

Small Multiply Charged Anions as Building Blocks in Chemistry

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I. Introduction

Chemists view most if not all ionic crystals as composed of *autonomously stable* negative and positive ions. These building block ions can be singly or multiply charged (e.g., NaCl(s) consists of Na⁺ and Cl⁻ ions, and MgSO₄(s) contains Mg²⁺ and SO₄²⁻ ions), but they are expected to be stable to the extent that they can be characterized in the laboratory. Dividing crystals, melts, and ionic molecules into positive and negative ions is usually performed via the octet rule. For example, K₂SO₄ salt is considered to be composed of K⁺ cations and SO₄²⁻ anions, within which all constituent atoms possess full octets of valence electrons. Within this point of view, chemists interpret the physical, reactivity, optical, and other properties of crystals, melts, and liquid ionic salts in terms of properties *intrinsic* to the corresponding positive and negative ions. For example, in NH₄Cl(s), one interprets Raman spectra in terms of crystal phonons as well as internal N–H vibrations belonging to the NH₄⁺ cation.

This widely accepted approach in chemistry is called into question when one recognizes that many multiply charged anions that occur frequently in salts do not exist as autonomously stable species in which the extra electrons occupy valence molecular orbitals. How then can one view the composition of an ionic material such as a salt in terms of building blocks that cannot be isolated and thus fully characterized? It is this difficulty that forms a primary focus of the present Account.

It is very difficult to experimentally prove or disprove the electronic instability of isolated multiply charged anions. The absence of corresponding signals in mass spectral data does not necessarily mean that the ions do not exist; it could be that, under the experimental source conditions, these anions are not formed. Alternatively, mass spectral peaks cannot

prove stability; the species may be metastable yet long-lived enough to survive to the ion detector.

The significant increase in the reliability of electronic structure computer techniques allows the question of the instability of multiply charged anions to be addressed using *ab initio* methods. Moreover, in recent years, substantial progress has been made in the *ab initio* study of multiply charged species, specifically. Three very good reviews on theoretical and experimental studies have appeared in the last three years.^{1,2} However, because the reviews were devoted primarily to studies of electronically *stable* multiply charged anions, many issues related to unstable anions were not included and thus need to be addressed in this work.

When we discuss the stability of multiply charged anions, we consider three types of stability. The first is electronic stability of the anion. If Aⁿ⁻, at its own optimal geometry, is more stable than the corresponding A⁽ⁿ⁻¹⁾⁻ at the *same* geometry, we consider Aⁿ⁻ to be *vertically electronically stable*. If Aⁿ⁻ at its optimal geometry is more stable than A⁽ⁿ⁻¹⁾⁻ at its own optimal geometry, we consider Aⁿ⁻ to be *adiabatically electronically stable*. In addition, there is the issue of geometrical stability. If Aⁿ⁻ has all real vibrational frequencies at its optimal geometry, it is *locally geometrically stable*. Finally, if Aⁿ⁻ is more stable than any possible dissociation fragment, it is *thermodynamically stable*. Clearly, if an anion is thermodynamically stable, it must also be electronically and geometrically stable.

Most small multiply charged anions are not thermodynamically stable, although many are electronically and locally geometrically stable and may have large barriers to dissociation or to autodetachment. Such anions can be studied experimentally because they are long-lived. However, many multiply charged anions that are only vertically electronically stable are very difficult to probe experimentally because of their very short lifetimes.

II. Electronically Stable and Unstable Multiply Charged Anions

A large extended molecular system with two distantly located electronegative radical centers can certainly attach two extra electrons; dianions derived

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from such systems (e.g., $^-OOC(CH_2)_nCOO^-$) have been recently reviewed.^{1,2} New experimental techniques, such as electrospray mass spectrometry^{3ab} and low-energy electron attachment^{3c,d} have made substantial progress in the study of multiply charged anions. However, when a molecule is composed of relatively few atoms, the Coulomb repulsion between the net charges due to the extra electrons cannot be overcome, so either electron detachment or molecular fragmentation takes place. In fact, during the last 10 years, theoreticians have accumulated a body of data indicating that many multiply charged anions, including many commonly proposed in condensed media, do not exist as stable moieties in the gas phase. In the next section, we briefly summarize the results of such calculations on both unstable and locally stable dianions.

II.1. Doubly Charged Anions. A. Atoms. While it is commonly accepted that multiply charged atomic anions such as O^{2-} , S^{2-} , and N^{3-} occur as building blocks of the solid state, melts, and liquids, there now is consensus that such free atoms cannot support two (or more) extra electrons because of the enormous Coulomb repulsion.^{1,2}

B. Diatomics. Doubly charged diatomic anions such as O_2^{2-} and C_2^{2-} are also considered as common species in the solid state. The existence of stable doubly charged diatomic anions has been examined,⁴ and it has been concluded that dianions with 10 valence electrons such as C_2^{2-} , BN^{2-} , and MgO^{2-} or with 14 valence electrons such as O_2^{2-} and S_2^{2-} represent the best candidates for electronic stability because (i) dianions from both groups are proposed in crystals [e.g., C_2^{2-} in Li_2C_2 , O_2^{2-} in Na_2O_2 , and S_2^{2-} in K_2S_2 ; see ref 4 for references], (ii) C, O, and S have positive high electron affinities (EA), and (iii) species with 10 and 14 valence electrons have closed-shell N_2 and F_2 type electronic configurations, respectively.

However, such dianions are found to be electronically unstable as a result of very high Coulomb repulsion energy. The bond lengths of the diatomics forming these dianions do not exceed 2.3 Å, so even if two excess charges were localized at the termini, the Coulomb repulsion would be ca. 5.3 eV. Therefore, it is concluded that all isolated diatomic dianions or other multiply charged diatomic anions are not stable to loss of an extra electron or fragmentation in their ground electronic states, although they may exist as resonance or metastable excited species.

C. Triatomics. Triatomic dianions (NCN^{2-} , $OBeO^{2-}$) with 22 valence electrons are likely the best candidates to be stable because (i) NCN^{2-} is proposed in crystals [e.g., Li_2NCN], (ii) these dianions have the closed-shell electronic configuration of CO_2 , (iii) $OBeO^-$ and $OMgO^-$ are valence isoelectronic to OBO , which possesses a very high electron affinity (and thus is a superhalogen⁵) [4.2 eV⁶ to 4.65 eV⁷], and (iv) the extra electrons are expected to be located at the termini. However, all such dianions have also been found to

be electronically unstable; as a result, we conclude that isolated triatomic dianions or other multiply charged triatomic anions do not occur as isolated species in which the extra electrons occupy valence molecular orbitals.

D. Linear Tetraatomics. A few linear tetraatomic dianions ($OCCO^{2-}$ and $SCCS^{2-}$) have been examined theoretically.⁴ In these species, the electronegative atoms (O or S) are placed at the termini to minimize the Coulomb repulsion. Moreover, the corresponding termini atoms $-O$ and $-S$ have unsaturated valences and quite high EAs. The $OCCO^{2-}$ dianion is also known as a structural unit in crystal salts. However, these linear dianions are also found to be electronically unstable.

E. Nonlinear Species. While *linear* tetraatomic dianions are not electronically stable, Sheller and Cederbaum⁸ showed that $AlkHal_3^{2-}$, where $Alk = Li-Cs$ and $Hal = F-I$, (e.g., LiF_3^{2-} , NaF_3^{2-} , KF_3^{2-} , and others; see Table 1) can exist as thermodynamically unstable, but electronically and locally geometrically stable, species. Because of large Coulomb barriers to dissociation and for detachment of an electron, these dianions should have significant lifetimes in the gas phase. The high stability of these dianions has been explained in the same manner as for the superhalogens.⁹ The *two* extra electrons occupy a nonbonding orbital, localized at the *three* halogen centers. Localization of less than one electron ($^{2/3}e$) per center thus helps overcome the Coulomb repulsion. Other dianions which satisfy such conditions have the general formula: $MHal_{k+2}^{2-}$, where M is a central atom and k is its formal maximal valence.¹⁰ LiF_3^{2-} and other doubly charged $AlkHal_3^{2-}$ anions studied by Sheller and Cederbaum fit this formula with $k = 1$.

For divalent electronegative ligands, the above formula is modified to $MX_{(k+2)/2}^{2-}$. For $X = O$ and $k = 4$, we have CO_3^{2-} , SiO_3^{2-} , GeO_3^{2-} , SnO_3^{2-} , and PbO_3^{2-} . The first dianion is isoelectronic with LiF_3^{2-} and is common in the solid state. However, they are also not electronically stable^{11,12} as isolated species.

Dianions such as SO_3^{2-} , SeO_3^{2-} , and TeO_3^{2-} are also proposed in condensed phases. However, theoretical calculations¹³ proved that these species cannot support two extra electrons and are thus electronically unstable.

Thus far, the tetraatomic $AlkHal_3^{2-}$ species are the smallest electronically and locally geometrically stable doubly charged negative ions known.

F. Larger Species. Larger linear dianions (with five or more atoms) have better chances to survive as electronically and geometrically stable species, because of the larger distance between their termini. However, among $Be_2O_3^{2-}$, $Be_2S_3^{2-}$, $Mg_2O_3^{2-}$, and $Mg_2S_3^{2-}$, only $Mg_2S_3^{2-}$ was found to be *slightly* vertically electronically stable (by 0.2 eV). It has been proposed on experimental findings^{14a} that C_7^{2-} is the smallest linear doubly charged anion, but this is not

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Table 1. Doubly Charged Anions

anion	proposed to exist in condensed phase	vertical electron detachment energy (eV)	method	proposed to exist in gas phase as a metastable species	anion	proposed to exist in condensed phase	vertical electron detachment energy (eV)	method	proposed to exist in gas phase as a metastable species
C ₂ ²⁻	yes ^a	-3.16 ^{b-d}	PMP4/6-311+G(2df)	no ^d	MgF ₄ ²⁻	-	+2.98 ⁿ	ADC(3)/TZVP-SP	yes ⁿ
Si ₂ ²⁻	-	-2.72 ^{b-d}	PMP4/6-311+G(2df)	no ^d	CaF ₄ ²⁻	-	+3.41 ⁿ	ADC(3)/TZVP-SP	yes ⁿ
MgO ²⁻	-	-1.46 ^{b,d}	PMP4/6-311+G(2df)	no ^d	SO ₅ ²⁻	-	-1.64 ^{b,e}	DFT/B3LYP/6-311+G(2d)	no ^e
MgS ²⁻	-	-2.52 ^{b,d}	PMP4/6-311+G(2df)	no ^d	CF ₆ ²⁻	-	+5.46 ^o	DFT/LFD/TZ2P	yes ^o
O ₂ ²⁻	yes ^a	-6.48 ^{b-d}	PMP4/6-311+G(2df)	no ^d	CCl ₆ ²⁻	-	+3.72 ^o	DFT/LFD/TZ2P	yes ^o
S ₂ ²⁻	yes ^a	-3.88 ^{b,d}	PMP4/6-311+G(2df)	no ^d	SiF ₆ ²⁻	yes ^g	+0.18 ^g	DFT/LFD/TZ2P	yes ^g
NCN ²⁻	yes ^a	-4.73 ^{b-d}	PMP4/6-311+G(2df)	no ^d	SiCl ₆ ²⁻	-	+4.28 ^o	DFT/LFD/TZ2P	yes ^o
OMgO ²⁻	-	-0.72 ^{b,d}	PMP4/6-311+G(2df)	no ^d	TiF ₆ ²⁻	yes ^g	+5.8 ^p	Koopmans	yes ^p
SMgS ²⁻	-	-1.17 ^{b,d}	PMP4/6-311+G(2df)	no ^d	TiCl ₆ ²⁻	yes ^g	+3.6 ^p	Koopmans	yes ^p
SO ₂ ²⁻	-	-5.19 ^e	DFT/B3LYP/6-311+G(2d)	no ^e	TiBr ₆ ²⁻	yes ^g	+2.9 ^p	Koopmans	yes ^p
OCCO ²⁻	yes ^a	-4.75 ^{b-d}	PMP4/6-311+G*	no ^d	TiI ₆ ²⁻	-	+2.4 ^p	Koopmans	yes ^p
SCCS ²⁻	-	-2.73 ^{b,d}	PMP4/6-311+G*	no ^d	ZrF ₆ ²⁻	yes ^g	+5.1 ^q	EPT3+/VDZP+diff.	yes ^q
OBEOBeO ²⁻	-	-0.39 ^{b,d}	PMP4/6-311+G*	no ^d	ZrCl ₆ ²⁻	yes ^g	+2.6 ^q	EPT3+/VDZP+diff.	yes ^q
OMgOMgO ²⁻	-	+1.39 ^d	PMP4/6-311+G*	yes? ^d	ZrBr ₆ ²⁻	yes ^g	+2.2 ^q	EPT3+/VDZP+diff.	yes ^q
SMgSMgS ²⁻	-	+0.20 ^d	PMP4/6-311+G*	no ^d	ZrI ₆ ²⁻	-	+1.7 ^q	EPT3+/VDZP+diff.	yes ^q
CO ₃ ²⁻	yes ^g	-3.75 ^{b,f}	PMP4/6-311+G*	no ^{b,h}	HfF ₆ ²⁻	yes ^g	+6.3 ^r	Koopmans	yes ^r
SiO ₃ ²⁻	yes ⁱ	-1.86 ^{b,j}	CISD/DZ2P+diff.	no ^j	HfCl ₆ ²⁻	yes ^g	+4.1 ^r	Koopmans	yes ^r
LiF ₃ ²⁻	-	+1.59 ^k	ADC(3)/TZ-D-SP	yes ^k	HfBr ₆ ²⁻	-	+3.3 ^r	Koopmans	yes ^r
NaF ₃ ²⁻	-	+2.17 ^k	ADC(3)/TZ-D-SP	yes ^k	HfI ₆ ²⁻	-	+2.7 ^r	Koopmans	yes ^r
KF ₃ ²⁻	-	+2.52 ^k	ADC(3)/TZ-D-SP	yes ^k	CrF ₆ ²⁻	yes ^s	+1.31 ^t	MCPFP/TZP	yes ^t
LiCl ₃ ²⁻	-	+1.50 ^k	ADC(3)/TZ-D-SP	yes ^k	MoF ₆ ²⁻	yes ^u	+0.58 ^v	CISD(Q)/TZP	no? ^v
NaCl ₃ ²⁻	-	+1.96 ^k	ADC(3)/TZ-D-SP	yes ^k	WF ₆ ²⁻	-	-0.92 ^{b,v}	CISD(Q)/TZP	no ^v
KCl ₃ ²⁻	-	+2.31 ^k	ADC(3)/TZ-D-SP	yes ^k	PtF ₆ ²⁻	yes ^w	+0.7 ^x	DVM-X _α DZ	yes? ^{w,x}
SO ₃ ²⁻	yes ^g	-2.85 ^e	DFT/B3LYP/6-311+G(2d)	no ^e	S ₂ O ₄ ²⁻	yes ^e	-2.23 ^{b,e}	DFT/B3LYP/6-311+G(2d)	no ^e
SO ₂ ²⁻	yes ^g	-1.34 ^{b,l}	QCISD(T)/6-311+G*	no ^{l,m}	S ₂ O ₆ ²⁻	yes ^e	+0.62 ^{b,e}	DFT/B3LYP/6-311+G(2d)	no ^e
SeO ₄ ²⁻	yes ^g	-0.72 ^{b,l}	QCISD(T)/6-311+G*	no ^l	S ₂ O ₈ ²⁻	yes ^e	+1.56 ^{b,e}	DFT/B3LYP/6-311+G(2d)	yes ^e
TeO ₄ ²⁻	-	-0.20 ^{b,l}	QCISD(T)/6-311+G*	no ^l	SeF ₆ ²⁻	-	+5.5 ^y	Koopmans	yes ^y
S ₂ O ₃ ²⁻	-	-1.33 ^{b,e}	DFT/B3LYP/6-311+G(2d)	no ^e	TeF ₆ ²⁻	yes ^z	+6.7 ^y	Koopmans	yes ^y
BeF ₄ ²⁻	yes ^g	+1.88 ⁿ	ADC(3)/TZVP-SP	yes ⁿ	TeCl ₆ ²⁻	-	+3.9 ^y	Koopmans	yes ^y

^a See references in ref 4. ^b Negative electron detachment energy means that the compact electronic wave function is not stable and the systems favors electron detachment. ^c Calculated in this work using the MP2(full)/6-31+G* geometry from reference 4. ^d Reference 4. ^e Reference 19. ^f At the MP2(full)/6-31+G* geometry. ^g Reference 21. ^h Also refs 11 and 20. ⁱ Reference 25. ^j Reference 12a. ^k Reference 8b. ^l Reference 16. ^m Also refs 11 and 19. ⁿ Reference 15. ^o Reference 26. ^p Reference 27. ^q References 28 and 29. ^r Reference 30. ^s Reference 31. ^t Reference 32a. ^u Reference 33. ^v Reference 32b. ^w Reference 34. ^x Reference 10. ^y Reference 17. ^z Reference 35.

in agreement with the recent ab initio calculations,^{14b-f} where the linear dianion was found to be vertically and adiabatically electronically unstable. Sommerfeld, Scheller, and Cederbaum^{14d} proposed a triangular C(C₂)₃²⁻ structure with D_{3h} symmetry, which was found to be electronically stable with respect to vertical and adiabatic autodetachment and stable with respect to all fragmentational pathways. Similar branched structures were found to be electronically stable for C₉²⁻^{14e,f} and for C₁₁²⁻.^{14f} Ab initio results on linear C₈²⁻ and C₉²⁻ are not conclusive, but C₁₀²⁻ was found to have positive vertical and adiabatic ionization energies.^{14b-f}

Nonlinear pentaatomic dianions of the form MF_{k+2}²⁻ (e.g., BeF₄²⁻, MgF₄²⁻, CaF₄²⁻; see Table 1) were predicted to have locally stable tetrahedral structures, to be stable to loss of an extra electron, but to be thermochemically unstable to loss of F⁻.¹⁵ These dianions are even more electronically stable than the AlkHal₃²⁻ species because the excess charges are delocalized over a larger number of halogen atoms. In contrast, the isoelectronic oxide dianions SO₄²⁻, SeO₄²⁻, and TeO₄²⁻ (from the MX_{(k+2)/2}²⁻ class of anions) do not support two electrons.^{11,16} It thus seems that having

halogens as ligands is an important factor for survival of doubly charged anions.

When the excess charge is delocalized through an even larger number of ligands, the electronic stability increases (see Table 1). For example, the vertical electron detachment energies of ZrF₆²⁻ and TeF₈²⁻ were predicted to be about 5 eV!^{17,18}

McKee¹⁹ recently presented ab initio results for electron detachment energies of some large sulfur oxide molecules: S₂O₃²⁻, SO₅²⁻, S₂O₄²⁻, S₂O₆²⁻, and S₂O₈²⁻. Only the last two dianions have positive vertical detachment energies, and only S₂O₈²⁻ has positive vertical and adiabatic electron detachment energies. Scheller and Cederbaum²⁰ predicted the existence of a large class of doubly charged fluorine- and chlorine-containing anions, which could be building blocks of melts and solutions.

II.2. Triply and Higher Charged Anions. Multiply charged anions with three or more extra electrons such as BO₃³⁻, PO₄³⁻, AlF₆³⁻, and LaF₆³⁻ are also considered as common species in the condensed phase. In Table 2 we list the mononuclear (i.e., with one central atom) triply charged anions which we expect to be the best candidates for survival in the gas phase because they all satisfy the MHal_{k+3}³⁻ or MO_{(k+3)/2}³⁻ formula. However, most if not all of these triply

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Table 2. Triply Charged Anions

anion	proposed to exist in condensed phase	vertical electron detachment energy (eV)	method	proposed to exist in gas phase
BO ₃ ³⁻	yes ^a	-8.72 ^{b,c}	PMP4/6-311+G*	no ^c
PO ₄ ³⁻	yes ^a	-5.33 ^{b,d}	Koopmans	no ^d
AsO ₄ ³⁻	yes ^a	-4.33 ^{b,d}	Koopmans	no ^d
SbO ₄ ³⁻	—	-3.52 ^{b,d}	Koopmans	no ^d
AlF ₆ ³⁻	yes ^a	-0.46 ^{b,e}	Koopmans	no ^e
GaF ₆ ³⁻	yes ^a	-0.24 ^{b,e}	Koopmans	no ^e
InF ₆ ³⁻	yes ^a	+0.41 ^{e,f}	Koopmans	no ^e
TlF ₆ ³⁻	yes ^a	+0.20 ^{e,f}	Koopmans	no ^e
ScF ₆ ³⁻	yes ^{a,g}	-1.78 ^{b,h}	MP2/VTZDZ+ddp	no ^h
YF ₆ ³⁻	yes ^g	-1.17 ^{b,h}	MP2/VTZDZ+ddp	no ^h
LaF ₆ ³⁻	yes ^g	-0.66 ^{b,h}	MP2/VTZDZ+ddp	no ^h
LaCl ₆ ³⁻	—	-0.12 ^{b,e}	PMP4/VDZ+diff.	no ^e

^a See references in ref 21. ^b Negative electron detachment energy means that the compact electronic wave function is not stable and the system favors electron detachment. ^c This work, at the MP2(full)/6-311+G* geometry. ^d Reference 16. ^e Reference 18. ^f InF₆³⁻ and TlF₆³⁻ both have negative orbital energies of the HOMO; however, we expect that electron correlation and electron relaxation corrections will decrease electronic stability by 1–2 eV, and therefore both anions are not electronically stable. ^g Reference 36. ^h Reference 23.

charged anions are found to not be electronically stable species (see Table 2). For two of them, LaF₆³⁻ and LaCl₆³⁻, the results are not conclusive; they are (barely) vertically electronically stable but probably will not be adiabatically stable after geometrical relaxation, although additional calculations need to be performed to make a final conclusion. Anions with four extra electrons such as MgF₆⁴⁻ are also considered in the condensed phase,²¹ but it is clear they will not be electronically stable as isolated species.

Numerous multiply charged *electronically stable* anions were considered in the review by Scheller, Cederbaum, and Compton^{1b} where it is shown that multiply charged anions can be stable if large numbers of halogen atoms are involved in the construction. All these species can be characterized by the simple formula M_mHal_{mk+n}ⁿ⁻ proposed in 1990 by Gutsev and Boldyrev,¹¹ where *m* is the number of central atoms M, *k* is the maximal valence of M, and *n* is the number of excess electrons.

II.3. Zintl Multiply Charged Anions. The Zintl anions E_mⁿ⁻ (where E are elements from group IVA or VA) are an important and large class of multiply charged anions.²² Cotton and Wilkinson report the existence of As₄²⁻, Sb₄²⁻, Bi₄²⁻, As₅³⁻, As₆⁴⁻, Sb₇³⁻, P₁₁³⁻, As₁₁³⁻, Ge₅²⁻, Sn₅²⁻, Pb₅²⁻, Sn₉³⁻, Sn₂Bi₂²⁻, and SnTi₄⁴⁻ in condensed phases. In view of the low electron affinities of the group IVA and VA elements, we do not expect any of these anions to survive in the gas phase.

We performed preliminary self-consistent-field (SCF) calculations for Bi₄²⁻ and Pb₄⁴⁻ Zintl anions, and our results are reported in Table 3. Both anions are geometrically stable when a medium-quality basis set (LANLDZ) is used. However, at this level of theory, the orbital energy of the highest occupied molecular orbital (HOMO) is positive. Hence, these anions are not electronically stable. When we added one set of diffuse basis functions (LANLDZ+D), Pb₄⁴⁻ was no

longer geometrically stable, but Bi₄²⁻ remained so. As more diffuse functions are added to the orbital basis set, the spatial extent of the Pb₄⁴⁻ electron charge distribution, measured by the mean value of *R*² (denoted as ⟨*R*²⟩ in Table 3), steadily increases. In contrast, the dianion Bi₄²⁻ remains geometrically stable as the orbital basis set is extended and the value of ⟨*R*²⟩ settles at ca. 300 Å. The positive HOMO orbital energy suggests, however, the electronic instability of this species. Certainly, more work should be done on the Zintl anions, but we suspect that these species will not be stable in the gas phase unless larger clusters are considered.

III. Comparison of Gas- and Condensed-Phase Properties

Many multiply charged anions that are electronically stable (for example, most of the doubly charged anions with general formula MHal_{k+2}²⁻) are also locally geometrically stable species, even though most are not thermodynamically stable. In these species, a large Coulomb potential barrier along the decomposition path produces an appreciable lifetime. Such barriers are due to avoided crossing of two dissociation channels: (i) MHal_{k+1}²⁻ + Hal, which is attractive, and (ii) MHal_{k+1}⁻ + Hal⁻, which is repulsive (see Figure 1). For some of these species, Scheller and Cederbaum predicted fragmentation lifetimes on the order of 10¹¹ years.⁸ In condensed phases, the solvent and/or counterion environment preferentially stabilizes the multiply charged anions, further slowing or even preventing their decomposition (i.e., by making the MHal_{k+1}⁻ + Hal⁻ channel higher in free energy).

Not surprisingly, the properties of isolated and electronically very stable anions obtained through *ab initio* calculations usually match well the corresponding experimental condensed phase results. However, for electronically weakly bound anions, the effect of the environment on the molecular geometry and vibrational frequencies may be very significant. In Figure 2 we compare (gas-phase) theoretical and condensed-phase experimental vibrational frequencies for the fully symmetric stretching (breathing) modes of a series of isoelectronic octahedral species.²³ For the electronically very stable WF₆ and TaF₆⁻ species, the discrepancy is within the range of the theoretical/experimental errors. This is not the case for ZrF₆²⁻ and, in particular, for LaF₆³⁻, where the discrepancies must be attributed to physicochemical effects occurring in the condensed phase. It is specifically in such cases that one should be careful about ascribing gas-phase molecular properties to those of the corresponding structural units embedded in condensed phases.

Many multiply charged anions (BO₃³⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻, etc.) commonly proposed in condensed media do not possess bound electronic states as isolated species. Nevertheless, it is often found that the geometries and vibrational frequencies calculated using modest, *ab initio*, bound-state-oriented methods are in qualitative agreement with corresponding condensed-phase data^{24–36} on these species. It is believed that by artificially constraining the description of the

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Table 3. Calculated Molecular Properties of Bi_4^{2-} and Pb_4^{4-} Zintl Anions

basis ^a	$E_{\text{HOMO}-1}$ (eV)	E_{HOMO} (eV)	R (Å)	$\langle R^2 \rangle$ (au)	
Pb_4^{4-} (T_d)	t_2	e			
LANLDZ	+9.93	+10.75	1.993	552	minimum
LANLDZ+D	+6.97	+7.78	2.022	706	not a minimum
LANLDZ+DD	+2.42	+4.82	1.967	1422	not a minimum
LANLDZ+DDD	-0.73	+2.67	1.959	3764	not a minimum
Bi_4^{2-} (D_{1h})	e_u	e_g			
LANLDZ	+1.28	+2.37	2.070	555	minimum
LANLDZ+D	+0.52	+1.63	2.070	570	minimum
LANLDZ+DD	+0.35	+1.52	2.071	589	minimum
LANLDZ+DDD	+0.30	+1.47	2.071	600	? ^b

^a For LANLDZ the LUMO has b_{2u} symmetry, and for LANLDZ+D the LUMO has e_u symmetry. ^b Failure of SCF convergence.

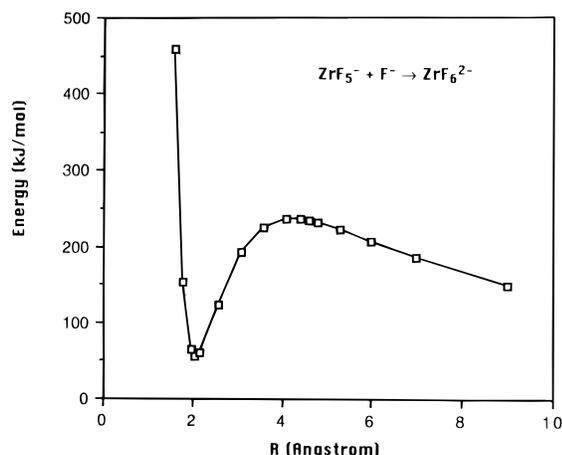


Figure 1. Potential energy curve for $\text{ZrF}_6^{2-} \rightarrow \text{ZrF}_5^- + \text{F}^-$ dissociation.

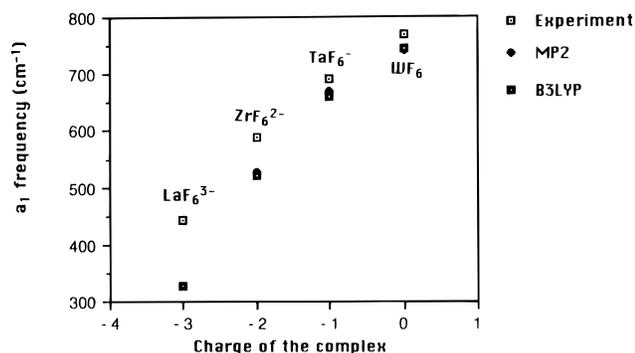


Figure 2. Dependence of the $\nu_1(a_1)$ frequency on the charge. anion's outermost electrons via a limited basis set, one can approximate the stabilizing influence of the condensed medium's solvent and/or counterions. How-

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ever, one is left with a not fully satisfactory approach for most rigorously bridging the gaps among gas-phase, light salvation, and fully condensed media situations.

IV. Reliability of the Theoretical Determination of Electronic Stability

The most crucial property of multiply charged anions discussed in this work is electronic stability. There are two methods for calculating electron stabilities: direct and indirect. In direct methods, the electronic stability is determined in *one calculation*. The simplest direct approach is the use of Koopmans' theorem in which the ionization energy is equal to the negative of the highest occupied orbital (HOMO) energy. In this method, electron relaxation and electron correlation are ignored. More sophisticated direct methods such as the electron propagator³⁷ and Green functions methods³⁸ are also available. In both of these methods, relaxation and electron correlation are taken into account, and when the atomic basis sets are large enough, these methods can provide accurate results.

With indirect methods, the ionization energy is calculated as a *difference* between total energies—that of the multiply charged anion and the same system with one fewer electron. A variety of indirect methods are currently in use, starting with the so-called Δ SCF approximation, where only the relaxation energy correction to Koopmans' theorem is taken into account upon ionization. Beyond the Δ SCF approximation, one frequently employs perturbation theory up to fourth and recently fifth order, configuration interaction methods, coupled cluster methods, and others.³⁹ Such more sophisticated methods require many computer resources and much computer time. Therefore, in many cases of relatively large systems, only the simplest direct (Koopmans') and indirect (Δ SCF) approximations can be used. Therefore, the question arises as to when conclusions made on Koopmans' theorem or the Δ SCF approximation can be trusted.

For example, if the HOMO orbital energy of a multiply charged anion is positive, does it mean that this anion is electronically unstable? To answer this question yes, the researcher must study the atomic

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Table 4. Calculated Vertical Electron Detachment Energies DE_v (eV)¹⁹

species	HOMO	Koopmans	Δ SCF	Δ PMP2	Δ PMP3	Δ PMP4	Δ QCISD	Δ QCISD(T)
SO ₄ ²⁻	1t ₁	+0.73	-1.10	-1.60	-1.13	-1.57	-1.10	-1.34
SeO ₄ ²⁻	1t ₁	+1.55	-0.91	-0.82	-0.54	-0.88	-0.51	-0.72
TeO ₄ ²⁻	1t ₁	+2.11	-0.47	-0.26	-0.03	-0.42	-0.12	-0.20

basis set dependence of this orbital energy. If the anion is not electronically stable, as the finite basis set size is increased by adding more and more diffuse functions, one finds that the most diffuse functions contribute substantially for the HOMO whose orbital energy converges to zero. According to the authors' experience, when electron relaxation and electron correlation are taken into account for multiply charged anions with positive HOMO energies, it is rare for the anion to become stable. Therefore, the positive orbital energy of the HOMO (when at least one set of diffuse functions were taken into account) is a good sign that the anion is not electronically stable. In this case a large set of diffuse functions may be used to simply allow an electron to "escape".

But what if the HOMO energy is negative; can one conclude that the anion is electronically stable? In Table 4 we present pertinent results for SO₄²⁻, SeO₄²⁻, and TeO₄²⁻. As follows from the table, the HOMO energies are quite negative (by up to 2 eV for TeO₄²⁻), but when relaxation is taken into account at the Δ SCF level, the anions become unstable. Even when electron correlation is included at the MP2, MP3, and MP4 levels, these anions remain electronically unbound. Therefore, if an anion has a negative HOMO energy, one cannot make a reliable conclusion about its electronic stability (except when the HOMO energy

is extremely negative). As seen from Table 4, the Δ SCF level of theory can also be misleading about electronic instability; usually, the Δ SCF level overestimates the instability. In summary, whenever the HOMO is negative, but less than 1–2 eV in magnitude, high-level ab initio calculations should be used to obtain reliable data.

V. Concluding Remarks

We believe that exploration of the nature of "structural units" which are electronically unstable in the gas phase yet stable in solution will continue to challenge theoretical chemists in the coming years. It is clear that, when solids, melts, solutions, and phase transitions are modeled, formal separation of materials into multiply charged anions and countercations may be misleading. This is true not only in chemistry, physics, and material science, but also in biochemistry, where multiply charged anions such as PO₄³⁻ are quite common species.

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