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FEATURE ARTICLE

Generation, Stability, and Reactivity of Small, Multiply Charged Ions in the Gas Phase

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Experimental and computational studies of small, multiply charged ions are of topical interest in chemistry and physics. Moreover, the increasing use of multiply charged ions in the analysis of environmental and biological samples calls for an improvement of the understanding of the fundamental properties of multiply charged ions at a molecular level. Mass spectrometric techniques in conjunction with advanced theoretical studies provide detailed insight into these aspects. This feature article describes the present state of research on small dications, dianions, and trications. Emphasis is given to thermochemically stable, multiply charged ions, with small trications in particular.

The often unusual bonding properties of diatomic dications have attracted the attention of chemists and physicists alike ever since Pauling's seminal paper from 1933.[1] Following a stimulating communication of Dunitz and Ha,[2] Beynon and co-workers demonstrated that even He_2^{2+} dication can be generated as a long-lived molecule in the gas phase.[3] Quite clearly, chemical bonding can thus overcome the strong electrostatic repulsion of the charge centers. Multiply charged ions are also assumed to play a role in extreme environments, as for example in the upper atmosphere; in this respect, metal ablation from meteorites and abandoned space crafts is particularly relevant because of the metals' low ionization energies.[4] An applied aspect of increasing importance evolves from the fact that the performance of numerous analytical methods, e.g., the characterization of biopolymers, crucially depends on the generation of long-lived, multiply charged ions.[5]

While several features of di- and polyatomic multiply charged ions are properly understood, contemporary research deals with fundamental questions regarding structures, stabilities, and the bonding schemes of small multiply charged ions in the balance between bonding and charge separation.[6] In this contribution, we limit ourselves to a discussion of a few of these fundamental aspects in small, long-lived polycations or polyanions with an emphasis on the interaction of the charge centers. In larger molecules, e.g., multiply ionized biomolecules, the repulsive interaction(s) of the multiple charges present can instead be treated as minor perturbations. Nevertheless, some implications derived from fundamental studies of small, multiply charged ions as described below are of crucial importance for the understanding of the behavior of larger molecules.

Generation

For many decades, (dissociative) electron ionization (EI) of volatile samples has served as a versatile means for the generation of long-lived multiply charged ions of small size. The multiply charged ions may either be formed directly from the neutral precursor by ejection of two electrons or in a stepwise manner with monocations as intermediates. Photoionization can also bring about formation of di- and trications;[7] however, the yields are often poor due to unfavorable Franck−Condon factors in the vertical transition from the neutral precursors to polycations which may cause prompt dissociation of the excited transient ions formed. Both techniques have in common that they permit the determination of thermochemical data of multiply charged ions by means of appearance-energy measurements and coincidence methods.[8,9] Since 1990, electrospray ionization (ESI) has been employed as an additional and quite efficient method to generate relatively small multiply charged ions.[10] A priori, the ESI approach is limited as far as highly reactive species are concerned because the ions emanate from solution, thereby only allowing generation of ions which do not react with the solvent(s) present.[11] Nevertheless, ESI has been used to generate some interesting multiply charged ions of moderate size in the gas phase, e.g., the $Ca(H_2O)_2^{2+}$ dication[12] and the $PtCl_6^{2-}$ dianion.[13]

Two other methods, charge stripping (CS) and double-charge transfer (DCT) spectroscopy, also provide some energetic information about multiply charged ions. In a typical CS experiment,[14] a mass-selected monocation AB^+ having several kiloelectronvolts of kinetic energy is collided with a stationary target gas to prompt ionization to the dication AB^{2+}. The energy required for the endothermic process $AB^+ \rightarrow AB^{2+}$ is taken from the kinetic energy of the projectile, resulting in a shift of the dication beam in the kinetic energy scale. This kinetic energy difference is referred to as the Q_{min} value,[5,14,15] and to a first approximation, Q_{min} corresponds to the vertical ionization energy (IE_v) of the cation AB^+. Thus, energy-resolved CS has been used to establish the energetics of numerous dications.[5,15] More sophisticated variants apply collision energies above 100 keV[16] and can assess rather short dication lifetimes. The DCT technique[17] follows a complementary approach in that a monocationic projectile P^+ having kiloelectronvolt energies is collided with the neutral target of interest, i.e., AB, while monitoring the anionic species P^- formed in the reaction $P^+ + AB \rightarrow P^- + AB^{2+}$. Provided that the transition $P^+ \rightarrow P^-$ is well understood, e.g., for atoms, kinetic energy analysis of the anion formed in DCT gives concise information about the various electronic states of the dication AB^{2+}; similarly, trications can be probed by triple-charge transfer (TCT) spectroscopy.[18] A fundamental drawback of DCT is, however, that it can only be applied to neutral molecules AB which exist

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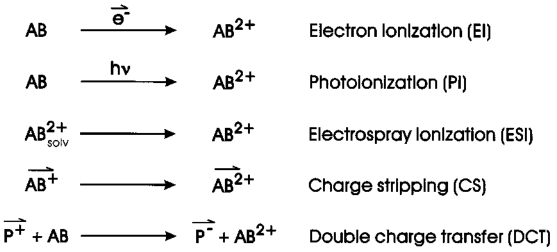

Figure 1. Survey of the most common methods used for the generation of dications. The half arrows indicate species of high translational energies.

as bulk compounds. Further, DCT is an indirect method in that the dicationic species themselves are not detected. In turn, DCT permits the examination of transient dications in the femtosecond regime which, due to facile dissociation, are not accessible at longer time scales.

Figure 1 gives a survey of the methods described in this section for the generation of molecular dications AB^{2+}. Higher polycations can be made analogously;[19] the generation of dianions is discussed in more detail further below.

Stability

A key aspect of multiply charged ions concerns the question of their thermochemical stability with respect to the asymptotes of the corresponding charge-separated fragments, i.e., $A^+ + B^+$ for a dication AB^{2+}, $A^- + B^-$ or $AB^- + e^-$ for a dianion AB^{2-}, and $A^{2+} + B^+$ for a trication AB^{3+}. The search for *thermochemically stable*, small dications and dianions has attracted considerable attention by both experimentalists and theoreticians, in particular because these studies provide insight into the nature of chemical bonding in the presence of multiple charges. "Thermochemical stability" is assigned to a diatomic dication for which the bound minimum AB^{2+} is lower in energy than the lowest atomic asymptotes, i.e., $A^+ + B^+$ and $A^{2+} + B$. Under thermal conditions, most of these multiply charged ions undergo rapid electron transfer in bimolecular collisions with neutral reactants because of the low ionization energies (IEs) of many neutral atoms and molecules in comparison with IE(AB^+). Accordingly, thermochemical stability is a property confined to isolated molecules, i.e., to an idealized environment as exists in gas-phase studies. Using diatomic dications as an example, these stability aspects are discussed next in some more detail; similar considerations apply for other multiply charged cations as well as anions.

Dications. As already recognized in 1955,[20] the prospect of generating thermochemically stable dications in the gas phase can be derived from some basic considerations which are best illustrated for rare gas dimers. Thus, a thermochemically stable dication AB^{2+} is predicted to exist, given that the lowest dissociation asymptote corresponds to $A^{2+} + B$, that is, IE(A^+) < IE(B). In such a situation, the mere electrostatic interaction between the dication A^{2+} and neutral B gives rise to a bound dication AB^{2+} as the global minimum (Figure 2a). A simple example is the thermochemically stable $XeHe^{2+}$ dication, for which IE(Xe^+) = 21.2 eV is much smaller than IE(He) = 24.5 eV.[21] Even if IE(A^+) exceeds IE(B), the corresponding dication AB^{2+} may be thermochemically stable, provided the binding energy $D(A^{2+}{-}B)$ compensates for the difference of the IEs (Figure 2b). For example, $KrHe^{2+}$ certainly is thermochemically stable, even though IE(Kr^+) = 24.6 eV slightly exceeds IE(He). Upon further increase of IE(A^+), the corresponding dication AB^{2+} becomes metastable with respect to the dissociation into A^+ and B^+. Despite a highly exothermic charge separation reaction ("Coulomb explosion"),[15] the presence of a barrier confines kinetic stability to the systems. The height of this barrier is essentially determined by the crossing of the attractive $A^{2+}{-}B$ potential with the repulsive Coulomb curve of the charge separation products $A^+ + B^+$. As a consequence of this barrier, many metastable dications reside in modest to fairly deep potential energy wells and are long-lived (Figure 2c). For example, a barrier of ca. 0.8 eV prevents the dissociation of metastable $ArNe^{2+}$ into monocations, although charge separation is by about 4.5 eV exothermic.[22] Even more extreme, the $He_2{}^{2+}$ dication mentioned above has a considerable barrier (1.4 eV) despite the >20 eV exothermicity of charge separation.[2,3] Once the potential energy curves of the charge-separated products cross the vicinity of potentially bound minima, the dication lifetimes drastically decrease, and these species may escape experimental detection (termed as "unstable" in Figure 2d). For example, an entirely repulsive potential curve has been predicted for the $^1\Sigma^+$ ground state of $Ne_2{}^{2+}$ dication.[23] However, even high above the Coulomb curves, metastable dications may exist that arise from excited states of the separate atoms (Figure 2e); here, the repulsive ground state asymptote can only be reached via radiative transitions.[16]

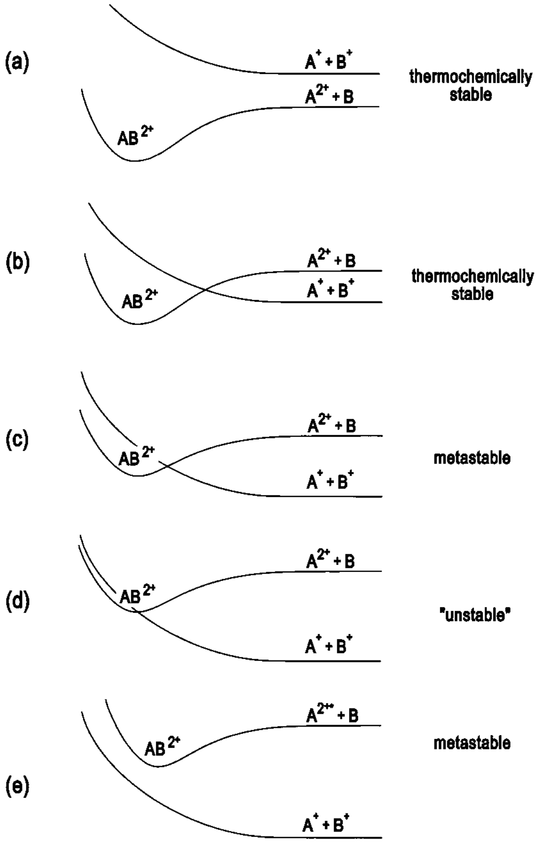

Figure 2. Schematic representation of potential energy curves for diatomic dications AB^{2+}: (a) thermochemically stable dication with IE(A^+) < IE(B); (b) thermochemically stable dication with IE(A^+) > IE(B); (c) metastable dication with IE(A^+) ≫ IE(B); (d) "unstable" dication in which the Coulomb curve crosses the charge polarization curve in the vicinity of the AB^{2+} minimum; (e) metastable dication in an electronically excited state.

This feature article deals primarily with energetically low-lying, multiply charged ions which arise from the corresponding ground state asymptotes of the charge-separated products. As far as thermochemical stability is concerned, in addition to rare gas clusters,[24,25] several thermochemically stable diatomic dications are found among the binary metal fluorides.[26,27] This is because many metal cations M^+ have relatively low IEs,

TABLE 1: Survey of Thermochemically Stable Diatomic Dications Described So Far

	theory	experiment
rare gas clusters	$BeHe^{2+}$,[a] $BeNe^{2+}$,[a] $BeAr^{2+}$,[a] BHe^{2+},[a] CHe^{2+},[a] $MgNe^{2+}$,[b,c] $MgAr^{2+}$,[d] $SiHe^{2+}$,[a] $SiNe^{2+}$,[e] $TiHe^{2+}$[f]	$GeNe^{2+}$,[g] $GeAr^{2+}$,[g] $GeKr^{2+}$,[g] $XeNe^{2+}$,[h] $PtHe^{2+}$[i]
fluorides	BeF^{2+},[j,k] MgF^{2+},[b] AlF^{2+},[l,m] SiF^{2+},[l,m] PF^{2+},[e] TiF^{2+},[n] ZrF^{2+},[n] UF^{2+}[o]	MgF^{2+},[p] AlF^{2+},[m] SiF^{2+},[m] TiF^{2+},[n] BaF^{2+},[q] UF^{2+}[o]
halides (except F)	$MgCl^{2+}$,[j] $CaCl^{2+}$,[r] $CaBr^{2+}$,[s] BaI^{2+}[t]	$MgCl^{2+}$,[p] $CaBr^{2+}$,[q] $FeCl^{2+}$,[u] $SrCl^{2+}$,[q] $BaCl^{2+}$,[q] $BaBr^{2+}$,[q] BaI^{2+}[q]
others	MgN^{2+},[b] [d]MgO^{2+},[b] ScN^{2+}[v]	UO^{2+}[w]

[a] Reference 24b,c and references therein. [b] Reference 24f. [c] Leung, A. W. K.; Julian, R. R.; Breckenridge, W. H. *J. Chem. Phys.* **1999**, *110*, 8443. [d] Reference 24g. [e] Reference 24d,e. [f] Reference 24a. [g] Reference 25c. [h] Reference 25a. [i] Reference 25b. [j] Reference 26a. [k] Ornellas, F. R.; Machado, F. B. C. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, 1993. [l] Reference 28. [m] Reference 29. [n] Reference 48. [o] Reference 51. [p] Reference 27a. [q] Reference 27b. [r] Wright, J. S.; Carpenter, D. J.; Alekseyev, A. B.; Liebermann, H.-P.; Lingott, R.; Buenker, R. J. *Chem. Phys. Lett.* **1997**, *266*, 391. [s] Alekseyev, A. B.; Liebermann, H.-P.; Lingott, R.; Buenker, R. J.; Wright, J. S. *Mol. Phys.* **1997**, *91*, 777. [t] Alekseyev, A. B.; Liebermann, H.-P.; Lingott, R. M.; Buenker, R. J.; Wright, J. S. *Spectrochim. Acta* **1999**, *A55*, 467. [u] Reference 33. [v] Kunze, K. L.; Harrison, J. F. *J. Phys. Chem.* **1991**, *95*, 6418. [w] Cornehl, H. H.; Heinemann, C.; Marcalo, J.; Pires de Matos, A.; Schwarz, H. *Angew. Chem.* **1996**, *108*, 950; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 891.

whereas the ionization energy of the fluorine atom is quite large (17.4 eV). As shown in Table 1, a series of other diatomic molecules are known to form thermochemically stable dications. This list can easily be extended by simple thermochemical considerations. For example, many halides and oxides of rare earth and actinide metals M exhibit the corresponding diatomic MX^{2+} dications (X = halogen, oxygen) as the global minima on the respective potential energy curves. This reflects the fact that $IE(M^{+})$ is often lower than IE(X) for these elements. Moreover, the strong covalent bonds between electropositive metals and electronegative elements may lead to thermochemically stable dications even if $IE(M^{+}) > IE(X)$. For example, in perfect agreement with a computational prediction,[28] the AlF^{2+} dication is thermochemically stable[29] although $IE(Al^{+}) = 18.8$ eV exceeds $IE(F) = 17.4$ eV. The thermochemical stability of AlF^{2+} can be traced back to the $^{1}\Sigma^{+}$ ground state of the dication which arises from perfect pairing of Al^{2+} (^{1}S) and F (^{2}P). This favorable bonding scheme gives rise to a reasonably strong Al–F bond in the dication, i.e., $D(Al^{2+}{-}F) = 3.4$ eV compared to $D(Al^{+}{-}F) = 3.2$ eV.[29] Interestingly, the situation is almost opposite in the SiF^{+}/SiF^{2+} congeners.[28,29] Thus, the monocation SiF^{+} has a $^{1}\Sigma^{+}$ ground state with the two remaining valence electrons on silicon occupying a nonbonding orbital which is by and large the 3s orbital of silicon. Upon ionization to SiF^{2+} ($^{2}\Sigma^{+}$), one of these electrons must be removed. Formally, this bonding situation corresponds to the perfect pairing of $F(^{2}P)$ with Si^{2+} (^{3}P) rather than the Si^{2+} (^{1}S) ground state of the silicon dication. This unfavorable binding situation in SiF^{2+} ($^{2}\Sigma^{+}$) leads to a considerable decrease from $D(Si^{+}{-}F) = 6.6$ eV in the monocation to $D(Si^{2+}{-}F) = 1.9$ eV in the dication.[29] Nevertheless, SiF^{2+} is still a thermochemically stable dication and even supports an excited SiF^{2+} ($^{2}\Pi$) state below the charge separation asymptote Si^{+} (^{2}P) + F^{+} (^{3}P).[28]

As far as slightly larger dications are concerned, there exist two opposing trends. Of course, additional atoms are likely to lower the IEs of the corresponding monocations. However, extension of the molecular systems also opens up new fragmentation channels which may be much lower in energy than the dissociation asymptotes in diatomic dications. Two simple examples may suffice to illustrate this dichotomy. (i) Despite very similar bonding situations in the FeO^{+}, FeS^{+}, and $FeNH^{+}$ cations,[30] the Q_{min} values of the monocations decrease from 18.3 ± 0.3 eV and 16.7 ± 0.5 eV for the diatomic molecules FeO^{+} and FeS^{+} to 16.3 ± 0.4 eV for the triatomic $FeNH^{+}$ cation.[30b,31] As a consequence, the corresponding bond strengths increase from $D(Fe^{2+}{-}O) = 2.0$ eV and $D(Fe^{2+}{-}S) = 2.7$ eV to $D(Fe^{2+}{-}NH) = 3.5$ eV. While FeO^{2+} and FeS^{2+} are metastable,[31] complementary data predict $FeNH^{2+}$ as a thermochemically stable dication.[30b] Compared to FeO^{2+} and FeS^{2+}, the increased stability of $FeNH^{2+}$ is attributed to the presence of the hydrogen atom, which facilitates the distribution of the positive charge. (ii) In contrast, triatomic $FeCl_2^{2+}$ is not thermochemically stable. The lowest-lying dissociation asymptote of $FeCl_2^{2+}$ corresponds to charge separation associated with rearrangement under concomitant Cl–Cl bond formation to yield $Fe^{+} + Cl_2^{+}$. The preference of this exit channel results from the ordering of the respective ionization energies in that $IE(Cl_2) = 11.5$ eV[32] is much lower than $IE(FeCl^{+}) = 15.9$ eV and $IE(Cl) = 13.0$ eV.[33]

Accordingly, many polyatomic dications are metastable because energetically lower lying charge separation asymptotes exist.[34] In particular, dications observed in the EI mass spectra of organometallic compounds are often not thermochemically stable because low-lying dissociation asymptotes are accessible. For example, the abundant dications $(c\text{-}C_5H_5)_2M^{2+}$ (M = Fe, Co, Ni) formed upon EI of neutral metallocenes are metastable and undergo unimolecular dissociation not only to the expected charge separation products $(c\text{-}C_5H_5)M^{+} + C_5H_5^{+}$ but also expel a metal cation M^{+} concomitant with formation of a $C_{10}H_{10}^{+}$ cation, thus demonstrating that ligand coupling can occur in metallocene dications.[35]

Dianions. Several aspects of multiply charged anions have been reviewed recently, including comprehensive lists of examples.[36] As far as stability is concerned, similar considerations as outlined above for dications apply for dianions. However, the criterion of thermochemical stability is much more strict than for multiply charged cations, because charge separation is usually associated with electron detachment, i.e., $AB^{2-} \rightarrow AB^{-} + e^{-}$. As quantum mechanical tunneling is facile for electrons, molecular dianions are therefore usually only stable, if the corresponding monoanions exhibit positive electron affinities, i.e., $EA(AB^{-}) > 0$. Note, however, that metastable dianions may also exist if electron loss is associated with considerable structural changes, thus exhibiting unfavorable Franck–Condon factors for electron detachment (see below).

Until very recently, small molecular dianions have predominately been a matter of theoretical studies. The limited number of experimental reports can primarily be attributed to the lack of appropriate experimental methods to generate small or medium-sized dianions. For example, while electron ionization is well-suited to generate multiply charged cations as well as monoanions, in the case of dianions there exists a fundamental conflict between generating reactive species having reasonably high EAs on one hand and the hyperthermal nature of the ionization method on the other hand. For illustration, let us discuss the gas-phase generation of dicarboxylate dianions $^{-}OOC{-}(CH_2)_n{-}COO^{-}$. Electron ionization would require volatile precursors, for example the diesters $ROOC{-}(CH_2)_n{-}COOR$, in which two reasonably strong R–O bonds need to be broken while attaching two electrons to the carboxyl residues. Energized electrons may well fulfill the first task, but the resulting species are too energetic to yield long-lived dianions

TABLE 2: Survey of Small, Long-Lived Triply and Quadruply Charged Molecular Cations Considered So Far

	theory	experiment
diatomic rare gas clusters	CNe^{3+},[a] NNe^{3+},[b,c] NAr^{3+},[d] $AlHe^{3+}$,[e] $AlNe^{3+}$,[e] $SiHe^{3+}$,[a] $SiHe^{4+}$,[a] PHe^{3+},[b] PNe^{3+},[d] SHe^{4+},[b] VHe^{3+},[e] YHe^{3+},[f] $LaHe^{3+}$,[g] $GdHe^{3+}$,[g] $LuHe^{3+}$,[g] $ThHe^{4+}$[e]	VHe^{3+}[h]
diatomic fluorides	CF^{3+},[a] OF^{3+},[b] F_2^{4+},[b] SF^{3+},[d] TiF^{3+},[i] ZrF^{3+},[i] UF^{3+}[j]	SF^{3+},[k] TiF^{3+},[i] VF^{3+},[l] UF^{3+}[j]
other diatomics	B_2^{3+},[m] BN^{3+},[n] CO^{3+},[o] OCl^{3+},[d] Al_2^{3+},[p] Cl_2^{3+},[q] Br_2^{3+},[q] I_2^{3+}[q]	B_2^{3+},[m] CS^{3+},[r] S_2^{3+},[s] Cl_2^{3+},[q] VO^{3+},[l] Br_2^{3+},[q] I_2^{3+}[q]
small polyatomics	$CFHe^{3+}$,[a] $CHeNe^{3+}$,[t] CHe_3^{3+},[a] CHe_4^{4+},[a] CNe_4^{4+}[a]	COS^{3+},[r] CS_2^{3+},[r,u] CSe_2^{3+},[p] SO_2^{3+},[v] UF_2^{3+}[l]

[a] Reference 24b and references therein. [b] Pyykkö, P. *Mol. Phys.* **1989**, *67*, 871. [c] An entirely repulsive curve for NNe^{3+} was reported by: Wong, M. W.; Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Chem. Phys.* **1989**, *91*, 2971. [d] Reference 24d. [e] Reference 24a. [f] Wesendrup, R.; Pernpointer, M.; Schwerdtfeger, P. *Phys. Rev. Lett.*, submitted. [g] Reference 46. [h] Reference 25b. [i] Reference 48. [j] Reference 51. [k] Nagesha, K.; Marathe, V. R.; Mathur, D. *Chem. Phys.* **1991**, *154*, 125. [l] Reference 50. [m] Wheathers, D. L.; McDaniel, F. D.; Matteson, S.; Duggan, J. L.; Anthony, J. M.; Douglas, M. A. *Nucl. Instrum. Methods* **1991**, *56*/*57*, 889. [n] Mahwinney, R. C.; Bruna, P. J.; Grein, F. *J. Phys. B: At. Mol. Opt. Phys.* **1995**, *28*, 4015. [o] The existence of metastable states is uncertain; see: Handke, G.; Tarantelli, F.; Cederbaum, L. S. *Phys. Rev. Lett.* **1996**, *76*, 896. [p] Bruna, P. J.; Wright, J. S. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, 1819 and references therein. [q] Ref 81. [r] Safvan, C. P.; Krishnamurti, M.; Mathur, D. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, L837. [s] Morvay, L.; Cornides, I. *Int. J. Mass Spectrom. Ion Processes* **1984**, *62*, 263. [t] Radom, L.; Gill, P. M. W.; Wong, M. W.; Nobes, R. H. *Pure Appl. Chem.* **1988**, *60*, 183. [u] Reference 18. [v] Lavollée, M.; Brems, V. *J. Chem. Phys.* **1999**, *110*, 918.

and vice versa. An earlier study of dicarboxylate dianions circumvented this problem by subjecting $ROOC-(CH_2)_n-COO^-$ monoanions to dissociative electron transfer in kiloelectronvolt collisions.[37] Several other small dianions which have been predicted to be stable, e.g., the elusive[38] BeF_4^{2-}, could not be made so far due to the lack of appropriate precursors to generate these species in the gas phase.[39,40]

A solution of this experimental dilemma has been provided by electrospray ionization, which not only can be used to smoothly generate dicarboxylate dianions[41] but has recently also been employed to generate counterion free dianions of the hexahalides MCl_6^{2-} and MBr_6^{2-} (M = Re, Os, Ir, Pt).[13] An elegant experimental device[42] has been used to study dianions by photoelectron spectroscopy, and despite its moderate size, the $PtCl_6^{2-}$ dianion has an electron detachment energy of 1.46 eV.[13] Thus, the experimental detection of other small elusive dianions, as for example T_d symmetrical BeF_4^{2-} as one of the smallest bound dianions,[38,43] seems to appear more as a mere matter of willingness by experimentalists to handle berrylium solutions than a fundamental problem.[39]

Trications. Except for atoms, the generation of small trications is much more challenging than that of dications, because third ionization energies are rather huge (often >30 eV) and, as a consequence of the stronger Coulomb repulsion, most molecular trications are unstable and expected to dissociate spontaneously.[44] No surprise, the majority of the diatomic trications do indeed exhibit entirely repulsive potential energy curves. Only very few long-lived trications of small or moderate size have so far been examined experimentally (Table 2). Surprisingly, also the number of theoretical studies on small trications is quite limited given the unusual bonding features typical for some of these systems. Note, however, that for trications a sufficient description of correlation effects in the computational studies becomes increasingly difficult and the number of low-lying states grows rapidly.[44,45]

Atomic data can again be used to predict the existence of thermochemically stable diatomic trications among rare gas compounds. For example,[46] the third ionization energies of some rare earth and actinide metals are lower than those of helium and neon, e.g., $IE(La^{2+}) = 19.2$ eV and $IE(Th^{2+}) = 18.3$ eV versus IE(He) = 24.5 eV and IE(Ne) = 21.6 eV. On the basis of these considerations, Pyykkö and co-workers have even predicted the existence of $ThHe^{4+}$ as an at least metastable, if not thermochemically stable, diatomic tetracation, because the bond strength $D(Th^{4+}-He)$ in the tetracation may compensate for the difference of the ionization energies, $IE(Th^{3+}) = 28.7$ eV versus IE(He) = 24.5 eV. As far as bonding features are concerned, these multiply charged rare gas compounds are somewhat trivial, however, because the bonding can by and large be attributed to mere electrostatic interactions between the multiply charged metal cores and the neutral rare gas ligands.

Our own recent interest in this field was triggered by some speculation about the possible existence of energetically low-lying diatomic trications having *covalent* bonds. Quite clearly, for a covalently bound diatomic trication AB^{3+} to be thermochemically stable, several requirements have to be met. (i) As the relationship $IE(A^{2+}) < IE(B)$ does not hold true for most, if not all systems, the difference of the IEs should be as small as possible. (ii) Irrespective of the actual charge distribution in AB^{3+}, large electronegativity differences of the building blocks will help to strengthen the bond between A and B. (iii) Triple ionization should not involve electrons engaged in the σ-bond between the atoms. By analogy to the thermochemically stable dications (see above), the combination of a metal atom with fluorine appears promising. As far as the choice of the metal is concerned, it should have few valence electrons in order to avoid any eventual repulsion between occupied orbitals at the metal and the 2p orbitals of fluorine. While early transition metals form strong bonds with fluorine[47] and also exhibit low ionization energies, the number of valence electrons must, however, at least correspond to four, one electron for σ-bond formation with fluorine and three electrons to be removed upon ionization to the corresponding trication.

Accordingly, our first choice was titanium fluoride, and TiF^{3+} can indeed be made by charge-stripping of the TiF^{2+} dication.[48] The experimentally measured $Q_{min}(TiF^{2+}) = 28 \pm 3$ eV agrees with $IE(TiF^{2+}) = 26.9$ eV, as predicted by CCSD(T) calculations using reasonably large and flexible basis sets for titanium and fluorine. As a consequence of its huge endothermicity, the charge-stripping process $TiF^{2+} \rightarrow TiF^{3}$ is, however, not very efficient. Given possible artifacts in sector mass spectrometers,[49] the nature of TiF^{3+} as a long-lived, diatomic trication may thus be questioned. While examination of the natural isotopes lends more credibility to the assignment, some ambiguity remains. Fortunately, a definitive proof of the existence of long-lived TiF^{3+} could be achieved by mass-selecting the tiny signal formally corresponding to $^{48}Ti^{19}F^{3+}$ ($m/z = 22.3$) from the ions exiting the source and subjecting it to a charge-exchange (CE) experiment (Figure 3). The mere observation of TiF^{2+} ($m/z = 33.5$) and TiF^{+} ($m/z = 67$) unambiguously demonstrates the existence of long-lived TiF^{3+} because only $z = 3$ can account for the observed mass-to-charge ratios. Considering the fact that $IE(Ti^{2+}) = 27.5$ eV is much larger than IE(F) = 17.4 eV, it is though not surprising that TiF^{3+} is metastable with respect to the charge separation into $Ti^{2+} + F^{+}$ by 6.2 eV. Nevertheless, the $^1\Sigma^+$ ground state of TiF^{3+} together with $r_{Ti-F} = 1.65$ Å in the trication (compared to 1.66 Å in TiF^{2+} and 1.81 Å in TiF^{+})

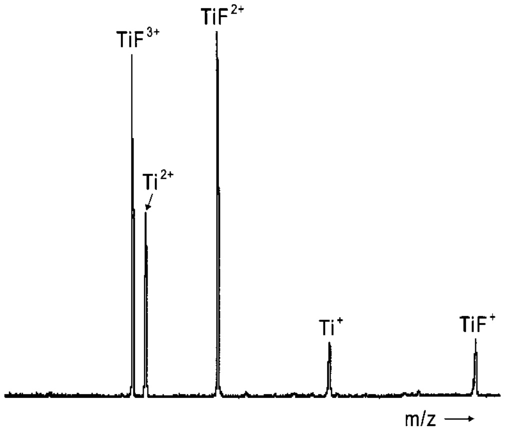

Figure 3. Charge exchange spectrum of mass-selected TiF^{3+} cations ($m/z = 22.3$) generated by electron ionization of gaseous TiF$_4$ (ref 48). In addition to Ti^{n+} fragments ($n = 1, 2$; $m/z = 48$ and 24, respectively), the characteristic charge exchange products, TiF^{2+} and TiF^{+} are observed at $m/z = 33.5$ and 67, respectively.

corroborates the description of TiF^{3+} as a covalently bound diatomic trication.

The attempt to increase the stability of MF^{3+} trications by switching to other 3d transition metals fails. For example, while scandium is more electropositive than titanium in that IE(Sc^{2+}) = 24.8 eV is notably lower than IE(Ti^{2+}) = 27.5 eV, the Sc^{3+} (^{1}S) cation with an argon-like core does not fit the bonding scheme outlined above because no valence electron is available to form a strong σ-bond with fluorine. Vanadium and later 3d metals have enough electrons but are poor choices because of the larger IE(M^{2+}), which disfavor the MF^{3+} trications. Accordingly, the experimentally observed[50] long-lived trications VF^{3+} and VO^{3+} are both assumed to be metastable with respect to charge separation. Progression to the 4d series is more promising, and theory predicts[48] that ZrF^{3+}, although still metastable, is only about 1 eV above the charge separation asymptote yielding Zr^{2+} + F^{+}. For 5d metals, however, formation of thermochemically stable trications becomes again less favorable because the ionization energies start to increase from the 4d to the 5d series due to the operation of relativistic effects, e.g., IE(Zr^{2+}) = 23.0 eV versus IE(Hf $^{2+}$) = 23.3 eV.

The f-elements are particularly promising candidates in that these metals have s^{1}f^n ground or low-lying excited states such that one electron is available for binding fluorine, while multiple ionization can occur from the more or less nonbonding f-manifold. In fact, UF^{3+} is predicted as the first thermochemically stable diatomic trication having a covalent bond, and its existence is unambiguously proven by CE experiments.[51] Figure 4 depicts the schematic potential-energy curves for UF^{n+} ($n = 1-3$) which indicate that at its minimum the tightly bound UF^{3+} trication is ca. 1.9 eV lower in energy than the charge separation products U^{2+} + F^{+}. Our work on UF^{3+}, however, also demonstrates the need for further research in this area. For example, as accurate higher ionization energies of atomic uranium have not yet been determined experimentally,[52] some ambiguity remains with respect to the quest for the thermochemical stability of UF^{3+}. Further, relativistic effects being of prime importance for uranium are covered only gradually in the computational study.[51]

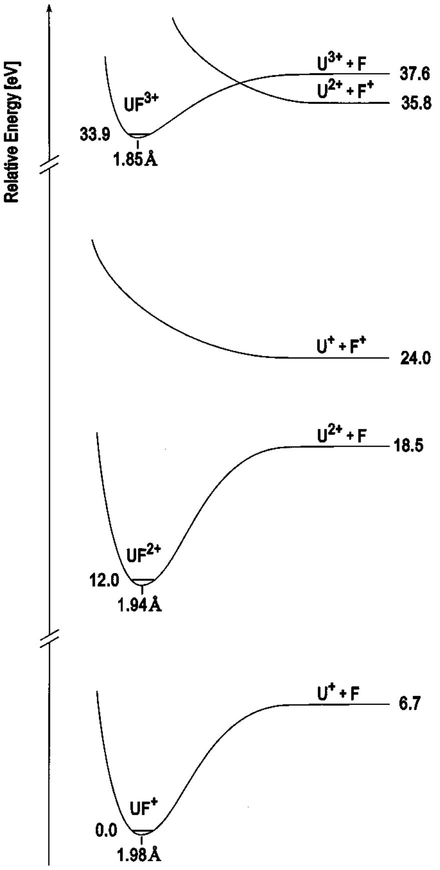

Figure 4. Calculated thermochemical data (in eV) of UF^{n+} diatomic cations ($n = 1-3$) (ref 51).

On the basis of the arguments outlined above for dications, the prospects of generating thermochemically stable trications with more than two atoms are quite limited. Perhaps, the long-lived UF$_2$$^{3+}$ trication[50] is also thermochemically stable, but the lack of reliable thermochemical data postpones a definitive assignment for this as well as other systems. Finally, by analogy to the metallocene dications discussed above, most trications generated by electron ionization of organometallic compounds are presumably metastable with respect to charge separation. Very large molecules, e.g., multiply protonated proteins, can, of course, experience thermochemical stability because Coulomb repulsion of the charge centers becomes almost negligible for large sizes.

Reactivity

Two aspects of unimolecular reactivity deserve particular attention for multiply charged ions and are discussed briefly. At first, multiple ionization is often associated with substantial structural changes and even leads to reversed stabilities in many cases. For example, the T_d symmetrical structure of carbon tetrachloride is not a minimum on the dication surface, and spontaneous rearrangement to a C_{2v} symmetrical [Cl$_2$C•Cl$_2$]$^{2+}$ structure occurs.[53] Another example is the [Cr,O$_2$]$^{2+}$ dication for which the most stable isomer is predicted to exhibit an O−O bond and can be described as a side-on [Cr•O$_2$]$^{2+}$ complex; the chromium dioxide structure O═Cr═O preferred in the anionic, neutral, and monocationic stages is higher in energy for the dication.[54] The second aspect of unimolecular reactivity concerns the details (e.g., dynamic aspects)[55] in the conversion of potential into kinetic energy in Coulomb explosions of multiply charged ions.[5,15] For example, Vékey and Szilágyi introduced an advanced method for the analysis of the experimental peak shapes associated with Coulomb explosions of metastable ions.[56] Thus, instead of the previously accepted estimation of the associated kinetic energy release from formal peak widths,[15] their approach includes the explicit analysis of the entire peak shape in order to extract the underlying kinetic energy release distribution (KERD). Their analysis of previously reported experimental data[57] for the charge separation reaction $HONO^{2+} \rightarrow NO^+ + HO^+$ implied a considerable revision of the intercharge distance at the crossing point compared to the previous estimate derived from the 'horns' of the peak. Interestingly, these results were in good agreement with the simple avoided-crossing model proposed by Gill and Radom in 1988.[58] Another timely topic concerns the possible role of tunneling in electron detachment from molecular dianions.[41,59] The examples given here may demonstrate that the unimolecular reactivity of multiply charged ions forms a continuously challenging area of research for experimentalists and theoreticians alike.

As far as the bimolecular reactivity of multiply charged ions with neutral substrates S is concerned, two extreme cases, which comprehend the most typical reactions of many multiply charged ions, deserve to be distinguished. In the first class of reactions, initial electron transfer prevails because the ionization energies of the substrates are much lower than the recombination energies of polycations (reaction 1) or the electron affinities of the substrates exceed those of the dianions (reaction 2a); in the latter case, the substrates may also bind to the anions, thereby inducing electron detachment (reaction 2b).

$$AB^{n+} + S \rightarrow AB^{(n-1)+} + S^+ \qquad (1)$$

$$AB^{2-} + S \rightarrow AB^- + S^- \qquad (2a)$$

$$AB^{2-} + S \rightarrow ABS^- + e^- \qquad (2b)$$

The second class of reactions comprises dications which have fairly low ionization energies and dianions with large electron affinities, respectively. These species behave similarly to singly charged ions in their reactions with neutral molecules in that various types of bond-formation and bond-breakening reactions may occur. This situation is to be expected if $IE(AB^+) < IE(S)$ or $EA(AB^-) > EA(S)$, respectively; because the condition $IE(AB^{2+}) < IE(S)$ can hardly be fulfilled, small trications are not considered here.[60] Prominent examples for this type of behavior are the reactions of the dications of early transition metals with various organic substrates in which charge transfer often constitutes a minor channel while bond-forming processes prevail (see below).[61]

Despite several interesting physical aspects,[62] reactions 1 and 2 can be described as simple outersphere charge-transfer processes; in particular, they do not bring about selective bond activations of the substrates which are difficult to achieve by other means of electron transfer. We do not pursue this ubiquitous type of reactivity any further. Instead, a few examples of bond-forming reactions of multiply charged ions are described.[63]

Although electron transfer is exothermic by several electronvolts, Newson and Price[64] have reported bond-forming reactions of some small dications as for example reaction 3. These and related studies[65] have demonstrated that $[CF_2 \cdot H_2]^{2+}$ can exist as a long-lived intermediate; doubly charged products with new bonds were not observed, however.

$$CF_2^{2+} + H_2 \rightarrow CHF_2^+ + H^+ \qquad (3)$$

Detailed analysis of reactivity studies such as reaction 3 can thus provide insight into the behavior of transient multiply charged ions which are difficult to generate otherwise.

As already mentioned, doubly charged transition metals sometimes lack electron-transfer pathways in their ion/molecule reactions.[61] For example, charge and anion transfers are minor channels in the reactions of Y^{2+} and La^{2+} with several simple alkanes; the major pathways are associated with metal-induced dehydrogenation of the hydrocarbons to afford multiply charged metal−alkene complexes. This behavior very much resembles the reactivities of the corresponding monocations, but due to their increased electrophilicities, the metal dications are significantly more reactive than their singly charged counterparts. Niobium dication, for example, even dehydrogenates methane (reaction 4), while none of the monocations of the 3d and 4d metals is capable of methane activation under thermal conditions.[66]

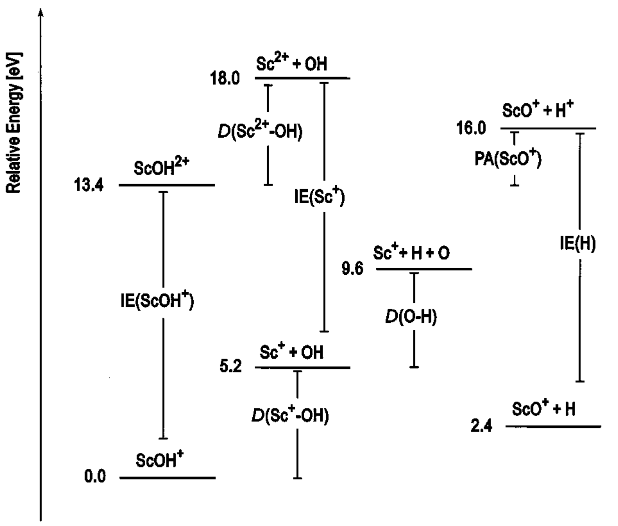

Figure 5. Deduction of the proton affinity of ScO^+ monocation using a thermochemical cycle. Data taken from refs 21, 67, and 68.

$$Nb^{2+} + CH_4 \rightarrow NbCH_2^{2+} + H_2 \qquad (4)$$

Obviously, the apparent suppression of electron- and anion-transfer channels with these metal dications can be associated with the low ionization energies of the early transition metals, but other factors also matter. Thus, the carbene ligand in $NbCH_2^{2+}$ significantly stabilizes the dication in that $IE(NbCH_2^+) = 10.6$ eV is by 3.7 eV lower than $IE(Nb^+) = 14.3$ eV. As a result, $NbCH_2^{2+}$ dication shows a remarkable thermochemical stability with $D(Nb^{2+}-CH_2) = 8.5 \pm 0.5$ eV and $D(Nb^+-CH_2^+) = 4.6 \pm 0.5$ eV.[34,61] Notwithstanding, $NbCH_2^{2+}$ is still quite reactive and continues to dehydrogenate further methane molecules up to products such as $NbC_5H_6^{2+}$ and $NbC_6H_6^{2+}$, which indicate the coupling of methane concomitant with formation of new C−C bonds.

The particular stability of dicationic metal compounds leads to another peculiar aspect in dication reactivity. Charge-stripping experiments of McCullough−Catalano and Lebrilla[67] predicted $IE(ScOH^+) = 13.4 \pm 0.2$ eV, which is quite close to $IE(Sc^+) = 12.8$ eV. The interesting speculation which comes into play evolves from consideration of additional thermochemical data[68] in terms of a thermochemical cycle (Figure 5). Thus, $ScOH^{2+}$ not only is a thermochemically stable triatomic dication with $D(Sc^{2+}-OH) = 4.6$ eV and $D(Sc^+-OH^+) = 4.8$ eV, but the scandium oxide monocation is further predicted to have a proton affinity of $PA(ScO^+) = 2.6$ eV. While proton transfer to neutral molecules is common and often a very facile process, for the ScO^+/H^+ system one arrives at the fascinating speculation that in fortunate cases small dications may be formed in a cation/cation process, e.g., reaction 5.

$$ScO^+ + H^+ \rightarrow ScOH^{2+} \qquad (5)$$

Of course such a process will have a considerable barrier associated with Coulomb repulsion and also requires some type of stabilization of the dication formed. The Coulomb barrier might be surmounted at elevated energies, and dication stabilization may be achieved by additional collision partners, radiative cooling, etc. Moreover, small cations with even larger proton affinities are conceivable. For example, preliminary data[50] suggest that the proton affinity of LaO^+ cation is on the order of that of methane, i.e., a commonly used protonation reagent in chemical ionization. At first sight, this conjecture of putative cation/cation reactions to yield dications appears as a mere "Gedankenexperiment". While this consideration constitutes a value in its own right, similar processes may in fact play a fundamental role in the multiple ionization of biomolecules. For example, cationization or anionization of an already charged molecule might occur upon successive evaporation of the droplets in electrospray ionization. Such a process would cause some deviation of the charge distribution sampled with ESI from that originally present in the liquid phase.[69] Moreover, the Coulomb barriers are not insurmountably high for larger molecules as recently documented in the controversy about the gas-phase acidities of doubly protonated α,ω-alkanediamines.[70] Even in the medium-sized $M(H_2O)_2^{2+}$ systems (M = Mg, Ca, Sr, Ba), the predicted barriers[12d] for cation protonation may be surmounted at hyperthermal energies. Within this context, exploration of possible cation/cation reactions of small ions appears as an interesting perspective of further research; no doubt, this is quite a challenge for both experimental and theoretical studies.

In contrast to the rich chemistry of monoanions in the gas phase, the bimolecular reactivity of small *dianions* has hardly been studied so far and forms a fascinating topic for future investigations. For example, the competition of substitution and elimination in the reactions of nucleophiles Y^- with alkyl halides (e.g., RCH_2CH_2X) according to reactions 6a and 6b formed the subject of numerous studies. While a distinction of the two reactions is a trivial matter in the condensed phase, it is not in gas-phase experiments because the chemically decisive reaction products are the neutral species formed, and these can often only be monitored indirectly.

$$Y^- + RCH_2CH_2X \rightarrow X^- + RCH_2CH_2Y \qquad (6a)$$

$$Y^- + RCH_2CH_2X \rightarrow X^- + RCH{=}CH_2 + HY \qquad (6b)$$

Instead, recently reported thermal ion/molecule reactions of medium-sized dianions of the type $^-Z{-}\text{spacer}{-}Y^-$ permit a direct observation of both the substitution and the elimination pathways, because the products remain charged (reaction 7).[71] Here, the spacer was a diphenylacetylene unit with a nonnucleophilic sulfonate residue and nucleophilic carboxylate or oxy groups in the terminal positions, i.e., $^-O_3S{-}p{-}C_6H_4{-}C{\equiv}C{-}p{-}C_6H_4{-}COO^-$ and $^-O_3S{-}p{-}C_6H_4{-}C{\equiv}C{-}p{-}C_6H_4{-}O^-$, respectively.

$$^-Z{-}\text{spacer}{-}Y^- + RCH_2CH_2X \rightarrow {}^-Z{-}\text{spacer}{-}YCH_2CH_2R + X^- \qquad (7a)$$

$$^-Z{-}\text{spacer}{-}Y^- + RCH_2CH_2X \rightarrow {}^-Z{-}\text{spacer}{-}YH + RCH{=}CH_2 + X^- \qquad (7b)$$

Another interesting variant, recently proposed by Gronert and Azebu,[72] involves $^-Z{-}\text{spacer}{-}Y^-$ dianions complexed to quarternary ammonium ions, e.g., $n\text{-}Bu_4N^+$, resulting in ion pairs that correspond to the net singly charged ions $[n\text{-}Bu_4N]^+[\text{Z-spacer-Y}]^{2-}$. Collision-induced dissociation of these ions inter alia affords losses of butene and thus provides a gas-phase analogue of the well-known Hofmann elimination. This reaction proceeds via an E1cB mechanism which involves a net cancellation of charges, i.e., an anion and a cation only yield neutral products. Usage of dianions allows this fundamental type of reaction mechanism to be studied by mass-spectrometric means for the first time. While Gronert and Azebu used ESI as the method of choice to generate the ions of interest, in this particular case fast atom bombardment and other ionization methods may be suitable as well. Most topics in dianion reactivity, in particular as far as small molecules are concerned, remain yet to be explored. A particular aspect is the interplay of Coulomb repulsion and tunneling in electron transfer from dianions to neutral substrates having significant electron affinities.

Challenges and Problems

In this section, we want to address some problems associated with the methods described above and also outline some perspectives of further research on multiply charged ions. This selection includes the discussion of some experimental shortcomings as well as chemical aspects of more general importance which are specific for small, multiply charged ions.

As far as the experimental methods for the generation of polyanions and polycations are concerned, their further development certainly is a general issue, but we do not consider it as a prime topic for fundamental studies because spectroscopists can hopefully benefit from the spinoff of other branches of chemistry and physics. Within this context, the development of electrospray ionization, basically driven by analytical interests, may serve as an example. One particular aspect in the generation of multiply charged cations deserves attention, however. Thus, gas-phase experiments probing species analogous to those responsible for the fascinating chemistry occurring in superacidic solutions[73] are scarce. Compared to the range of other multiply charged ions studied so far, the species detected in superacids do not seem too outrageous from an energetic point of view, and the available ionization techniques would probably allow them to be generated in the gas phase. For example, dissociative electron ionization of nitric acid allows the elusive protonitronium dication HNO_2^{2+} to be accessed and characterized in the gas phase.[57] Interestingly, the prototype superelectrophile HNO_2^{2+} cannot be obtained by charge stripping of the corresponding monocation HNO_2^+ because its vertical ionization to the dication surface leads to prompt Coulomb explosion. The generation and characterization of many other superelectrophiles in the gas phase was, however, so far impossible due to the lack of appropriate precursors. Let us consider doubly protonated water as an example. Although Coulomb explosion of H_4O^{2+} dication into the monocations $H_3O^+ + H^+$ is quite exothermic, T_d symmetrical H_4O^{2+} is a local minimum with a barrier of about 1.6 eV preventing charge separation.[73a,74] Accordingly, H_4O^{2+} is predicted as a viable species in the gas phase. However, as the oxygen is hypervalent in H_4O^{2+}, no appropriate covalent precursors exist and ionization of van der Waals type complexes such as $H_2O{\cdot}H_2$ or $H_3O^+{\cdot}H$ is unlikely to reach the local minimum of H_4O^{2+}. Here, ESI of superacidic solutions may offer an entirely new approach. Despite some apparent corrosion problems, the promise of generating superelectrophiles in the gas phase seems worthy of experimental effort.

A pertinent problem in experimental studies of dications in the gas phase is associated with the calibration schemes applied in charge-stripping measurements. It is obvious from the experimental boundary conditions that the energy deficits in CS reactions need to be calibrated against a reference system. Presently, there exist two different calibration schemes, a multiplicative and an additive one.[14,15] Moreover, commonly only two reference monocations are used, the toluene cation radical ($Q_{\min} = 15.7$ eV)[14,15] for electron ionization and chemical ionization sources and Mg^+ ($Q_{\min} = 15.1$ eV)[67] for sputtering sources. Considering the experimental error in the determination of $Q_{\min}$ values (≥ 0.2 eV), both calibration schemes agree with each other for these references because the $Q_{\min}$ values are close to one another. For much smaller or significantly larger $Q_{\min}$ values, the discrepancies increase and the need for a more extensive scale of absolute references is obvious. Unfortunately, highly resolved double- and eventually triple-photoionization spectra of neutral molecules do not provide very suitable references for calibration in this respect; what matters instead are photoionization spectra of mass-selected monocations. At this point, we shall not dwell upon further details of charge stripping, such as Franck−Condon effects, collisional broadening, reproducibility, etc. Rather, a brief discussion of another issue is indicated which is of prime importance and directly associated with the calibration problem. Specifically, the usually applied ionization techniques for the generation of the monocation precursors in CS experiments, e.g., electron ionization or chemical ionization, do not necessarily give rise to ground state ions. The presence of electronically excited monocations may substantially obscure $Q_{\min}$ measurements, because the cross sections drastically decrease with increasing endothermicities of the charge-stripping processes. In fact, small percentages of electronically excited monocation precursors may govern the CS spectra[29,75] because ionization of the excited monocations to dications is less energy demanding. Accordingly, the presence of excited states will generally lead to a significant *underestimation* of the ionization energies of the monocations. Complementary theoretical studies are extremely valuable in this respect because they can add credibility to the assignment of the processes observed; in addition, theoretical data can be used to correlate the vertical ionization energies with the corresponding adiabatic properties.[29−33,48,51]

The seemingly straightforward calibration of $Q_{\min}$ data by means of atomic ions cannot be applied because contributions from excited states are particularly pronounced for atoms.[75a,c,d] Ion thermalization in the source, on the other hand, is not necessarily trivial for small, reactive ions. For example, in addition to the $^1\Sigma^+$ ground states of CF^+ and SiF^+ ions, electron ionization of CF_4 and SiF_4, respectively,[29,75b] gives rise to considerable amounts of the excited states CF^+ ($^3\Pi$) and SiF^+ ($^3\Pi$) which cannot be quenched with rare gases on one hand, while excited and ground-state ions react with many other conceivable quenching reagents on the other hand.[76] With regard to the possible interferences by electronically excited states in charge-stripping measurements, the reluctance on toluene standard mentioned above finds a justification in that excited toluene ions are prone to undergo facile dissociation[77] and can thus be considered of having an internal thermometer.

As far as the chemical reactivity of dications in ion/molecule reactions is concerned, doubly charged metal fragments deserve continuous attention.[61] In particular, the enhanced electrophilicities of dications enable the activation of relatively robust substrates. The activation of methane by Nb^{2+} (see above) is one example, but several other interesting target molecules which are difficult to activate otherwise have not been examined so far, e.g., carbon dioxide, dinitrogen, fluorinated hydrocarbons, etc. In extrapolation of a recently outlined scenario,[78] the activation of carbon dioxide appears particularly promising with dianionic species. A prime aspect in reactivity studies remains, however, to achieve some control over the balance of bond-forming versus electron-transfer pathways. In this respect, the nowadays exploratory reactivity studies with multiply charged metal fragments need continuation in order to achieve a more complete survey.

As mentioned above, the chemical behavior of small dianions is by and large unknown and further reactivity studies are highly recommended. Before speculating about the promises of dianion chemistry, already now there appear two challenges which are closely related to each other and need to be addressed. (i) What is the relationship between the vertical electron detachment energies determined spectroscopically[42] and the corresponding adiabatic properties? For example, Wang and co-workers derived $EA_a(S_2O_8^-) = 1.7 \pm 0.2$ eV from detailed analysis of the photodetachment spectra of the peroxodisulfate dianion;[79] this figure is in obvious disagreement with a theoretically predicted adiabatic electron affinity of only 0.35 eV.[80] (ii) What is the nature of the neutral products formed upon electron detachment? This aspect is crucial from a chemical point of view, because as with other multiply charged ions, dianions may exhibit structures which are unfavorable for the singly charged or neutral counterparts. In the case of alkanedicarboxylate dianions, for example, photodetachment of one of the electrons may be associated with decarboxylation, hydrogen transfer to the oxygen-centered radical, or recoil of the alkyl chain, thereby leading to other than the expected products.

As with dianions, many properties of small trications remain to be explored. A prime issue with regard to the achievement of more accurate thermochemical data is the settlement of the calibration schemes used in charge stripping. While the deviation of the additive and multiplicative calibration schemes in the charge stripping of monocations to dications may still be acceptable, for trications the errors imparted by the calibration exceed the tolerable uncertainty of the experimentally measured energy deficits. For example, about two-thirds of the error bar in $Q_{\min}(TiF^{2+}) = 28 \pm 3$ eV associated with the transition $TiF^{2+} \rightarrow TiF^{3+}$ arises from the uncertainty of the calibration scheme.[48] Moreover, it is questionable whether charge stripping of toluene as a reference is still appropriate for the charge stripping of dications because the calibration primarily accounts for focusing conditions which obviously also are a function of the net charge. Therefore, some absolute measurements of suitable reference compounds are highly desirable. Note, however, that the thermalization issue discussed above for the charge stripping of monocations is even more severe for dicationic precursors. Thus, the number of low-lying states usually increases from mono- to dications, and thermalization of small dications in the ion source is difficult to achieve because their generation requires hyperthermal conditions by definition. For the time being, experimentalists should therefore recommendably add confidence to their results by complementary theoretical studies.[48,51,81]

Finally, a hitherto only partially addressed effect is the relationship between the measured vertical transitions of singly to multiply charged ions and vice versa and the corresponding adiabatic properties; in charge stripping, the relationship between $Q_{\min}$ and IE_v represents another forthcoming topic. In the future, more advanced treatments may allow explicit consideration of Franck−Condon envelopes and also for temperature effects, collisional broadening, etc. to be accounted for in mass spectrometric experiments with multiply charged ions.

Conclusions

Small, multiply charged ions combine a manifold of interesting chemical and physical features. Fundamental studies on these admittedly somewhat unusual species not only ameliorate our understanding of chemical bonding in the presence of multiple charges but may also have substantial input into other areas of research in which multiply charged ions are involved. In particular, the rapid development of supramolecular and biological chemistry demands for a more detailed understanding of multiply charged ions, not only with respect to analytical applications but also with regard to fundamental properties. Moreover, small polycations and even dianions[36b] are species in their own right because of their roles in extreme environments such as the upper atmosphere and interstellar regions. Thereby, the study of multiply charged ions will continue to represent a formidable challenge for chemistry and physics in the decades to come.[82]

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