dipole moment. Such classes of dianions are now understood to be mixed valence–dipole bound dianions, since one excess electron is valence and the second dipole bound.¹²⁰ Recently, theoretical evidence was given for the existence of a bidipole-bound dianion.¹²¹ Although the parent neutral molecule possesses no net dipole moment, two excess electrons are bound to two polar ends with opposite dipole direction of a linear molecule, both ends of which are capable of binding one electron in their dipole field. The first molecule that can bind two extra electrons at one dipole site has also been discovered not long ago.¹²²

In some recent experimental and theoretical investigations, the influence of solvent molecules and counterions on the geometrical and electronic proper-

ties of multiply charged anions has been studied (see also section III.I). The hydration of the electronically unstable sulfate dianion SO_4^{2-} has been examined by mass spectrometry,¹⁸ as well as photodetachment photoelectron spectroscopy.⁶⁹ Unequivocally, it has been reported that at least three water molecules are needed to stabilize SO_4^{2-} and that the properties of the hydrate are dominated by the sulfate dianion. Analogously, the hydrates of dianionic diphosphates¹²³ and of dicarboxylate dianions¹²⁴ have been investigated experimentally. A recent theoretical quantum chemical treatment of MCAs in water has clearly shown that unstable MCAs are strongly stabilized in aqueous solution.¹²⁵ For example, sulfate is electronically stabilized by about 11 eV to give rise to a very stable entity.

In a similar fashion, the influence of counterions on MCAs has been addressed. Wang et al. found within their experimental studies of singly and doubly charged alkali metal sulfate ion pairs that the electronic features of the cation–dianion complexes are all very similar and correlate well with the molecular orbital energy levels of “free” SO_4^{2-} .¹²⁶ In a recent mass spectrometric experiment $[\text{CsC}_9]^-$ complexes have been used to selectively produce pure carbon dianions in the gas phase by collision-induced dissociation.¹²⁷ A theoretical study of the structures of the cation–dianion complexes $[\text{CsC}_n]^-$ ($n = 7, 9$) between Cs^+ and pure carbon dianions C_7^{2-} and C_9^{2-} has given clear evidence that the cesium cation interacts only electrostatically with the dianions and strongly stabilizes them.¹²⁸ The structures of the $[\text{CsC}_n]^-$ cation–dianion complexes give first hints on possible crystal structures or the structure of ion pairs in solution.

III. Recent Developments

A. Alkaline Earth Tetrahalides

As early as 1991 the existence of the free, stable beryllium tetrafluoride dianion BeF_4^{2-} has been predicted theoretically by Weikert et al.⁶⁰ An extension of their studies revealed that the isoelectronic species of the heavier elements of the alkaline earth metals and halogenes EX_4^{2-} ($\text{E} = \text{Be, Mg or Ca}$; $\text{X} = \text{F or Cl}$) represent as well long-lived dianions in the gas phase.⁶¹ As an example, the tetrahedral structures of BeF_4^{2-} and MgF_4^{2-} are displayed in Figure 4.

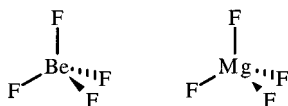


Figure 4. BeF_4^{2-} and MgF_4^{2-} have been predicted theoretically by Weikert et al.,^{60,61} and afterwards, their existence has been confirmed experimentally by Middleton and Klein.⁶²

Using high-level ab initio methods, they examined the stability of the T_D symmetric dianions with respect to electron emission and with respect to dissociation. All examined dianions correspond to electronically stable systems; for instance, the vertical EDE of BeF_4^{2-} has a value of about 1.8 eV and

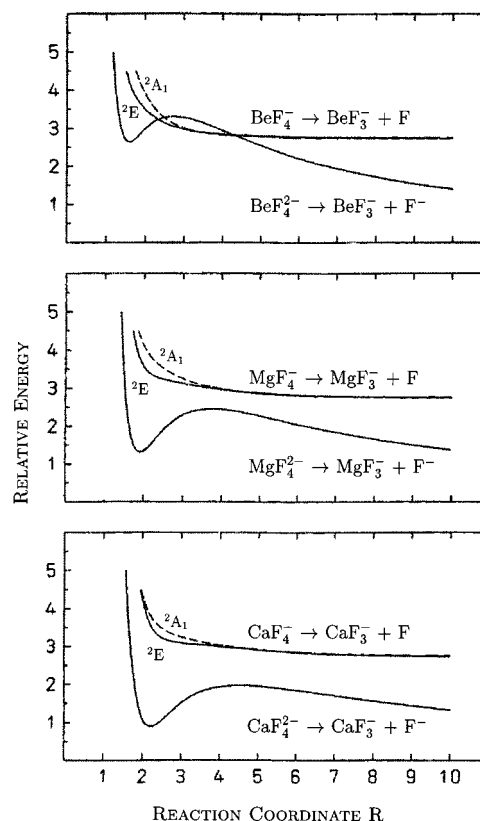


Figure 5. Energetically lowest potential energy surfaces of the dianionic alkaline earth tetrafluorides EF_4^{2-} ($\text{E} = \text{Be, Mg or Ca}$) and the corresponding monoanions EF_4^- along their dissociation pathways into F^- and F , respectively, and the trifluoride anions EF_3^- . The geometrical parameters of the dianionic fragmentation channels have been optimized along the paths. The reaction coordinate R is given in Å, and the energies relative to the dissociation limit are in eV. Reprinted with permission from ref 61. Copyright 1993 American Institute of Physics.

increases with increasing ionicity of the systems to about 3.3 eV for CaF_4^{2-} . Electron loss can thus be excluded as relevant decay channel for the dianionic alkaline earth tetrahalides.

In contrast, all these systems are thermodynamically unstable with respect to fragmentation into EX_3^- and X^- , i.e., splitting off one halide anion. For example, the energy of the fragments F^- and BeF_3^- is about 2.6 eV lower than the total energy of the dianion BeF_4^{2-} (Figure 5). Calculation of the dissociation pathways of the dianions has shown that an energy barrier hinders the fragmentation of the dianions, which increases from 0.6 to 1.2 eV from the lighter BeF_4^{2-} to the heavier CaF_4^{2-} . Similar results have been found for the chloride systems.

Except for BeF_4^{2-} , the total energies of the monoanions EX_4^- ($\text{E} = \text{Mg or Ca}$) are always larger than the energy of the dianions along the dissociation pathways, but arguments are given that the crossing of the BeF_4^- and BeF_4^{2-} PES (upper part of Figure 5) may be an artifact of the applied SDCI (singles plus doubles configuration interaction) method.⁶¹ By shifting the BeF_4^- such that the asymptotic tail correctly describes the electron affinity of the fluorine atom, the crossing of the BeF_4^- and BeF_4^{2-} curves disappears.

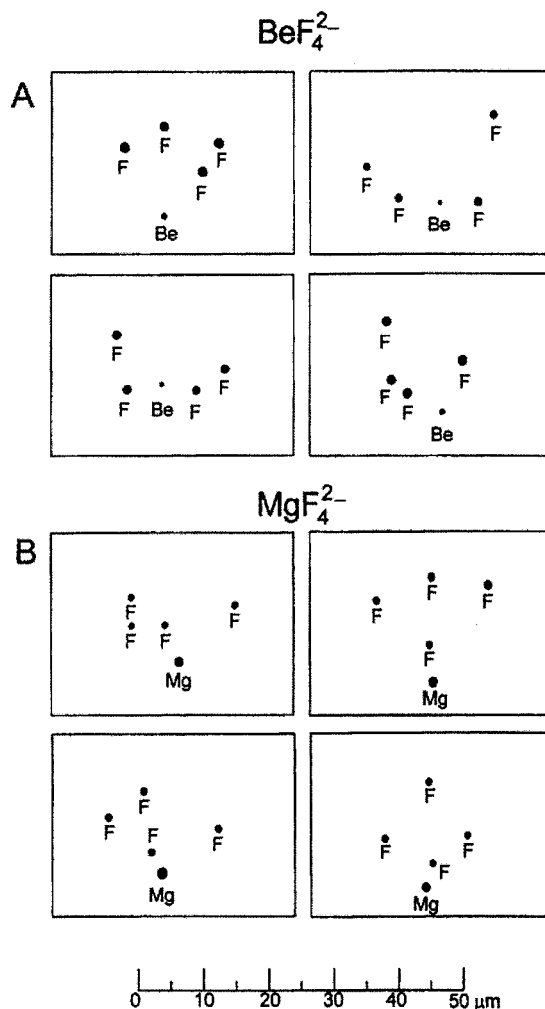


Figure 6. Coulomb explosion images of BeF_4^{2-} (A) and MgF_4^{2-} (B). Each box represents a single photograph that has been oriented so that the track left by the alkaline earth metal ion, readily distinguishable from the fluorine ion, is at the bottom. Reprinted with permission from ref 62. Copyright 1999 American Physical Society.

Although the absolute barrier heights are only small compared with neutral systems, the corresponding widths of the barriers are very large (several Å) due to the Coulomb repulsion between the anionic fragments. Therefore, the corresponding tunneling process of the fluorine anion through the broad barrier is very unlikely and the lifetime of the dianions with respect to fragmentation is extremely long. On the basis of these findings, Weikert et al. have predicted the existence of the long-lived alkaline earth tetrahalides in the gas phase.^{60,61}

The explicit calculation of the dissociation lifetimes of the alkaline earth tetrahalide dianions has confirmed their long lifetimes.⁵⁹ Moreover, the number of long-lived vibrational states increases markedly when going from BeF_4^{2-} to the heavier CaF_4^{2-} by a factor of 10^5 . Therefore, the observation of the heavier species is more likely than the lighter ones, since the temperature is usually very high in typical experimental setups, due to the highly energetic generation processes of the dianions, e.g., sputtering or laser ablation.

Nevertheless, 8 years after the theoretical prediction of BeF_4^{2-} and MgF_4^{2-} , Middleton and Klein have

reported their observation in a mass spectrometer.⁶² They have employed a cesium sputter source to produce the dianions in the gas phase by sputtering BeF_2 or MgF_2 and used accelerator mass spectrometry to identify the dianions. They have provided further experimental evidence for the existence of the gas-phase dianions BeF_4^{2-} and MgF_4^{2-} in the form of Coulomb explosion images (CEI) (Figure 6). The CEIs allow one to distinguish between the elements and give hints on the structure of the systems. Having a closer look at Figure 6, the composition of the detected clusters BeF_4^{2-} and MgF_4^{2-} is evident, and the structure is likely to be tetrahedral.

The experimental observation of the theoretically predicted alkaline earth tetrahalides finally proves their existence, and even more important, places confidence into the theoretical formalism applied to investigate a large number of multiply charged anions by ab initio methods.

B. Mixed Silicon–Carbon Dianions

Searching for new free stable gas-phase dianions, mixed silicon–carbon dianions have been theoretically investigated with standard quantum chemical methods.^{74,75} Since pure carbon clusters form free stable dianions (see section II), substitution of one or two carbon atoms of these dianions with silicon may lead to stable isoelectronic silicon–carbon dianions.

The smallest silicon–carbon dianion that has been found to be a clearly stable gas-phase dianion is a D_{3h} symmetric starlike SiC_6^{2-} system (Figure 7). This system is structurally closely related to the smallest C_7^{2-} carbon dianion, in which the central carbon atom is replaced by Si.

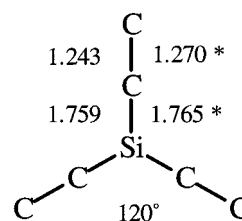


Figure 7. Geometrical parameters of the smallest stable silicon–carbon dianion SiC_6^{2-} . The dianion is D_{3h} symmetric and has been optimized at the single-particle level of RHF (restricted Hartree–Fock) as well as at the highly correlated level of CCSD(*) (coupled cluster singles plus doubles).⁷⁵

Due to the optimized bond lengths, the Si–C bonds of the SiC_6^{2-} dianion possess mainly single bond character, while the C–C bonds are clearly triple bonds. Thus, it can be seen as central Si atom to which three electron affine C_2 units are attached.

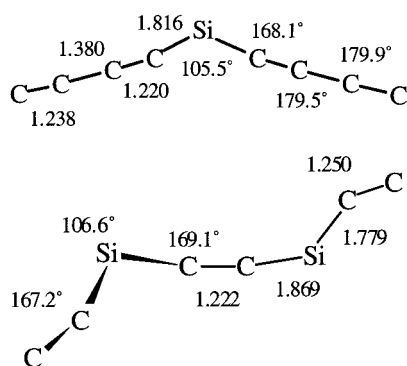
At highly correlated levels of theory, vertical as well as dynamic electron emission can be excluded for SiC_6^{2-} ; i.e., it is clearly stable with respect to electron emission (Table 1), since the vertical EDE has values of around 1.1 eV at the best theoretical levels and the adiabatic EDE is clearly positive.

Due to the covalent character of the silicon–carbon dianions, fragmentations do not play relevant roles for the decay of the silicon–carbon dianions. For

Table 1. Vertical and Adiabatic Electron Detachment Energies (EDE) of the Star-like Dianion SiC_6^{2-} and the Chain-like Dianions $\text{Si}_2\text{C}_6^{2-}$ and SiC_8^{2-} at Different Levels of Theory

theoretical method ^a	EDE/eV		
	SiC_6^{2-}	$\text{Si}_2\text{C}_6^{2-}$	SiC_8^{2-}
vertical			
KT	1.77	1.55	1.57
ΔSCF	1.08	1.12	1.35
ΔMP2	1.98		
ΔSDCI	1.27	1.10	1.09
ΔCCSD	1.05		
OvGF	1.24	0.98	
adiabatic			
ΔSCF	0.587	0.73	0.04
ΔSDCI	0.861	0.75	

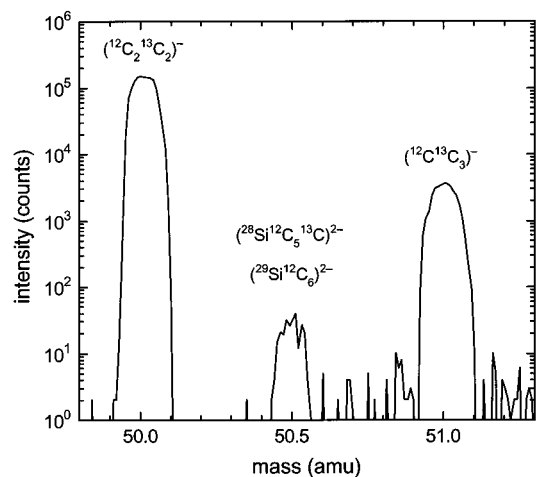
^aThe most reliable numbers are those at the ΔCCSD (coupled clusters singles plus doubles) and OvGF (outer valence Green's function) levels of theory. (The data are taken from).^{74,75}

**Figure 8.** Geometrical structures of the chainlike silicon-carbon dianions $\text{Si}_2\text{C}_6^{2-}$ (bottom) and SiC_8^{2-} (top), which both represent stable dianions in the gas phase. The SiC_8^{2-} is a planar C_{2v} symmetric system, while the $\text{Si}_2\text{C}_6^{2-}$ dianion possesses C_2 symmetry.

instance, the SiC_6^{2-} dianion has been found to be thermodynamically stable with respect to the most relevant fragmentation channel into SiC_4^- and C_2^- by 2.4 eV. Since SiC_6^{2-} is stable with respect to electron loss and fragmentation, it represents a free stable dianion in the gas phase.

In analogy to the starlike SiC_6^{2-} dianion, also chainlike silicon-carbon dianions have been examined in detail, and a free stable $\text{Si}_2\text{C}_6^{2-}$ dianion as well as a SiC_8^{2-} system have been found to represent stable dianionic systems in the gas phase (Figure 8). Both dianions are clearly stable with respect to electron loss, and due to the covalent character of the involved bonds, also stability with respect to fragmentation of the nuclear framework is given.

Comparing the structures of Si-C dianions with those of typical neutral Si-C clusters, a remarkable structural difference becomes evident. In neutral carbon rich systems the Si atoms are placed mainly at the outer positions such that the number of strong C-C bonds is maximized.¹²⁹⁻¹³¹ In contrast, in dianionic species the Si atom is in the central position. This phenomenon is directly related to the criteria of stability of dianions. In contrast to neutral species, electronic stability is the ultimate requirement for the existence of a given dianion. For example, there exist several energetically more favorable isomers of the SiC_6^{2-} dianion, such as a linear chain with the

**Figure 9.** Anionic mass spectrum recorded after sputtering SiC in the range of 50.5 amu, which corresponds to the doubly charged SiC_6^{2-} cluster anion. Reprinted with permission from ref 76. Copyright 1999 American Physical Society.

silicon at the outer position. These structures are stable with respect to fragmentation, but they are not stable with respect to electron autodetachment. Thus in small stable dianions, the position of the Si atoms, i.e., the whole geometrical structure, is not controlled by a total energy criterion but by the necessity to bind both extra electrons.

Motivated by the theoretical prediction of the existence of mixed silicon-carbon dianions in the gas phase, Gnaser investigated experimentally the occurrence of these species in the gas phase.³⁹ It has been shown that free doubly charged negative clusters SiC_n^{2-} ($n = 6, 8, 10$) do exist and have average lifetimes of at least 15 μs . The dianions were generated by sputtering of a solid SiC specimen with an energetic 14.5 keV Cs^+ ion beam and analyzed by high-resolution mass spectrometry. Thereby, the dianions SiC_n^{2-} ($n = 6, 8, 10$) were unambiguously identified, which have to appear at half-integral mass numbers in the spectrum. The range of the mass spectrum around 50.5 amu corresponding to the SiC_6^{2-} peak is displayed in Figure 9.

Summarizing, the existence of the mixed silicon-carbon dianions in the gas phase has been firmly established by a rigorous quantum chemical treatment as well as by thorough mass spectrometric investigation.

C. Mixed Beryllium-Carbon Dianions

In 1999, Klein and Middleton detected a new class of free stable dianions: the mixed beryllium-carbon dianions BeC_{2n}^{2-} ($n = 2-7$) and $\text{Be}_2\text{C}_n^{2-}$ ($n = 6, 10$).⁷⁷ The detection of these dianions was serendipitous, since Klein and Middleton actually wanted to measure the lifetimes of metastable pure carbon anions and dianions. Surprisingly, they observed two peaks in the carbon mass spectrum at 52.5 and 64.5, which could only be assigned to the BeC_8^{2-} and BeC_{10}^{2-} dianions. Since the only source of Be in the apparatus was "cross-talk" from a preceding recalibration of the facility with Be^- ions, the observed beryllium-carbon dianions must be very stable entities. This conclusion

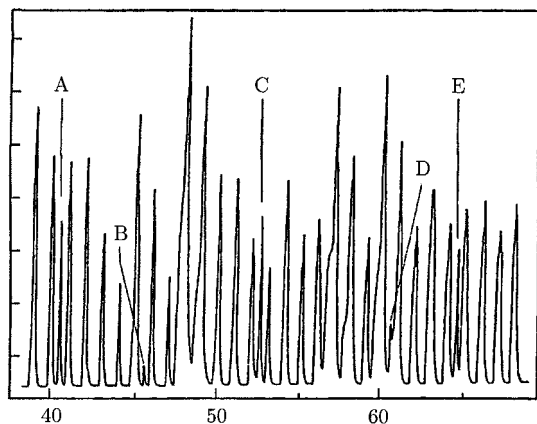


Figure 10. Portion of the anionic mass spectrum that has been obtained after sputtering a cathode containing equal weights of powdered graphite and beryllium metal powder with 8 keV Cs^+ ions. The nonintegral mass peaks belong to dianionic species. A BeC_6^{2-} ; B $\text{Be}_2^{13}\text{C}^{12}\text{C}_5^{2-}$; C BeC_8^{2-} ; D $^{13}\text{C}^{12}\text{C}_9^{2-}$; and E BeC_{10}^{2-} . Reprinted with permission from ref 77. Copyright 1999 Elsevier Science.

has been confirmed by replacing the carbon cathode with a cathode containing equal weights of powdered graphite and beryllium metal powder. The obtained anionic mass spectrum is displayed in Figure 10 in the mass range from 38 to 68 atomic mass units, where the peaks corresponding to the dianions BeC_{2n}^{2-} ($n = 3-5$), $\text{Be}_2^{13}\text{C}^{12}\text{C}_5^{2-}$, and $^{13}\text{C}^{12}\text{C}_9^{2-}$ are evident.

Astonishingly, only mixed beryllium-carbon dianions with an even number of carbon atoms have been observed. The composition of the clusters has further been confirmed by Coulomb explosion imaging. Meanwhile, photodissociation investigation of the most abundant BeC_6^{2-} dianion has shown that it is bound by more than 1.165 eV with respect to any photodetachment or dissociation channel.⁷⁸

Inspired by the experimental discovery of the mixed beryllium-carbon dianions, various isomers of the smallest observed species BeC_4^{2-} and BeC_6^{2-} have been examined using quantum chemical ab initio methods.⁷⁹ In contrast to pure carbon dianions and mixed silicon-carbon dianions (see sections II and III.B), the only stable isomers of the BeC_4^{2-} and BeC_6^{2-} dianions exhibit strictly linear geometries (Figure 11).

The beryllium atom is placed in the middle of the chain such that electron affine C_2 units are retained. This results in a C_2BeC_2 structure for BeC_4^{2-} and a C_2BeC_4 structure for BeC_6^{2-} . The surprising linear structure of these dianions can be rationalized by the fact that BeC_4^{2-} and BeC_6^{2-} are isoelectronic to the neutral pure carbon clusters C_5 and C_7 , which are known to possess linear ground-state structures.¹³²

Investigating the electronic stability of the linear BeC_4^{2-} dianion at highest level of theory, one cannot unambiguously decide whether this dianion is electronically stable or not, since the electron detachment energy (EDE) oscillates around 0 eV (Table 2).

The first clearly stable gas-phase dianion of the mixed beryllium-carbon clusters is the linear isomer of the BeC_6^{2-} dianion, which exhibits a vertical and adiabatic EDE of about 0.75 and 0.6 eV, respectively. Another relevant decay channel for dianions is fragmentation into two monoanionic fragments, which

	1.6347	1.2658
	<i>1.6350</i>	<i>1.2761</i>
	<i>1.6453</i>	<i>1.2448</i>
$\text{C}-\text{C}-\text{Be}-\text{C}-\text{C}$		
	1.2727	1.6610
	<i>1.2747</i>	<i>1.6384</i>
	<i>1.2441</i>	<i>1.3911</i>
$\text{C}-\text{C}-\text{Be}-\text{C}-\text{C}-\text{C}-\text{C}$		
	1.6257	1.2462
	<i>1.6142</i>	<i>1.2577</i>
	<i>1.6188</i>	<i>1.2315</i>

Figure 11. Structures and geometrical parameters of the BeC_4^{2-} and BeC_6^{2-} dianions. The parameters have been optimized at the RHF level (plain text), MP2 (Møller-Plesset perturbation theory of second order) level (italic), and CCSD level (bold face) and are given in Ångströms. Reprinted with permission from ref 79. Copyright 2000 American Institute of Physics.

Table 2. Vertical and Adiabatic Electron Detachment Energies (EDE) of the Linear BeC_4^{2-} and BeC_6^{2-} Dianions Computed at the CCSD Optimized Geometries

theoretical method ^a	EDE/eV	
	BeC_4^{2-}	BeC_6^{2-}
vertical		
KT	0.324	1.061
ΔSCF	-0.504	-0.005
ΔMP2	0.181	1.227
ΔSDCI	-0.194	0.486
ΔCCSD	0.014	0.740
$\Delta\text{CCSD(T)}$	-0.002	
ΔCCSDT	-0.005	
OVGF	0.084	0.766
adiabatic		
ΔCCSD	-0.026	0.627

^a The adiabatic EDE of BeC_6^{2-} has been calculated at the separately MP2-optimized geometries of the dianion and monoanion. A DZP basis set has been used that is additionally augmented with one s- and two p-type diffuse functions on carbon and one s- and one p-type diffuse function on beryllium. The most reasonable numbers are those at the ΔCCSD level and below. The data are taken from.⁷⁹

can be excluded for these species due to the covalent character of the involved bonds. A calculation of the fragment energies of BeC_2^- and C_2^- , which represent the energetically most favored fragmentation channel for BeC_4^{2-} , has shown that the fragments are 1.5 eV higher in energy than the total energy of the dianion, i.e., the BeC_4^{2-} dianion is thermodynamically stable with respect to fragmentation.

Due to the mutual electronic instability of BeC_4^{2-} , it is surprising that this species has been observed in a mass spectrometer. This possible discrepancy between theory and experiment can be explained by taking the repulsive Coulomb barrier (RCB), which hinders the electron emission from a multiply charged anion, into account. The height and width of the RCB has been calculated with different local ab initio approximation schemes, which will be described later in section G. Using these potentials for the calculation of the electronic lifetime of BeC_4^{2-} in the framework of semiclassical WKB theory, it has been clearly proven that electron emission is very unlikely and does not play a relevant role in the above experiment. For instance, given an EDE larger than

−0.47 eV, the lifetime with respect to electron emission is longer than 10^{-5} s, which is the limit of experimental observation, and assuming an EDE of −0.02 eV (the adiabatic EDE of BeC_4^{2-}), the lifetime increases enormously to be about 10^{17} years.

D. Dianions Containing Tetrahedrally Coordinated Oxygen Atoms

A recent theoretical investigation of the structures, electron binding, and fragmentation of oxocarbon dianions of general formula OC_6^{2-} and OC_8^{2-} has shown that the smallest free stable dianion of OC_6^{2-} is a D_{3h} symmetric system, which consists of a central oxygen atom to which three equivalent C_2 units are bound.^{80,82} This seven atomic dianion is structurally closely related to the D_{3h} symmetric C_7^{2-} (section II) and SiC_6^{2-} (Figure 7 in section B) dianions. The OC_8^{2-} system possesses plenty of electronically stable isomers, for example, two chainlike isomers, $\text{C}_2\text{OC}_6^{2-}$ and $\text{C}_4\text{OC}_4^{2-}$, and a triangular isomer, $(\text{C}_2)_2\text{OC}_4^{2-}$.

Furthermore, a stable tetrahedral isomer $\text{O}(\text{C}_2)_4^{2-}$ exists that possesses a tetrahedrally coordinated central oxygen atom (Figure 12). To our best knowl-

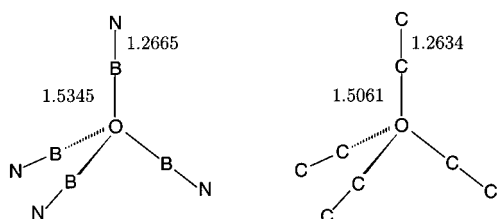


Figure 12. Structure of the long-lived tetrahedral dianions $\text{O}(\text{BN})_4^{2-}$ and $\text{O}(\text{C}_2)_4^{2-}$. The displayed bond lengths have been optimized at the CCSD level of theory. The data are taken from ref 81.

edge this isomer of OC_8^{2-} is the first single molecule with a tetrahedral oxygen atom in a covalent bonding situation.⁸¹ An analogous tetrahedral molecule has been identified when the C_2 units of $\text{O}(\text{C}_2)_4^{2-}$ are replaced by isoelectronic BN ligands (Figure 12). To illustrate the unique chemistry of free stable dianions in general, the results for the two tetrahedral dianions $\text{O}(\text{C}_2)_4^{2-}$ and $\text{O}(\text{BN})_4^{2-}$ will be presented in more detail.

Optimization of the geometrical parameters of the dianions $\text{O}(\text{C}_2)_4^{2-}$ and $\text{O}(\text{BN})_4^{2-}$ gives bond lengths for the O–C and O–B bonds that indicate that they possess covalent single bond character. The C–C and B–N bonds of the dianions correspond to triple bonds. The optimized bond lengths are given at the theoretical level of coupled clusters singles plus doubles (CCSD) in Figure 12. The covalent character of the O–C and O–B bonds of both systems has further been corroborated by an analysis in the framework of the natural bond orbital (NBO) approach.

The examination of the electronic stability of these dianions unambiguously proves their electronic stability, since the vertical EDE is about 2 eV for both systems (Table 3).

A further requirement a stable gas-phase dianion has to possess is stability with respect to fragmentation of the nuclear framework. Both dianions $\text{O}(\text{C}_2)_4^{2-}$

Table 3. Vertical Electron Detachment Energies of the Dianions $\text{O}(\text{BN})_4^{2-}$ and $\text{O}(\text{C}_2)_4^{2-}$ (from ref 81)

theoretical method	EDE/eV	
	$\text{O}(\text{BN})_4^{2-}$	$\text{O}(\text{C}_2)_4^{2-}$
KT	2.77	2.63
ΔSCF	2.07	1.66
ΔMP2	2.14	2.33
ΔCCSD	2.03	2.06

and $\text{O}(\text{BN})_4^{2-}$ have been found to be thermodynamically unstable with respect to fragmentation into $\text{O}(\text{C}_2)_3^-$ and C_2^- , and $\text{O}(\text{BN})_3^-$ and BN^- , respectively. However, closer inspection of the dissociation pathway shows the existence of an energy barrier along the path. Exemplary, the calculated dissociation pathway for $\text{O}(\text{BN})_4^{2-}$ is depicted in Figure 13.

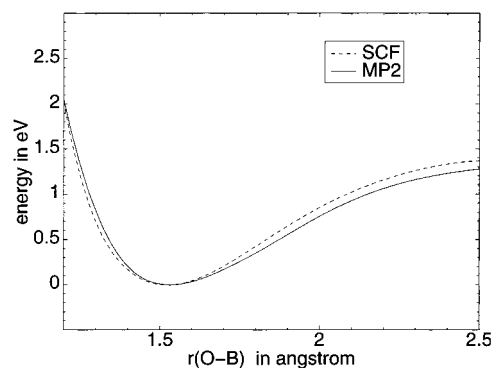


Figure 13. Potential barrier along the dissociation pathway of $\text{O}(\text{BN})_4^{2-}$ into $\text{O}(\text{BN})_3^-$ and BN^- , which has been estimated at the theoretical levels of SCF and MP2. All geometrical parameters have been allowed to relax during the dissociation process. Reprinted with permission from ref 81. Copyright 2001 American Chemical Society.

Since the dissociation pathway is known to be of the form $1/r$ at large distances due to the electrostatic repulsion between the monoanionic fragments, it is sufficient to estimate the energy barrier in the area of the equilibrium geometry, where single reference methods such as RHF and MP2 are appropriate. Because of the broadness of the barrier, the corresponding tunneling process is very unlikely and therefore, the dissociation of $\text{O}(\text{BN})_4^{2-}$ and $\text{O}(\text{C}_2)_4^{2-}$ can be assumed to be extremely slow. Note that a similar dissociation behavior has been predicted previously for the BeF_4^{2-} dianion, and this system was experimentally detected afterward (see section A). For this reason, the estimated barrier height for $\text{O}(\text{BN})_4^{2-}$ and $\text{O}(\text{C}_2)_4^{2-}$ coincides with a very long lifetime of the dissociation process and is no relevant decay channel. In summary, the tetrahedral dianions $\text{O}(\text{BN})_4^{2-}$ and $\text{O}(\text{C}_2)_4^{2-}$ represent free stable dianions and are predicted to exist in the gas phase.

Analysis of the charge distribution of the dianions $\text{O}(\text{BN})_4^{2-}$ and the $\text{O}(\text{C}_2)_4^{2-}$ in the framework of the NBO approach reveals that the central oxygen atom is clearly negatively charged. In the case of the $\text{O}(\text{C}_2)_4^{2-}$ dianion, the oxygen atom possesses a partial charge of −0.43, the inner carbon atoms of −0.16, and the outer ones of −0.25. Since the inner oxygen is already negatively charged by −0.43, only −1.57 charges need to be distributed equally over four C_2 units. This reduces the electrostatic repulsion of the

excess negative charges drastically. The situation is different for the $O(BN)_4^{2-}$ system, where the oxygen has a partial charge of -0.99 , the boron of $+0.8$, and the nitrogen of -1.1 . This strong polarization is due to the differences of the electronegativities of the elements. Even if these numbers overestimate the real charge distribution, the trend is clear, and it is a sequence of alternating negative and positive charges that strongly stabilizes the excess negative charges of the dianion.

E. The Stability of Derivatives of the *closo*-Borate Dianion $B_6H_6^{2-}$

After their theoretical prediction and chemical synthesis, polyhedral *closo*-borates are a vivid field of research in inorganic chemistry (see, for example, ref 89 and references herein). $B_6H_6^{2-}$ has been predicted to exist in condensed phases as early as 1954^{133–135} but evaded chemical preparation for 10 years until 1964.¹³⁶ Since then, theoretical effort has been made to investigate the relative stabilities of the members of the *closo*-borate dianions,^{85–87} and $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ have turned out to show enhanced stability. It is now well-established that the *closo*-borate dianions are unstable with respect to electron loss in the gas phase up to a size of 12 boron atoms.⁸⁵ $B_{12}H_{12}^{2-}$ is the first stable dianion, while $B_{13}H_{13}^{2-}$ is again unstable, but from then on all larger systems are clearly stable with respect to electron emission. This is clearly due to the reduced intramolecular Coulomb repulsion of the two excess electrons within these systems.

In a recent theoretical study, the question has been addressed whether it is possible to stabilize the excess negative charges of the small *closo*-borate dianion $B_6H_6^{2-}$ by substitution of the hydrogen atoms through appropriate ligands and, thereby, to find a stable gas-phase *closo*-hexaborate dianion.⁸⁸ For this reason, the vertical and adiabatic electron detachment energies (EDEs) of various derivatives of these dianions have been computed at a high level of theory. The vertical EDEs of a small selection of the examined species are given in Table 4, and the octahedral structure of the *closo*-hexaborates is exemplarily shown for $B_6(CN)_6^{2-}$ in Figure 14.

While the fluoro-substituted hexaborate $B_6F_6^{2-}$ remains clearly unstable with respect to electron loss, the chloro-substituted species $B_6Cl_6^{2-}$ is slightly stable. Although the vertical EDE is clearly negative at all levels of theory when the standard DZP basis set is used, it turns to positive values when diffuse

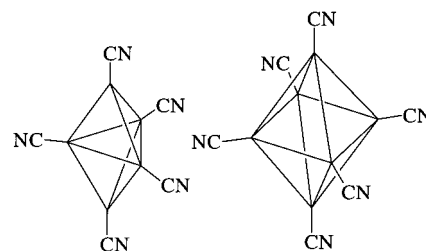


Figure 14. The free stable *closo*-borates $B_5(CN)_5^{2-}$ and $B_6(CN)_6^{2-}$ possess the typical trigonal bipyramidal and octahedral symmetries, respectively.

functions are included in the employed basis set. The CN^- and BO^- -substituted species $B_6(CN)_6^{2-}$ and $B_6(BO)_6^{2-}$ represent electronically very stable dianions, since they possess large vertical electron detachment energies of about 2 eV already when the nondiffuse DZP basis set is used within the calculations (Table 4). Theoretical examination of possible fragmentation channels for smaller borate dianions has shown that fragmentations do not play relevant roles for the dianions' decay. Thus, stability with respect to fragmentation can be taken for granted for the dianionic *closo*-borate family.

A reduction of the number of ligands of the very stable $B_6(CN)_6^{2-}$ dianion has shown that also the D_{4h} symmetric dianion $B_6H_2(CN)_4^{2-}$ is stable with respect to electron loss, whereas only two CN ligands are not sufficient to stabilize the dianion $B_6H_4(CN)_2^{2-}$; i.e., this dianion is electronically unstable. The same trend holds for the BO -substituted *closo*-borate dianions.

To find even smaller *closo*-borate dianions, *closo*-pentaborate systems have been investigated in the same fashion. Also for this system, the CN and BO ligands have been found to be very successful in stabilizing the excess charges of the dianions. Both dianions $B_5(CN)_5^{2-}$ and $B_5(BO)_5^{2-}$ have been found to represent stable dianions in the gas phase, showing a vertical EDE of about 0.6 eV and stability with respect to fragmentation. The structure of $B_5(CN)_5^{2-}$ is displayed in Figure 14.

On the basis of these *ab initio* results the *closo*-hexa- and pentaborates $B_6L_6^{2-}$ ($L = Cl, CN$ or BO) and $B_5L_5^{2-}$ ($L = CN$ or BO) can be predicted to exist as stable dianions in the gas phase. Note that no *closo*-pentaborate derivative has been synthesized so far either in condensed phase or in the gas phase. Due to the increased system size and the thereby reduced intramolecular Coulomb repulsion, the hexaborate dianions are electronically more stable than the analogous pentaborate systems.

There are two reasons for the electronic stabilization of the hexaborate $B_6H_6^{2-}$ and pentaborate $B_5H_5^{2-}$ systems through the exchange of the hydrogen atoms with CN or BO ligands. First, the diameter of the molecule increases markedly from the H-substituted to the CN- and BO-substituted species, and thus, the repulsion between the excess negative charges is significantly diminished. Second, the CN and BO ligands possess strong electron-withdrawing inductive and mesomeric effects that allow one to efficiently distribute the excess negative charges in the π -system of the ligands.

Table 4. Vertical Electron Detachment Energies for the Octahedral *closo*-Borates $B_6L_6^{2-}$ ($L = H, F, Cl, CN,$ or BO) Calculated at the Theoretical Level of Koopman's Theorem, ΔSCF , and $OVGF^a$

	H	F	Cl	CN	BO
KT	-1.495	-1.011	0.647	3.145	3.304
ΔSCF	-2.474	-1.824	-0.301	2.118	2.206
OVGF	-2.081	-1.809	-0.475	2.003	1.953

^a Within these calculations, a standard DZP basis set has been used. Note that the vertical EDE of $B_6Cl_6^{2-}$ turns to slightly positive values when diffuse functions are added to the applied basis set.

F. Photodetachment Photoelectron Spectroscopy of Multiply Charged Anions

One of the most important experimental advances in the research field of multiply charged negative ions (MCAs) in the past few years was made by Wang et al., who applied photodetachment photoelectron spectroscopy to MCAs for the first time. This has become possible by combining an electrospray ionization (ESI) source with a time-of-flight photoelectron analyzer.¹⁰¹ Anions formed in the ESI source are accumulated in a quadrupole ion trap, perpendicularly extracted, and mass analyzed by a time-of-flight mass spectrometer. The mass-selected MCAs are then intercepted by a laser beam of appropriate energy and thereby photodetached. The photoelectrons are finally analyzed with a magnetic-bottle photoelectron analyzer, and the PES spectra of the MCAs are recorded. Using this unique apparatus, Wang et al. reported the first photoelectron spectrum (PES) of a multiply charged anion (MCA), which was taken from the dianion of citric acid¹⁰² (Figure 15).

Analyzing the PES spectra of the citric acid and the aliphatic dicarboxylate dianions $^{-}\text{OOC}(\text{CH}_2)_n\text{COO}^{-}$ ($n = 3-10$), Wang et al. have given conclusive experimental evidence for the existence of the repulsive Coulomb barrier (RCB).^{103,104,109} The PES spectrum of the dianion of citric acid has been recorded at 3.49 and 4.66 eV laser energy (Figure 15).¹⁰² Although the energy of the laser is in both cases larger than the electron binding energy of feature A, it is clearly observable only in the 4.66 eV spectrum. This observation can be rationalized with the existence of a potential barrier, the RCB, which the electrons must overcome in addition to the electron

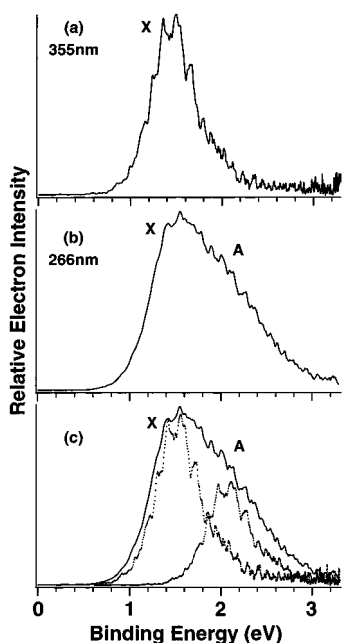


Figure 15. First reported photoelectron spectra of a MCA that has been taken from the citrate acid dianion recorded at (a) 355 nm (3.49 eV) and (b) 266 nm (4.66 eV) laser energy. The increased spectral width in the 266 nm spectrum is due to an additional detachment channel, as indicated in c. Reprinted with permission from ref 102. Copyright 1998 American Physical Society.

binding energy. Only in the spectrum recorded at 4.66 eV laser energy is this condition satisfied for feature A. In the PES spectra of aliphatic dicarboxylate dianions, spectral features were observed whose relative intensities depend on the laser energy, indicating tunneling processes through the repulsive Coulomb barrier.¹⁰⁵

When Wang et al. examined the tetraanion of copper phthalocyanine tetrasulfonate with their photodetachment photoelectron spectrometer, they made a sensational observation: a signal corresponding to a negative electron binding energy was measured (Figure 16).^{109,110}

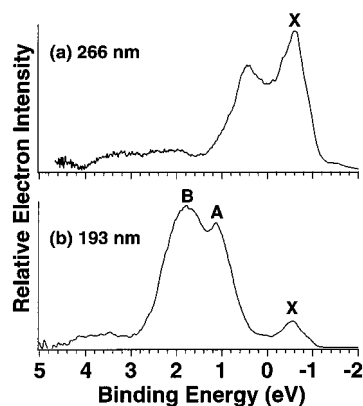


Figure 16. Photodetachment photoelectron spectrum of the tetraanion of copper phthalocyanine tetrasulfonate at laser wavelengths of 266 and 193 nm. Note the feature X exhibits a negative electron binding energy of about -0.5 eV. Reprinted from ref 110. Copyright 2000 American Chemical Society.

This surprising observation can again only be explained with the existence of the RCB, which hinders the unbound electrons of the tetraanion to escape from the molecule. The electrons have to tunnel through this energy barrier, and this process is unlikely and strongly dependent on the energy of the applied laser beam. In Figure 16, the signal X is strongly pronounced at lower laser energy of 4.66 eV compared with features A and B (upper part (a)), since at this laser energy only the unbound electrons gain enough energy to overcome the barrier. At higher laser energy of 6.42 eV (lower part (b)) also the bound electrons of feature A and B obtain enough energy to cross the RCB and are thus strongly pronounced in the higher energy spectrum.

A negative electron binding energy has also been observed for the square-planar tetrahalogenoplatinate dianions PtCl_4^{2-} and PtBr_4^{2-} .^{23,108} Wang et al. have estimated the adiabatic electron binding energies to be -0.25 and -0.05 eV for PtCl_4^{2-} and PtBr_4^{2-} , respectively. In analogy to the previously described results, this observation can again only be rationalized by the existence of the RCB.

A first theoretical calculation of a PES of a multiply charged anion has been reported for the BeF_4^{2-} dianion,¹³⁷ which has been described in detail in section A. A complete valence-shell ionization spectrum has been calculated at a highly correlated level of theory.

G. The Repulsive Coulomb Barrier

In previous sections, the repulsive Coulomb barrier (RCB) has already been described to be a general phenomenon in multiply charged anions. The RCB is always present in MCAs and hinders the emission of one of the excess electrons. We have seen that the RCB is responsible for the observation of electronically unstable MCAs in the gas phase, since the escaping electron has to tunnel through this barrier potential. Considering the electrostatic forces present, the RCB emerges through the combination of the short-range electron binding and the long-range electrostatic repulsion between the emitted electron and the remaining anion.

Although the RCB is clearly dominated by the electrostatics, it is a nonlocal and energy-dependent potential¹¹⁶ and closely related to scattering potentials. In analogy to scattering potentials, an exact theory for the RCB can be derived in the framework of Green's function theory.¹¹⁶ It is well-known that the one-particle Green's function, $\mathbf{G}(E)$, of the complete system (emitted electron and remaining anion) contains all physical information of the emission process. The Green's function $\mathbf{G}(E)$ obeys the following well-known Dyson equation

$$\mathbf{G}(E) = \mathbf{G}(\mathbf{0})(E) + \mathbf{G}(\mathbf{0})(E) \Sigma(E) \mathbf{G}(E) \quad (1)$$

Here, $\mathbf{G}(\mathbf{0})(E)$ is the free GF calculated for the unperturbed remaining anion, and E is the energy of the full system, the remaining anion, and the outgoing electron. The Dyson equation relates the GF for the total system $\mathbf{G}(E)$ to the free GFs of the unperturbed anion via its kernel $\Sigma(E)$, which is called self-energy. The Dyson equation can be formally solved exactly by inversion, giving

$$\mathbf{G}(E) = (\mathbf{E}\mathbf{1} - \mathbf{e} - \Sigma(E))^{-1} \quad (2)$$

The unit matrix $\mathbf{1}$, the diagonal matrix of energies \mathbf{e} of the outgoing electron, and $\Sigma(E)$ are matrixes in the configuration space of the escaping electron. $\Sigma(E)$ corresponds to the exact potential that an electron experiences when it is emitted from the electronically unstable MCA, and can thus be identified with the repulsive Coulomb barrier (RCB).¹¹⁶

The self-energy consists of a static part $\Sigma(\infty)$, not depending on E , and a dynamic part, depending on E :

$$\Sigma(E) = \Sigma(\infty) + \mathbf{M}(E) \quad (3)$$

The static part has a simple interpretation. In spatial representation it can be written as

$$\Sigma(r, r', \infty) = W + \delta(r - r') \int \frac{\rho(\vec{r}, \vec{r})}{|\vec{r} - \vec{r}|} d\vec{r} - \frac{\rho(r, r')}{|r - r'|} \quad (4)$$

where ρ is the exact one-particle density of the ground state of the anion, and W is the interaction potential of the outgoing electron with the nuclei. The static part can thus be seen as the static-exchange interaction of the outgoing electron with the correlated remaining anion. Unfortunately, the exact self-energy, i.e., an exact RCB, is not straightforward

to compute, and due to its nonlocal, energy-dependent, and probably complex nature it is not easily depictable. Such calculations would be desirable, but they are out of reach at the moment, since the needed computer programs are not yet developed. To illustrate the nature of the RCB and to make first ab initio calculations, approximations have to be made to circumvent the nonlocality and energy-dependence of the RCB.

Simons et al. have shown that a simple Coulomb-energy model can be applied to roughly estimate the height of the RCB of compact stable and metastable MCAs.¹¹⁵ These barrier heights have been used in a simple model radial potential to estimate tunneling lifetimes of metastable di- and trianions, such as sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}).

Beyond this simple Coulomb-model, the RCB can be computed in the framework of local ab initio approaches. In the first approach, the RCB can be calculated directly by using the Hartree–Fock ground-state wave function of the dianion. One electron is taken out of the highest occupied orbital (the orbital from which the electron is emitted) and the electrostatic potential is calculated by summing up the nucleus–electron attraction and electron–electron repulsion via

$$V_{\text{DFOSA}}(r) = - \sum_{a=1}^K \frac{Z_a}{|r - R_a|} + \sum_{i=1}^N \int \frac{\phi_i^* \phi_i}{|r - r_i|} d\tau \quad (5)$$

In this equation the first term of the right-hand side describes the electrostatic attraction between K nuclei and the outgoing electron, while the second term corresponds to the electrostatic repulsion between the outgoing electron and the N remaining electrons in their molecular orbitals of the dianion. Within this approach, the energy dependence of the exact RCB is circumvented by formally setting the energy of the outgoing electron to the negative of the electron detachment energy. Furthermore, the exchange interaction between the outgoing electron and those of the residual anion is neglected. This approximation scheme is called the dianion frozen orbital static approach (DFOSA), since the molecular orbitals of the dianion that do not interfere with the emitted electron are used within the calculation. As an example, the RCB of BeC_4^{2-} dianion calculated with the DFOSA approximation is shown in Figure 17.

It has been described in section C that the linear dianion BeC_4^{2-} has been observed experimentally, although the vertical EDE possesses slightly negative values at high levels of theory. Only the RCB that hinders the electron to detach explains the observability of this small dianionic species.

A second possibility to calculate the RCB in a straightforward and natural way is to compute the total energy of the monoanion in the presence of a negative point charge, which may represent the outgoing electron. If the negative point charge is placed at varying distances r to the monoanion, one readily obtains a complete potential energy surface, which reflects the repulsive Coulomb barrier. The

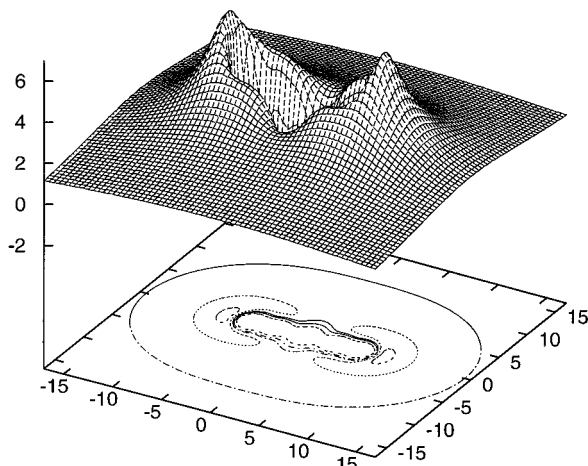


Figure 17. Two-dimensional picture of the RCB of the linear BeC_4^{2-} dianion (see also section C) calculated with the DFOSA approach. Contour lines are projected in the xy -plane for several heights of the barrier. The energy is given in eV, the lengths in Å. Adapted from ref 79. Copyright 2000 American Institute of Physics.

RCB is then given by the simple equation

$$V_{\text{PCM}}(r) = E_0(r) - E_0 \quad (6)$$

Here, $E_0(r)$ corresponds to the total energy of the monoanion in the presence of the negative point charge at the distance r , while E_0 is the total energy of the free monoanion, i.e., in the absence of the negative point charge. Using this approach to calculate the RCB, one takes account of electron relaxation and can easily apply ab initio methods beyond Hartree–Fock, which makes correlation between the N electrons of the monoanion accessible. This point charge model (PCM) correctly describes the remaining anion at large distances between the point charge and the monoanion; thus, the PCM reveals the correct shape of the RCB far away from the monoanion. At short distances this method, of course, possesses weaknesses. From a certain distance on, when the electrostatic repulsion between the monoanion and the point charge exceeds the binding energy of the anionic electron, the monoanion always detaches.¹¹⁶ Hence, at short distances the monoanion–point charge system represents a resonance state that can in principle not be correctly computed with bound state methods, and therefore, the obtained RCB potentials are not well-defined. Thus, the quality of the RCB can be low at shorter distances, and care must be taken of how to compute it.¹¹⁶ Nevertheless, the usefulness of this conceptually appealing approach has been demonstrated through the calculation of the RCB of BeC_4^{2-} ⁷⁹ and of PtCl_4^{2-} ¹¹³ with the help of the PCM. The obtained barrier potentials have been used to calculate the tunneling rate and lifetime of the dianions with respect to electron emission in the framework of WKB theory. The calculated values are in excellent agreement with the experimental findings. Other applications of the PCM are found in ref 116.

Comparing the DFOSA method and the PCM, the latter reveals the correct shape of the RCB at large distances between the residual anion and the out-

going electron, because the anion is described correctly for this situation. DFOSA yields a more reliable RCB in the inner region, when the detaching electron is close to the anion, since the orbitals of the dianion are used within the DFOSA approach. Both methods seem to complement one another to give a more complete picture of the repulsive Coulomb barrier.

A third approach to the RCB consists of computing directly the local contribution of the static self-energy, which is called local static approach (LSA). Neglecting in eqs 3 and 4 the dynamic part and the exchange of the outgoing electron with the remaining anion, one obtains the local static potential

$$V_{\text{LSA}}(r) = - \sum_{a=1}^K \frac{Z_a}{|r - R_a|} + \int \frac{\rho(\vec{r}, \vec{r})}{|r - \vec{r}|} d\vec{r} \quad (7)$$

The one-particle density ρ of the anion can be computed with any ab initio method. The response of the target's density to the projectile electron included in the PCM is, of course, absent in $V_{\text{LSA}}(r)$. However, the latter potential has advantages compared to the other approaches, since it does not depend on the choice of the basis set and is well-defined in the limit of an infinite basis set.¹¹⁶ In all three local approaches discussed above, the exchange interaction between the electron and the anion can in principle be taken into account by using local approximations such as those done in density functional theories.

Using all three ab initio approximation schemes to calculate local RCB potentials of the linear C_8^{2-} dianion, one still remaining puzzle of the pure carbon cluster dianions could be solved:¹¹⁶ Although the peak of the linear C_8^{2-} is one of the most abundant peaks in the mass spectrum of the carbon dianions, the dianion has been found to be adiabatically unstable with respect to electron emission by about 0.1 eV.⁴¹ In contrast, C_7^{2-} , which is the smallest observed carbon dianion, possesses a D_{3h} starlike structure and is electronically stable,^{42,43} but its peak in the mass spectrum is less intense than that of C_8^{2-} .

The local RCB potentials of C_8^{2-} have been calculated using the DFOSA approach at the level of restricted Hartree–Fock and, with the help of the PCM and LSA methods, at the level of coupled-clusters singles plus doubles. It is assumed that the outgoing electron leaves the molecule along the minimum energy path that is along the horizontal mirror plane of the $D_{\infty h}$ symmetric molecule. The potential barriers along this path are displayed in the lower part of Figure 18. These potentials can now be used in the framework of semiclassical WKB theory to estimate the tunneling lifetimes for electron emission along the minimum energy path. Although the potentials obtained with the three approaches are quite different, the calculated lifetimes are very similar, as can be seen in the upper part of Figure 18. To be explicit, independent of which potential is used in the calculation of the lifetime, the lifetime is markedly longer than 10^{-5} s when the electron energy is lower than 0.35 eV (corresponding to an electron detachment energy of -0.35 eV); 10^{-5} s is

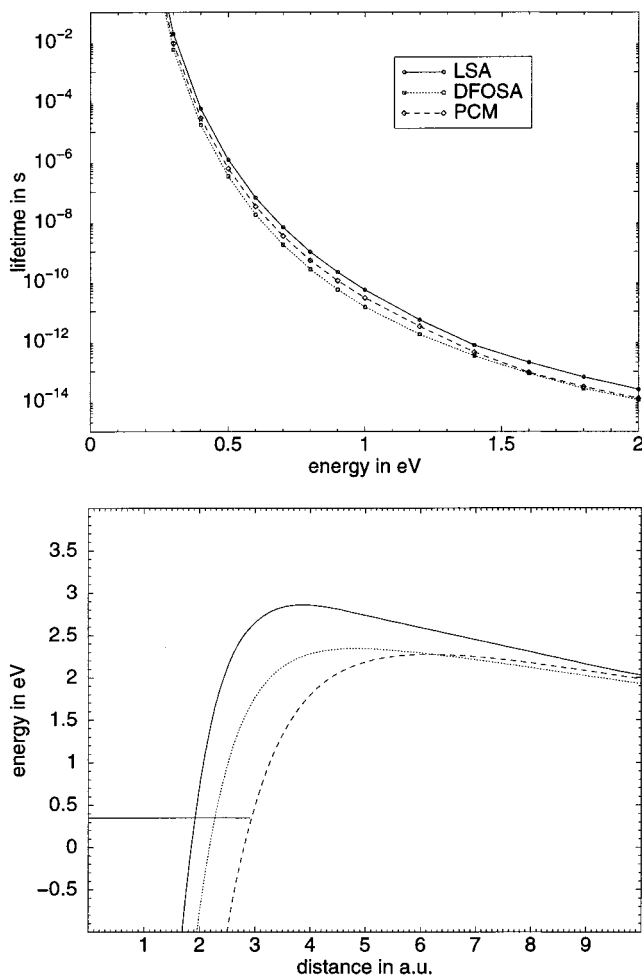


Figure 18. In the upper part, the computed lifetimes are displayed as a function of the energy of the emitted electron. For the calculation of the lifetime, the LSA (full line), DFOSA (dotted line), and PCM (dashed line) potentials have been used, which are shown in the lower part. For electron energies below 0.35 eV (indicated by the horizontal line in the lower part), the lifetime of the C_8^{2-} dianion is computed to be longer than 10^{-5} s, which is the lower limit for experimental observation. Reprinted with permission from ref 116. Copyright 2001 American Physical Society.

usually the minimum lifetime for experimental observation in a mass spectrometer.

Watts and Bartlett have found that the C_8^{2-} dianion is vertically stable with respect to electron emission but adiabatically unstable by about 0.1 eV.⁴¹ Assuming 0.1 eV to be the energy of the outgoing electron, we obtain a very long tunneling lifetime of about 2×10^{11} s for the C_8^{2-} system; thus, no significant electronic decay should be observed in the experiment. Since the linear isomers of the carbon dianions are thermodynamically more favorable than the branched isomers such as, e.g., C_7^{2-} , it is now clear that the abundance of the peaks of C_7^{2-} and C_8^{2-} in the mass spectrum is determined by the thermodynamically committed generation rate and not by the electronic stability of these dianions.

Finally, we would like to mention that the height of the RCB strongly depends on the electrostatic repulsion between the excess negative charges. Therefore, higher negatively charged species, e.g., trianions, in general possess higher repulsive Coulomb

barriers than lower charged species, e.g., dianions. Due to this higher RCB potential, one is tempted to believe that higher charged species may exhibit longer lifetimes. But this is in general not true, because the electron binding energy of the excess charges is also influenced by their electrostatic repulsion and may decrease substantially. Typically, we expect higher charged anions to possess a higher RCB potential but a much lower electron binding energy resulting in a shorter lifetime.

H. A Long-Lived Molecular Trianion: $N(BF_3)_4^{3-}$

Experimental observations or theoretical predictions of higher than doubly charged negative ions in the gas phase are scarce in the literature (see section II). In a recent theoretical study, conclusive evidence has been presented for the existence of a long-lived $N(BF_3)_4^{3-}$ trianion in the gas phase,⁹⁸ which is to our best knowledge the first small long-lived covalent trianion so far.

The structure of the examined $N(BF_3)_4^{3-}$ trianion is shown in Figure 19. It has T symmetry, since all

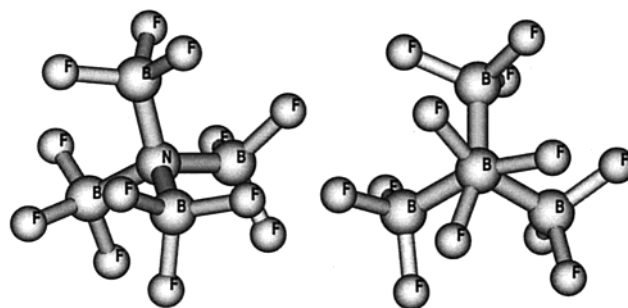


Figure 19. The structure of the T symmetric covalent trianion $N(BF_3)_4^{3-}$ is shown in side view (left part) and along one of the four C_3 axis of the molecule (right part), where the rotation of the BF_3 units around the C_3 axes of the molecule by about 40° can easily be recognized. Reprinted from ref 98. Copyright 2001 American Chemical Society.

BF_3 units are rotated about 40° along the four C_3 axes of the system, thus disturbing the higher T_d symmetry. The trianion possesses a closed-shell 1A_1 electronic ground state. Geometry optimization of the structure at the theoretical levels of restricted Hartree–Fock (RHF) and Møller–Plesset perturbation theory of second order (MP2) revealed that the N–B bonds as well as the B–F bonds have clearly single-bond character.

The geometrical parameter are given in Table 5. An analysis of the harmonic frequencies at both levels of theory has proven that the T symmetric structure corresponds to real minima on the potential energy surfaces.

To establish electronic stability of the system, the vertical electron detachment energy (EDE) has been computed at different levels of theory for the RHF-optimized as well as for the MP2-optimized geometry. Using a nondiffuse standard DZP basis set within the calculations, the vertical EDE possesses values of about -0.3 eV at the best levels of theory [coupled-cluster singles plus doubles (CCSD) and the outer-valence Green's function (OVGF); see Table 5] for the

Table 5. Geometric Parameters of the Trianion $N(\text{BF}_3)_4^{3-}$ Optimized at the Theoretical Levels of RHF and MP2 Using a Standard DZP Basis Set and Additionally Augmented with Diffuse s- and p-type Functions

geometry ^a	RHF	MP2	vertical EDE ^b	RHF	MP2
$r(\text{N}-\text{B})$	1.599	1.603	KT*	1.514	1.815
$r(\text{B}-\text{F})$	1.402	1.427	KT	1.304	1.611
$\angle(\text{N}-\text{B}-\text{F})$	112.12	111.98	ΔSCF^*	-0.449	-0.112
$\angle(\text{B}-\text{N}-\text{B}-\text{F})$	40.16	40.12	ΔSCF	-0.782	-0.236
			ΔMP2^*	-0.097	0.170
			ΔMP2	-0.441	-0.177
			ΔCCD	-0.384	-0.100
			ΔCCSD	-0.593	-0.325
			OVSF	-0.522	-0.262

^a The bond lengths are in Ångströms and the angles in degrees. ^b The vertical electron detachment energies have been calculated for both optimized geometries using the DZP basis set and the DZP+sp basis set (*) and are given in eV.

MP2 optimized geometry. Due to the size of the system, augmentation of the basis set with diffuse functions is only accessible at the MP2 level of theory. Having a look at the EDE values obtained with and without diffuse basis functions at lower levels of theory, it becomes clear that the trianion is stabilized by about 0.2 eV when diffuse functions are used. Taking this stabilization of the EDE into account for the best methods, the vertical EDE has a value of about 0 eV at the MP2 optimized geometry, and it is not clearly decidable whether the trianion is electronically stable or not.

As we have seen in the previous section G, a repulsive Coulomb barrier (RCB) hinders the emission of one of the excess electrons. Calculation of the RCB with the DFOSA method and estimation of the tunneling lifetime along the minimum energy path for electron emission in the framework of WKB theory reveals that the $N(\text{BF}_3)_4^{3-}$ is long-lived with respect to electron emission. For EDEs greater than -1 eV (corresponding to 1 eV electron energy), the trianion lives clearly longer than the limit for experimental observation in a mass spectrometer, which usually is 10^{-5} s (Figure 20).

We have seen that the EDE is close to zero (Table 5), and assuming an EDE of -0.1 eV, the lifetime of $N(\text{BF}_3)_4^{3-}$ would be on the order of 10^{15} s. Thus, no electronic decay should be observable in mass spectrometric experiments.

In analogy to previously described dianions, e.g. BeF_4^{2-} (section A) or $\text{O}(\text{C}_2)_4^{2-}$ (section D), the $N(\text{BF}_3)_4^{3-}$ trianion is found to be thermodynamically unstable with respect to fragmentation. The energetically most favored dissociation channel is splitting off one fluorine anion, but this channel is connected with a sufficiently high potential barrier. The corresponding tunneling process is due to the high mass of the fluorine anion, and because of the broadness of the barrier, progress is very unlikely. Thus, fragmentation of the $N(\text{BF}_3)_4^{3-}$ trianion can be excluded as relevant decay channels.

Summarizing the theoretical results, the covalent trianion $N(\text{BF}_3)_4^{3-}$ is long-lived with respect to electron emission as well as with respect to fragmentations of the nuclear framework. Therefore, its ob-

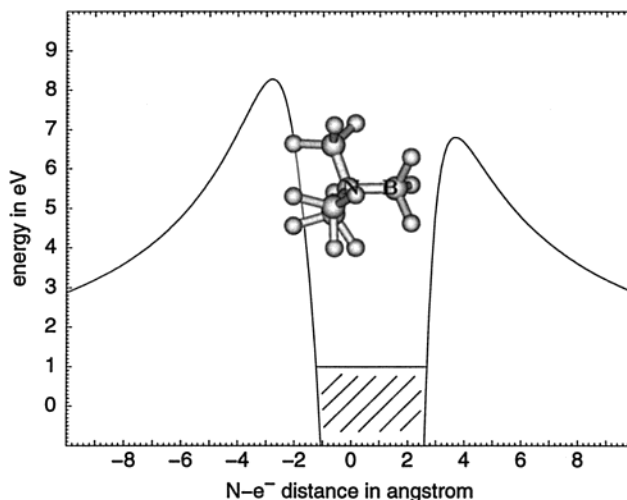


Figure 20. One-dimensional cut through the RCB of $N(\text{BF}_3)_4^{3-}$ along one of the C_3 axes of the molecules, which corresponds to the minimum energy path for electron emission. The zero-point of the x-axis is set to the position of the nitrogen atom, and for a better orientation, the trianion is displayed in the length scale of the potential. For electron energies below 1 eV, the trianion lives longer than 10^{-5} s, which is indicated by a horizontal line. Reprinted from ref 98. Copyright 2001 American Chemical Society.

servability in mass spectrometric experiments is predicted. Photodetachment photoelectron spectroscopy as described in section F would be a very useful tool to investigate the electronic structure of the trianion, and in analogy to PtCl_4^{2-} or the tetraanion of copper phthalocyanine tetrasulfonate, a possibly negative electron binding energy could be observed.

I. On the Transition to Condensed Phases

Since the early beginning of the research field, several groups investigated the influence of solvent molecules or counterions on the geometric and electronic structures of isolated MCAs to bridge the gap between gas phase and condensed phases.

To study the transition from gas phase to solution, Blades and Kebarle examined the hydration of the sulfate (SO_4^{2-}), dithionate ($\text{S}_2\text{O}_6^{2-}$), and peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) using an electrospray ionization source combined with a mass spectrometer.¹⁸ They observed that at least three water molecules are needed to stabilize the electronically unstable isolated SO_4^{2-} dianion, while $\text{S}_2\text{O}_6^{2-}$ and $\text{S}_2\text{O}_8^{2-}$ represent free stable dianions. In analogy, dianionic diphosphates have been examined and their hydration energies estimated.¹²³ Wang et al. investigated the hydration of SO_4^{2-} experimentally using a photodetachment photoelectron spectrometer as well as theoretically and provided the first direct information about the electronic stability of the hydrates as a function of solvation.⁶⁹ While mass spectrometric observations such as those of Blades and Kebarle do not provide information about the stability of the observed species, Wang et al. have given conclusive experimental evidence that at least three water molecules are needed to stabilize the sulfate dianion. Furthermore, they have shown that further addition of water molecules successively stabilizes the dianion,

Table 6. Calculated Bond Lengths and Vertical Electron Detachment Energies of Several "Textbook" MCAs in the Isolated State (I) and in Water (W), Where the Relaxation of the Solvent Reaction Field on the Detachment of the Dianion Is Not Taken into Account (EDE(v)) and Is Taken into Account (EDE(a))^a

	$r(\text{M}-\text{O}) \text{ \AA}$	EDE(v) eV	EDE(a) eV
O ²⁻ (I)		-6.9	
O ²⁻ (W)		7.5	3.5
CO ₃ ²⁻ (I)	1.31	-3.4	
CO ₃ ²⁻ (W)	1.30	9.9	5.7
SO ₄ ²⁻ (I)	1.52	-1.6	
SO ₄ ²⁻ (W)	1.51	9.6	6.7
BO ₃ ³⁻ (I)	1.43	-8.2	
BO ₃ ³⁻ (W)	1.41	8.5	5.2
PO ₄ ³⁻ (I)	1.60	-5.5	
PO ₄ ³⁻ (W)	1.57	8.5	5.7

^a The calculations were performed at the level of Møller–Plesset perturbation theory of second order, and the effects of the solvent were taken into account by the generalized conductor-like screening model (GCOSMO). The data are taken from ref 125.

while the main electronic features of the hydrates are retained and can be attributed to the "free" sulfate dianion. Using the same technique, the hydration of dicarboxylate dianions has been studied analogously.¹²⁴

In a recent theoretical examination, Stefanovich et al. examined the stabilization of multiply charged anions in water.¹²⁵ The influence of the solvent on the geometry as well as the electronic stability and the stability with respect to fragmentations was studied using the generalized conductor-like screening model (GCOSMO) to include the solvent effects within an ab initio treatment. Due to their calculations, electronically unstable MCAs are tremendously stabilized by the solvent, and also fragmentation channels are clearly suppressed. For instance, the vertical electron detachment energy (EDE) of sulfate (SO₄²⁻) increases by about 11.2 eV from -1.6 eV to 9.6 eV in water and the EDE of phosphate (PO₄³⁻) by about 14 eV from -5.5 eV to 8.5 eV (see Table 6).

The influence of counterions on the properties of stable and unstable dianions has been investigated as well, which can be regarded as a first step toward crystals and more important solutions where cation–dianion complexes are probably present. Wang et al. have studied free singly and doubly charged alkali metal sulfate ion pairs, [M(SO₄)]⁻ and [M(SO₄)₂]²⁻ (M = Na, K), with photodetachment photoelectron spectroscopy.¹²⁶ Clear experimental evidence is given that the electronic features of the cation–dianion complexes are all very similar and correlate well with the molecular orbital energy levels of "free" SO₄²⁻. Thus, the complexes can be considered as a distorted sulfate that interacts electrostatically with the alkali metal cations as it is found in bulk sulfate solids. The effect of the counterions on sulfate is very similar to the effect of water, which has been reported previously.

In a recent mass spectrometric experiment, which has been proposed by Compton, cesium carbon cluster anions [CsC₉]⁻ have been generated by sputtering graphite and served as precursors to selectively

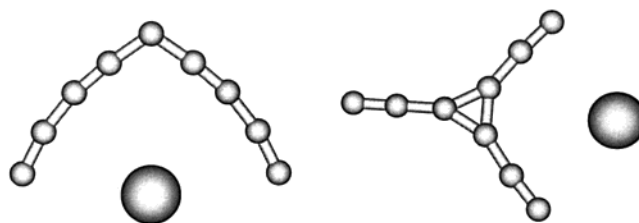


Figure 21. Structures of two stable isomers of [CsC₉]⁻. While fragmentation of the left isomer into Cs⁺ and C₉²⁻ leads to an electronically unstable C₉²⁻ isomer, fragmentation of the right structure results in the free stable C₉²⁻ isomer displayed in Figure 1. Reprinted with permission from ref 128. Copyright 1999 American Institute of Physics.

produce the dianionic carbon cluster C₉²⁻ by collision-induced dissociation.¹²⁷ The anionic fragmentation products were finally analyzed with a mass spectrometer, and C₉²⁻ was unambiguously identified.

In a thorough quantum chemical investigation of the structures of the cesium carbon clusters [CsC₉]⁻ and [CsC₇]⁻, it has been pointed out that the structures of the known pure carbon dianions C₉²⁻ and C₇²⁻ are mainly retained.¹²⁸ The cesium cation only electrostatically interacts with the dianions and strongly stabilizes them, so even unstable isomers of C₉²⁻ and C₇²⁻ become electronically stable within the cation–dianion complex. Dissociation of such [CsC₉]⁻ complexes within the experiment leads to electronically unstable dianions that spontaneously emit one electron. For instance, dissociation of the [CsC₉]⁻ complex displayed on the left-hand side of Figure 21 would lead to an electronically unstable chainlike C₉²⁻. In contrast, the [CsC₉]⁻ complex displayed on the right-hand side of Figure 21 leads to the stable D_{3h} symmetric C₉²⁻ dianion (Figure 1), which can finally be detected. Since the structures of the [CsC₉]⁻ and [CsC₇]⁻ cation–dianion complexes are ruled by electrostatics, they are related to possible crystal structures and represent a first step toward this direction.

IV. Future Perspectives

Looking back onto about one decade of research in the field of multiply charged anions (MCAs) since the experimental detection of small dianionic carbon clusters in a mass spectrometer and the first reliable theoretical predictions of stable metal fluoride dianions, the field was dominated by the search for the smallest system that can bind two excess negative charges. To date, the smallest predicted long-lived dianion is the trigonal LiF₃²⁻ system, which until now evaded experimental verification. The smallest detected dianions so far are the pentaatomic systems BeC₄²⁻, BeF₄²⁻, and PtCl₄²⁻. From a theoretical point of view, the detection of LiF₃²⁻ or preferably the heavier KF₃²⁻ may be possible when new experimental techniques allow the generation of multiply negatively charged species in the gas phase at lower temperatures. One totally different ansatz to gain experimental data about the LiF₃²⁻ species in the gas phase might be by scattering fluoride off the very stable LiF₂⁻ anion. The question whether even smaller or less electron rich MCAs exist still remains a challenge to experimentalists as well as theorists.

With the development of photodetachment photoelectron spectroscopy (PES) of MCAs and the technical development of ion traps and storage rings, the door has been opened to study properties of multiply charged anions and to obtain experimental data about their electronic structure. Today, only MCAs are accessible to PES that can be produced with an electrospray ionization source. Thus, only such MCAs can be investigated for which appropriate precursors are available in solution. Since many theoretically predicted dianions do not exist in condensed phases and can only be generated by high-energy processes such as laser ablation or sputtering, the combination of a photodetachment photoelectron spectrometer with such sources would be of great interest. A further experimental challenge for the future is the application of spectroscopical methods different from PES to MCAs to obtain information about, for example, the geometrical structures, which are today not yet available from experiment.

The most important requirements for the existence of a small, free, stable MCA are stability with respect to electron autodetachment as well as stability with respect to fragmentation of the nuclear framework. A glance at the structures of the nowadays known small, stable, gas-phase dianions reveals that electronic stability can be reached in two different ways. Linear or chainlike dianions gain electronic stability by localizing the excess negative charges in electron affine groups at the ends of the chain, whereby the electrostatic repulsion between the excess electrons is minimized. More efficient for the binding of excess electrons is a compact polarized structure, which is characterized by a central positively charged atom or group of atoms, to which several negatively charged ligands are bound. The electrostatic attraction between the positively charged center and the negatively charged ligands strongly stabilizes the excess negative charges of the MCA. These two concepts, of course, display borderline cases, and some of the known small gas-phase MCAs show characteristics of both. A natural question is whether there exist different binding mechanisms for excess charges that have not been considered yet. To answer this challenging question is a remaining task for researchers in this field.

A first step into this direction may be the search for the smallest covalent open-shell dianion, since all small covalent dianions described so far are closed-shell systems. First calculations on open-shell dianionic systems indicate that correlation seems to play an important role for the appropriate theoretical description of open-shell dianions. Another point that will be addressed in the future is the calculation of electronic spectra of MCAs to corroborate the experimental PES findings and to understand the influence of the excess charges on the spectra.

After much effort has been made to investigate and study the ground state properties of small multiply charged anions in the gas phase, it will be interesting to look for electronically excited states of small MCAs that are long-lived with respect to electron emission. To be long-lived, the excitation energy of such states has to be smaller or only slightly larger than the

electron detachment energy of the respective MCA. The excited state will be stable with respect to electron emission if the energy of the excited state is lower in energy than the ground state of the corresponding monoanion and may be long-lived if it is slightly larger. In the latter case, the emission of an electron from the excited state will be hindered by a repulsive Coulomb barrier, giving rise to a finite and possibly long lifetime. We would like to note that recently unexpected PES features have been observed in the large organic tetraanion of copper phthalocyanine tetrasulfonate and have tentatively been interpreted as excited states of MCAs.¹¹⁰

In summary, the variety of known small, stable or long-lived dianions in the gas phase has grown remarkably, and one can assume that still many different classes of such MCAs exist and wait to be detected. Furthermore, only little is known about higher than doubly charged system: long-lived trianions are scarce in the literature, and nearly nothing can be found on tetraanions, pentaanions, etc. Although the research field has rapidly developed during the last years, it is still at its beginning and plenty remains to be done.

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