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Microsolvation of metal ions: on the stability of $[Zr(CH_3CN)]^{4+}$ and other multiply charged ions

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Dedicated to Helmut Schwarz on the occasion of his 60th birthday,
in warm appreciation of his contribution to (gas phase ion) chemistry.

Abstract

The stability of highly charged gas phase metal ion solvates $[M(Sol)_n]^{z+}$ ($z > 2$) is discussed based on a simple electrostatic model and density functional theory computations. It is often assumed that the observation of such ions will be increasingly difficult as z increases because they will be less and less stable, i.e., that they will have an increasing tendency to undergo spontaneous charge-separating dissociation into fragment ions of lower charge. It is shown here that for carefully chosen metal ions such as Zr^{4+}, this need not be the case—many highly charged metal solvates, such as $[Zr(CH_3CN)]^{4+}$, should exist with very significant metastable lifetimes. However, it may be difficult to isolate and identify such ions experimentally without the interference of competing processes such as charge-separating dissociation or charge reduction through electron transfer during collisions with other molecules in the ion source.

Keywords: Multiply charged ions; Metal solvates; Computation

1. Introduction

The gas-phase properties of multiply charged ions often differ significantly from those in solution. This is mainly due to the fact that charge–charge interactions are extremely strong in the gas-phase, in the absence of an attenuating dielectric environment. As a result, fragmentation (or "Coulomb explosion") of a dication into two monocations releases a strong repulsive force and qualitatively changes the whole shape of the relevant potential energy surfaces. Likewise, detachment of an electron from a multiply charged anion is usually highly exothermic except for quite large species. As a result, many small dications or dianions, even those whose electronic structure would a priori indicate very favourable bonding properties, are either completely unstable in the gas phase, or, if they can be formed, undergo more or less rapid exothermic unimolecular dissociation processes, and are thus termed metastable. For example, although the He_2^{2+} ion has the same very stable $^1\Sigma_g^+$, σ_g^2, electronic configuration as the H_2 molecule, it is much *less* stable than two separated He^+ ions. The peculiar features of the potential energy curve for this molecule, which has a local, metastable, minimum well *above* the dissociation asymptote, were predicted by Pauling

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[1] long before the ion was first observed experimentally [2]. The sulfate dianion, $[SO_4]^{2-}$ ion, which is of course very stable in solution, undergoes autodetachment of an electron to give the at first sight much less stable monoanion-radical [3]. As well as the great intrinsic interest concerning the physics and chemistry of multiply charged cations and anions, they also play an important role in the chemistry of plasmas [4,5].

Solvent stabilization of charge, together with the reduction of Coulombic interactions through dielectric screening, play a large role in establishing the very large differences between gas-phase and solution properties of multiply charged ions. Unusual in the gas-phase, these species are commonplace in polar solvents such as water. Nevertheless, some of the features of the unsolvated chemistry do persist in solution. For example, highly charged species have a tendency to undergo charge-separation processes, such as hydrolysis $[M(H_2O)_n]^{z+} \rightarrow [M(H_2O)_{n-1}(OH)]^{(z-1)+} + H^+_{aq}$. Also, some highly charged organic intermediates, or superelectrophiles, have been shown to have a much higher reactivity than the more conventional singly charged species commonly involved in organic reaction mechanisms [6]. The reactivity and properties of such organic polycations have been much better understood thanks to fundamental studies of these species in the gas phase [7]. The advantage of this approach is that it enables the existence of these otherwise highly elusive species to be established, and that their intrinsic properties can be the object of combined experimental and computational studies. Helmut Schwarz's group has made many pioneering mass spectrometric and computational contributions to this area.

In recent years, studies of gas-phase polycations have developed along several different pathways. On the one hand, many thermodynamically stable diatomic cations have been characterized—such as AlF^{2+} [8]—and the principles affecting the stability of very small, typically diatomic, ions have been more systematically tested, leading for example to the experimental demonstration that even diatomic trications—such as TiF^{3+}—can have arbitrarily long metastable lifetimes and thus be in all practical terms stable entities in unimolecular terms [9]. Indeed, some trications have been shown to be thermodynamically *stable* (i.e., lower in energy than the *lowest* atomic asymptote), as in UF^{3+} [10]. This is another area of research in which many contributions have come from Helmut Schwarz and his group. Another very active field of research has been the *reactivity* of dications [11], with the observation of bond-forming reactions such as $Ar^{2+} + CO \rightarrow ArC^{2+} + O$ [12] being a typical intriguing observation. Finally, enormous interest has focussed on the microsolvation of metal ions to give small clusters $[M(Sol)_n]^{z+}$ [13]. As the number of solvent ligands is increased, these ions increasingly approach the condensed-phase limit, and so they provide a useful model for understanding the differences between the gas-phase and liquid environments. As well as a host of doubly charged metal ion solvates such as $[M(H_2O)]^{2+}$ ($M = V$ [14], Cu [15]), $[Au(Ar)]^{2+}$ [16] and $[Mg(CO_2)_4]^{2+}$ [17], recent studies have shown that tricationic species, e.g., $[Y(DMSO)_n]^{3+}$, $n > 4$ [18], (where DMSO is $(CH_3)_2SO$) and $[In(DMSO)_4]^{3+}$ [19] can also be formed.

Much of the research in this area has given great weight to the issue of stability (or kinetic metastability) of the metal solvates $[M(Sol)_n]^{z+}$. A more or less general observation, indeed an implicit assumption in many cases, has been that their stability is intrinsically low, especially when the number of solvent molecules, n, is low, or when the charge of the ion, z, is high. In this paper, pursuing our interests in the structures and energetics of metal solvates such as $[Fe(C_6H_6)]^{2+}$ [20], we will use qualitative arguments, as well as density functional theory (DFT) computations on a set of model tricationic and tetracationic solvates of zirconium, to show that this assumption is in many respects incorrect if it is taken to refer to the intrinsic *kinetic* stability of the isolated ions in the dilute gas phase. Instead, it is argued that many of the constraints occur at the level of the process leading to formation of the gas-phase ions, and are due to the fundamental *thermodynamic* instability of many of these multiply charged ions.

2. Computational details

All computations in this paper have been carried out using the Jaguar 4.1 package [21], the standard B3LYP hybrid density functional [22] as implemented in Jaguar, together with the standard double-zeta LACVP* basis on all atoms. This involves the Los Alamos ECP on Zr (and Y) to describe the innermost 28 electrons, and the associated double-zeta basis to describe the outermost 4s and 4p electrons, as well as the valence 4d (and 5s) electrons [23]. For H, C, N and O, the all-electron 6-31G* basis was used [24], with *d* polarization functions on C, N and O (only the five spherical harmonic components of the *d* functions were used). Full geometry optimization was carried out on all species, using restricted "wavefunctions" both for singlet species such as $[Zr(H_2O)]^{4+}$ and for doublets such as $[Zr(H_2O)]^{3+}$. All energetics have been computed from differences in total energies. Whilst certainly not of quantitative value, due to the neglect of zero-point corrections, the limited basis sets used, and the intrinsic unpredictability of DFT, we believe our results are more than accurate enough for the mainly qualitative purposes of this study. Dipole moments and polarisibilities of the solvent species were computed using finite-difference methods, with the same B3LYP level of theory, but the larger 6-311 + G** basis set [24].

3. Metal ion solvates: qualitative model

First of all, we discuss the trends in stability of multiply charged metal ion solvates as the metal charge increases, using a simplified version of the electrostatic model used by Stace et al. [16,25]. The interactions in a $[M,Sol]^{z+}$ system can be schematically presented as occurring on two potential energy surfaces, one corresponding to $M^{z+} + Sol$, and one to $M^{(z-1)+} + Sol^+$. The former surface is typically higher-lying at the dissociation asymptote, by an amount Δ equal to $IE(M^{(z-1)+}) - IE(Sol)$. However, this surface is also attractive at long range, due to charge–dipole and charge–induced dipole interactions, until a certain distance r_{min} beneath which short-range Pauli repulsion effects of the two electron clouds dominate. The second surface, in contrast, is repulsive even at long range, due to charge–charge Coulombic repulsion (slightly modified by charge–dipole and charge–induced dipole interactions, which we neglect here). Both surfaces are of course strongly repulsive at short range due to steric repulsion. The question is, which surface lies lower at r_{min}? If it is the repulsive curve V_{rep} (case (a) in Fig. 1), then the electronic ground state of the complex is unbound, and, although the system could in principle have a short metastable lifetime on the upper, bound surface, in practice, this is unlikely to be at all significant for the polyatomic species considered here, and such an ion will not be observed. If it is instead the attractive surface V_{att} which lies lower, then provided the crossing with the repulsive curve lies at large enough r_c, such that $V(r_c)$ is significantly higher than the energy on the attractive curve at r_{min}, then the ion may have an observable metastable lifetime—provided it can be made in the first place!

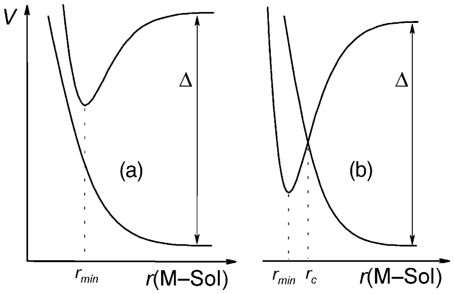

Fig. 1. Possible relation between attractive (M^{z+}–Sol) and repulsive ($M^{(z-1)+}$–Sol^+) potential energy curves.

A rough numerical estimate for $V_{att}(r)$ and $V_{rep}(r)$ can be obtained from the charge z on the metal, the IEs (and hence Δ), together with the dipole moment μ and polarizability α of the solvent species. The value of r_{min} can either be derived from experimental ionic and van der Waals radii, or from ab initio computations. Thus, using an energy scale on which $V_{rep}(\infty) = 0$, one obtains $V_{rep}(r_{min}) \approx (z-1)/r_{min}$, and $V_{att}(r_{min}) \approx \Delta - (z\mu/r_{min}^2 - (z^2\alpha)/(2r_{min}^4)$ (these equations are in atomic units). To take the example of the $[Zr(H_2O)]^{4+}$ and $[Zr(CH_3CN)]^{4+}$ cations: the dipole moment μ_z and polarizability α_{zz} along the z axis of H_2O are calculated at the B3LYP/6-311 + G** level to be respectively 0.86 and 7.8 atomic units. The r_{min} value of 3.78 a.u. is derived from the B3LYP optimized geometry of the complex (see below), with the assumption that the oxygen atom is the site of the dipole. Δ is computed to be 0.840 a.u. (IE(Zr^{3+}) is computed to be 35.13 eV, with IE(H_2O) computed as 12.28 eV). Taken together, these parameters give $V_{\mathrm{rep}}(r_{\mathrm{min}}) = 0.794$ a.u. and $V_{\mathrm{att}}(r_{\mathrm{min}}) = 0.294$ a.u.—the latter is significantly lower, so this ion is predicted to reside in a metastable minimum. The crossing of the two curves is predicted to occur for $r_{\mathrm{c}} = 4.99$ a.u., with $V_{\mathrm{c}} = 0.602$ a.u. For acetonitrile, $\mu_z = 1.60$, $\alpha_{zz} = 38.91$, $\Delta = 0.855$, and $r_{\mathrm{min}} = 4.83$, all in a.u. (and with the latter value taken somewhat arbitrarily to the mid-point of the C–N bond in the B3LYP optimized geometry), giving $V_{\mathrm{rep}}(r_{\mathrm{min}}) = 0.621$ a.u. and $V_{\mathrm{att}}(r_{\mathrm{min}}) = 0.009$ a.u.—here too, the ion is predicted to have a metastable minimum, in fact, this ion is predicted to be almost thermodynamically stable, with energy only just above the charge-separation asymptote. However, this prediction from the model should not be taken too literally given that the short-range repulsive interactions are not included. The crossover r_{c} occurs at 6.22 a.u., with $V_{\mathrm{c}} = 0.482$ a.u.

The model used by Stace et al. [13,16,25] is more sophisticated, in that it allows for charge–dipole and charge–induced dipole interactions also for V_{rep}, and not just for V_{att}. However, it uses the same values of the dipole and of the polarizibility for the neutral and the cation, which is probably not a very good approximation. In our opinion, greater accuracy would require taking into account the different geometries of the neutral and cationic solvent species, and the fact that their preferred angle of approach to the metal may be different—and such modifications would destroy the simple, one-dimensional nature of the model. For the qualitative purposes of the present work, we have therefore used the simplest possible form of the model, which here leads to the remarkable conclusion that the two monosolvated tetracationic systems, $[Zr(H_2O)]^{4+}$ and $[Zr(CH_3CN)]^{4+}$, should be associated with fairly long-lived metastable minima.

Is this result surprising? To answer this, it is instructive to consider how the different terms in this model vary as a function of the charge z on the metal ion. Considering first Δ, it clearly increases with z, due to the increasing value of IE_z (or IE($M^{(z-1)+}$)) of the metal, and this is the main reason why metal ion complexes are usually held to become less stable with increasing charge. For hydrogenic atoms, IE_z varies as z^2, but for many-electron atoms, as the charge of the ion increases, the remaining electrons screen the nucleus more effectively, so that the effective nuclear charge felt by the electron which is removed does not in fact increase proportionately to z and IE_z scales more softly also. For example, it can readily be evaluated that the IEs of the 29-electron systems Rb, Ba^+, Y^{2+}, Zr^{3+}, Nb^{4+} and Mo^{5+} [26] increase roughly as $z^{1.57}$. Δ increases more steeply than this, especially for small values of z, so overall this term becomes increasingly unfavorable for the stability of the metal ion solvates bearing higher and higher charges, although perhaps not as rapidly as one might expect. It should be noted that the metal polycations discussed here, including the Zr^{4+} system which is the focus of the DFT computations, have not been chosen at random but instead picked as the most favorable cases, based on their electronic configurations. For example, IE_4(Zr) is 34.34 eV, whereas IE_4(Al) and IE_4(Fe), to pick just two of the many less favourable cases at random, are respectively 120 and 54.8 eV [26]—the chances of making the corresponding metal solvates are probably quite low!

Despite the quite sharp increase in IE with z, metal ion solvates may have metastable minima in favorable cases, because all the other terms comprising V_{att} and V_{rep} also increase with z: the charge–dipole attractive term increases linearly with z, and the charge–induced dipole interaction also associated with V_{att} increases quadratically with z. The repulsive term between fragment ions increases as $(z - 1)$, as does the charge–dipole component of V_{rep}, omitted here; the other term which we have not included, corresponding to charge–induced dipole interactions, increases as $(z - 1)^2$. In fact, the increase in all these terms will be *larger* than linear or quadratic, as the foregoing relates to their increase at a given, fixed, value of r, whereas r_{min} will tend to decrease with z, simply because more highly charged ions have a smaller radius. This effect is hard to quantify but it is important: the computed r_{min} for $[\mathrm{Y(CH_3CN)}]^{3+}$, defined as for the isoelectronic $[\mathrm{Zr(CH_3CN)}]^{4+}$ as the distance between the metal and the C–N bond midpoint, is of 5.12 a.u., i.e., 0.29 a.u. longer than for the more highly charged ion. If V_{att} is recomputed at this larger value of r, it is significantly higher, at 0.158 a.u. (versus 0.008 a.u. for the “true” r_{min} of 4.83 a.u.). Overall, therefore, the electrostatic terms at the corresponding r_{min}, which tend to favor V_{att} over V_{rep}, increase somewhat more than linearly with z, and Δ does too.

What happens for more highly solvated ions, $[\mathrm{M(Sol)}_n]^{z+}$? The repulsive interaction V_{rep} between $[\mathrm{M(Sol)}_{n-1}]^{(z-1)+}$ and Sol^+ will remain almost constant, whereas the attractive force will be decreased due to unfavorable dipole-dipole and steric interactions between the different solvent ligands. However, Δ will also decrease, as the ionization energy of the partially solvated metal fragment is smaller than that of the metal ion (see examples below). At least within the first solvation shell, then, the stability of higher solvates is likely to be higher than that of the mono-solvate—as is indeed found experimentally, and computationally, below. This may not be true for molecules in the second solvation shell, where r_{min} is much larger.

The overall conclusion of this section is that as the charge on a metal ion (or solvate) increases, the possibility of it forming kinetically metastable complexes with solvent molecules decreases, due to the increase in the difference Δ between the ionization energies of the fragments, Sol and $[\mathrm{M(Sol)}_{n-1}]^{(z-1)+}$. However, this increase is much slower than might be expected, because the solvation energy also increases rapidly with z, as does the height of the repulsive Coulombic barrier between the fragment ions, and these latter terms tend to favor the formation of metastable minima on the attractive potential energy surface, lying *below* the repulsive surface. Therefore, provided that these ions can be generated in some way, many highly charged metal ion solvates should in principle be isolable in the gas phase, even in the presence of only a small number of solvent molecules. This conclusion is well supported by experiment, and from computations, for dicationic and tricationic systems. However, the model suggests it should also be so for more highly charged species, such as tetracations. In the next section, DFT computations are used to check this prediction.

4. Computational results

The Zr^{4+} ion was chosen as a test case to check the conclusions of the previous section. Two different solvent molecules were chosen, acetonitrile and water. The computed energetics of the $[\mathrm{Zr(Sol)}_n]^{z+}$ system ($\mathrm{Sol} = \mathrm{CH_3CN}$, $\mathrm{H_2O}$, $n = 0$–6, $z = 3, 4$) are summarized in Tables 1 and 2. The optimized geometries are by and large unremarkable. For the cations with 4, 5 and 6 solvent molecules, approximately symmetric structures of a tetrahedral, trigonal bipyramidic and octahedral nature, respectively, have been obtained. These geometries are found as local minima, but based on previous results from other groups, it is not impossible that the global minimum for these clusters has a lower symmetry, with some waters moving into the second solvation shell [13]. Whilst such changes are clearly important to consider where any specific ion is of interest, especially in the light of the discussion below on Coulomb explosion for species with partially

Table 1
B3LYP computed energetics (eV) for the $[\mathrm{Zr(CH_3CN)}_n]^{3,4+}$ systems

n	IE_4	BDE(4-0)	BDE(3-1)
0	35.13	–	–
1	24.61	18.92	−4.35
2	22.18	9.73	−3.02
3	19.73	7.09	−3.23
4	17.79	5.81	−2.06
5	16.59	3.81	−2.12
6	15.63	3.24	−1.49

IE_4 is the IE of the trication, BDE(4-0) is the bond dissociation energy for “charge-conserving” dissociation of $\mathrm{CH_3CN}$ from $[\mathrm{Zr(CH_3CN)}_n]^{4+}$ to give $[\mathrm{Zr(CH_3CN)}_{n-1}]^{4+}$, and BDE(3-1) that for the “charge-splitting” dissociation to give $\mathrm{CH_3CN}^+$ and the trication.

Table 2
B3LYP computed energetics (eV) for the $[Zr(H_2O)_n]^{3,4+}$ systems

n	IE_4	BDE(4-0)	BDE(3-1)	BDE(H^+)	BDE(H_3O^+)
0	35.13	–	–	–	–
1	30.19	11.59	−11.25	−12.25	–
2	26.93	8.36	−9.55	−9.68	−11.52
3	24.49	6.67	−7.98	−7.66	−10.64
4	22.61	5.60	−6.60	−6.33	−9.69
5	21.17	4.22	−6.11	−5.18	−9.74
6	19.89	3.79	−5.09	−4.02	−9.01

IE_4, BDE(4-0) and BDE(3-1) are as in Table 1. BDE(H^+) is the energy for loss of H^+ to give $[Zr(H_2O)_{n-1}(OH)]^{3+}$, and BDE($H_3O^+$) is the energy for loss of H_3O^+ to give $[Zr(H_2O)_{n-2}(OH)]^{3+}$.

occupied second solvation shells, we did not explore such structures in this study. For the di- and tri-solvated species, the lowest energy structures were not as symmetric as one might expect: distortion occurred from linear (roughly $D_{\infty h}$) and triangular ($\sim D_{3h}$) structures, respectively, to give bent ($\sim C_{2v}$) and non-planar ($\sim C_{3v}$) structures, respectively. Such distortion prevents the individual dipole moments of the solvent molecules from canceling out. The symmetric structures, in which the net electric field at the metal atom from the solvent dipoles is zero by symmetry, were very slightly higher in energy. In all structures, the high charge on the metal atom induces a small distortion of the solvent with respect to the free molecule, as shown for the monosolvates in Fig. 2.

The remarkable thing to point out, though, is that all these species are local minima, which do not spontaneously undergo Coulomb explosion. This was confirmed for the monosolvates and a few other species by frequency computations, and given that no symmetry constraints were imposed during optimization, is likely to be the case for the larger clusters also. This confirms the above predictions concerning the fact that these tetracations are good candidates for preparation as metastable multiply charged ions!

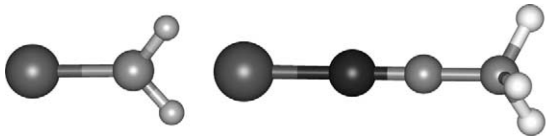

Fig. 2. B3LYP optimized geometries of $[Zr(H_2O)]^{4+}$ (left) and $[Zr(CH_3CN)]^{4+}$ (right). Sample bond lengths and angles (in parentheses, optimized for the free solvent molecule): Zr–O, 2.00 Å, O–H, 1.11 Å (0.97°), H–O–H 100.7 Å (103.8°); Zr–N, 1.92 Å, N–C, 1.27 Å (1.16°).

The energetics are worthy of more comment. First of all, it can be seen that the computed ionization energy of Zr^{3+}, 35.1 eV, is in fair agreement with the experimental value of 34.3 eV [26]. The computed ionization energies of water and acetonitrile (12.3 and 11.9 eV, respectively), are also in agreement with the experimental values [27] (12.6 and 12.2 eV).

Next, the energetics for the monosolvates are in fair agreement with the predictions of the simple electrostatic model for V_{att} at r_{min}. Combined with Δ, the model predicted a “charge-conserving” BDE(4-0) of 14.9 and 23.0 eV for $[Zr(H_2O)]^{4+}$ and $[Zr(CH_3CN)]^{4+}$, respectively, in reasonable agreement with the computed values of 11.6 and 18.9 eV. The DFT bond energy is smaller than that derived from the simple model because the latter neglects the steric short-range repulsive interactions. This qualitative agreement between the computational and model results lends support to the latter. The values of these bond energies also underline how strong metal ion–solvent interactions are when the ion is multiply charged. As expected, the values of BDE(4-0) decrease quite sharply as more solvent molecules are added, due to the unfavorable dipole-dipole and steric interactions.

It can be seen next that none of the tetracations in Tables 1 and 2 are thermodynamically stable in the sense of lying lower in energy than the charge-separated dissociated species, i.e., the “charge-splitting” BDE(3-1) is negative in all cases. That this is true even for the most strongly solvated species, $[Zr(CH_3CN)_6]^{4+}$, suggests that for highly charged metal ions, it will be extremely difficult to obtain thermodynamically stable ions in the gas phase, and the implications of this for the behavior in solution are discussed below. Nevertheless, these charge-separation processes do become progressively less favorable as solvent molecules are added, and it is noteworthy that with acetonitrile, BDE(3-1) is only slightly negative even for the monosolvate.

The fourth ionization energies of the solvated ions also decrease as more solvent molecules are added, reflecting the fact that the solvents bind on average more strongly to the tetracation than to the trication. Thus, the fourth ionization energies for the higher solvates are within the same energy range as the second or even first ionization energies of typical bare metal ions or solvent molecules.

For both types of cluster, there are of course many competing pathways for dissociation, involving bond-breaking and forming amongst the ligand solvent molecules. We have mostly not considered these pathways, despite the fact that they are known to be important experimentally, because it is fairly easy to recognize that their energetics are likely to be of the same order of magnitude as those we have computed, which are therefore of sufficient qualitative value on their own. For example, $[Zr(CH_3CN)]^{4+}$ can undergo dissociation [28] to $CH_3{}^+$ and $[ZrNC]^{3+}$ (the latter is computed to be more stable than the $[ZrCN]^{3+}$ isomer). This charge separation is computed to be exothermic by 6.89 eV, i.e., roughly the same as the BDE(3-1) considered in Table 1. The BDE(2-2) of this monosolvate (i.e., the energy for dissociation into Zr^{2+} and triplet CH_3CN^{2+}), −8.15 eV, is also of the same order of magnitude as BDE(3-1). Larger acetonitrile complexes can follow still more dissociation paths, e.g., $[Zr(CH_3CN)_2]^{4+}$ could dissociate to $[Zr–N=C=CH_2]^{3+}$ and protonated acetonitrile CH_3CNH^+ [28], with a computed exothermicity of 6.55 eV.

For the water complexes, there are two very important dissociative pathways of this type, involving bond breaking in the ligand molecules, which we have considered for all the solvates: loss of a proton, as in BDE(H^+), and loss of a protonated water molecule, as in BDE(H_3O^+). As can be seen in Table 2, both of these processes are exothermic for all water complexes, confirming that the latter are metastable in more than one way. In fact, loss of H_3O^+ remains quite strongly exothermic even for the larger clusters. This was very apparent when we attempted to optimize a structure for the heptasolvate, $[Zr(H_2O)_7]^{4+}$, in which six molecules of water were arranged in an octahedron surrounding the metal, and the seventh was hydrogen bonded to one of them, forming a second shell. This ion underwent “spontaneous” dissociation to H_3O^+ and the corresponding trication upon minimization. This observation is at first sight surprising given the metastable nature of the minima with less water molecules, because one might expect that with more solvent molecules, and hence more charge stabilization, the solvated ions should be more stable. In a *thermodynamic* sense, this is clearly true for the Zr^{4+} solvates: BDE(H_3O^+) becomes less negative as the cluster grows. However, unlike for metals with a lower charge, this dissociation energy remains very negative, even for the hexa-aquo complex, due to the high charge (and charge/radius ratio) on Zr. Therefore, what is most relevant here is the kinetic stability of the ion solvates, which can easily be understood to be different for water molecules in the first and second solvation shells. For the molecules in the first shell, dissociation of H_3O^+ follows a complex pathway involving initial de-ligation followed by proton transfer [13,29]. Such pathways undoubtedly exist for the complexes in Table 2, but will involve an energy barrier due to high energy cost of desolvation. For the putative hepta-aquo complex we sought to locate, however, where the last water molecule is in the second solvation shell, only the proton transfer needs to take place for dissociation to occur. Our calculations suggest that the barrier to this proton transfer is very small or nonexistent.

5. Discussion

What message can be taken from the above results? First of all, we believe that it is wrong to conclude that metal ion solvates have a tendency to become intrinsically less stable, in all meanings of the word, in the gas phase, when the charge on the metal ion increases. It is true that all the ions characterized computationally here are thermodynamically unstable, that is, that one or more of the charge-separated dissociation asymptotes lies lower in energy for all of them. This need not mean, however, that they will undergo spontaneous and rapid dissociation, as there are clearly energy barriers towards such steps, and these may well be relatively high. In general, provided the metals are chosen such that the corresponding ionization energy is not too large, and strongly solvating solvent molecules are considered, many multiply charged metal ion solvates may display kinetically metastable minima on the potential energy surface, or even approach thermodynamic stability with respect to at least some of the charge-separation asymptotes.

However, the mere fact that such minima exist does not guarantee that they can be observed. For this to be done, any multiply charged ion must first be produced in the gas phase, which places severe practical limitations on which ions can be observed. Multiply charged solvated metal ions can be produced in three fundamentally different ways [4,13]: by removing electrons from a neutral metal solvate or one with a lower charge, by collisional association of a solvent molecule with a naked or less highly solvated ion, or by evaporation (mainly of solvent) from a larger solvate or droplet. The first of these methods may lead to rather “hot” ions due to the typically shorter bond lengths in the more highly charged ions, so that these ions may have enough internal energy to cross the barriers to metastable dissociation. Collisions between highly charged metal ions or solvates and most solvent molecules will typically lead to rapid charge transfer rather than to stabilization by further collisions. The last type of approach, typified by electrospray methods, might encounter a similar problem, due to charge transfer occurring between the ion and the solvent molecules as the latter evaporate. It is instructive to consider the likelihood of this occurring.

First of all, the ions a priori most likely to be formed, i.e., those which are most “stable”, are those with a nearly complete first solvation shell. Evaporation of solvent to form these species therefore occurs from the second and higher solvation shells. This means that quite large values of r_{min} need to be used to assess whether V_{att} or V_{rep} is most stable for the $[\mathrm{M(Sol)}_{n+1}]^{z+}$ cluster—solvent molecule complex which is undergoing dissociation. The larger r_{min} is, though, the lower in energy the V_{rep} curve is likely to lie, and the higher V_{att} will be. In other words, second shell solvent molecules are inherently more likely than first shell ones to undergo charge transfer upon dissociation from a metal ion solvate complex, provided it is thermodynamically favorable. Another aspect of this is that electron transfer from the solvent molecule to the metal can be mediated by the first solvent-shell molecules. This means that at the large M–Sol distances at which electron transfer occurs, the non-adiabatic electron-transfer coupling element between the wavefunctions corresponding to V_{att} and V_{rep} will be much larger than in the case of dissociation of a first shell solvent molecule, where electron transfer needs to occur through the vacuum if it is to take place at such large distances (or the solvent needs to dissociate via an indirect pathway in which it first moves into the second solvation shell). An example of this is provided by our study of the $[\mathrm{Zr(H_2O)_7}]^{4+}$ species, for which geometry optimization did not show a metastable minimum but instead led spontaneously to dissociation into $\mathrm{H_3O^+}$ and $[\mathrm{Zr(H_2O)_5(OH)}]^{3+}$.

Another, connected point to be made concerns the nature of the Coulombic repulsion “barrier” to metastable dissociation. The existence of this barrier is a key to the existence of such ions with a finite lifetime, and its height, for highly charged species, is fundamentally due to the multiplicative nature of Coulomb’s law: dissociation of a trication into a monocation and a dication involves a Coulombic repulsive force, at the same distances, which is twice as large as that for dissociation of a dication into two monocations. However, this also means that dissociation barriers for highly charged species are likely to be “thinner” than those for dications, because the Coulomb repulsion energy will also decay more rapidly as the distance between the fragment ions increases. Therefore, the distance at which electron transfer, leading to a “hop” from V_{att} to V_{rep}, becomes favorable, is smaller than for dications. This in turn means that electron transfer will occur more easily during solvent evaporation and similar collision processes.

For these reasons, it may be difficult to observe quadruply charged ions discussed in this paper and/or similar ones. The sheer thermodynamic instability of many of them will mean that many exothermic charge-separation or -transfer processes can occur during or after the ion generation process. In many respects, this low stability of quadruply charged ions is true in solution also. For example, the standard potential for the Ce^{4+}/Ce^{3+} couple in water, $+1.61\,V$, means that this ion is thermodynamically unstable in water (the O_2/H_2O standard potential is only $+1.23\,V$). Equally, the hydrolysis constant for the $Zr^{4+}{}_{(aq)}$ ion is one of the smallest known, so that Zr(IV) tends to exist in solution as $[Zr(OH)(H_2O)_n]^{3+}{}_{(aq)}$ except at very low pH values. This is an additional reason why it may be difficult to generate quadruply charged metal ion solvates in the gas phase: the precursor solutions may not contain discrete ions of such high charge—they may be present only in lower oxidation states, or as fully or partly hydrolyzed or solvolyzed species, or as lower-charged ions in which the metal is tightly bonded to a formal "counterion" such as chloride.

6. Conclusions

In conclusion, we have shown that the electrostatic model used explicitly or implicitly by many groups studying gas-phase multiply charged metal ion solvates predicts that there should be many kinetically "stable" species—in the sense of metastable ions with a significant lifetime towards charge-separating dissociation—even for highly (+3, +4, and maybe +5) charged ions. Of the ions of this type discussed here, the $[Zr(CH_3CN)]^{4+}$ monosolvate appears to be a good candidate for experimental observation. DFT computations on this and other ions confirm the conclusion that these ions could have high metastable lifetimes. However, it is acknowledged that the *generation* of these ions may be problematic.

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References

[1] L. Pauling, J. Chem. Phys. 1 (1933) 56.
[2] (a) M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenović, P.V.R. Schleyer, J. Phys. B 17 (1984) L605;
(b) M. Guilhaus, A.G. Brenton, J.H. Beynon, M. Rabrenović, P.V.R. Schleyer, J. Chem. Soc. Chem. Commun. (1985) 210.
[3] (a) A.T. Blades, P. Kebarle, J. Am. Chem. Soc. 116 (1994) 10761;
(b) X.-B. Wang, J.B. Nicholas, L.-S. Wang, J. Chem. Phys. 113 (2000) 10837.
[4] For a general review of the gas-phase chemistry of multiply charged ions, especially cations, see D. Schröder, H. Schwarz, J. Phys. Chem. A 103 (1999) 7385.
[5] For a review of the gas-phase chemistry of poly-anions, see A. Dreuw, L.S. Cederbaum, Chem. Rev. 102 (2002) 181.
[6] (a) G.A. Olah, Angew. Chem. Int. Ed. Engl. 32 (1993) 767;
(b) G.A. Olah, T. Mathew, E.R. Marinez, P.M. Esteves, M. Etzkorn, G. Rasul, G.K.S. Prakash, J. Am. Chem. Soc. 123 (2001) 11556.
[7] K. Lammertsma, P.V.R. Schleyer, H. Schwarz, Angew. Chem. Int. Ed. Engl. 28 (1989) 1321, and references therein.
[8] C. Heinemann, D. Schröder, H. Schwarz, J. Phys. Chem. 99 (1995) 16195.
[9] D. Schröder, J.N. Harvey, H. Schwarz, J. Phys. Chem. A 102 (1998) 3639.
[10] D. Schröder, M. Diefenbach, T.M. Klapötke, H. Schwarz, Angew. Chem. Int. Ed. 38 (1999) 137.
[11] (a) See e.g., N. Tafadar, D. Kearney, S.D. Price, J. Chem. Phys. 115 (2001) 8819;
(b) L. Mrázek, J. Žabka, Z. Dolejšek, J. Hrušak, Z. Herman, J. Phys. Chem. A 104 (2000) 7294.
[12] P. Tosi, R. Correale, W. Lu, S. Falcinelli, D. Bassi, Phys. Rev. Lett. 82 (1999) 450.
[13] For a review, see A.J. Stace, J. Phys. Chem. A 106 (2002) 7994.
[14] D. Schröder, M. Engeser, H. Schwarz, J.N. Harvey, Chem. Phys. Chem. 3 (2002) 584.
[15] D. Schröder, H. Schwarz, J.L. Wu, C. Wesdemiotis, Chem. Phys. Lett. 343 (2001) 258.
[16] N.R. Walker, R.R. Wright, P.E. Barran, H. Cox, A.J. Stace, J. Chem. Phys. 114 (2001) 5562.
[17] N. Walker, M.P. Dobson, R.R. Wright, P.E. Barran, J.N. Murrell, A.J. Stace, J. Am. Chem. Soc. 122 (2000) 11138.
[18] A.T. Blades, P. Jayaweera, M.G. Ikonomou, P. Kebarle, Int. J. Mass Spectrom. Ion Proc. 101 (1990) 325.
[19] A.A. Shvartsburg, J. Am. Chem. Soc. 124 (2002) 12343.
[20] M. Kaczorowska, J.N. Harvey, Phys. Chem. Chem. Phys. 4 (2002) 5227.
[21] Jaguar 4.1, Schrodinger, Inc., Portland, OR, USA, 2000.
[22] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[23] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[24] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265, and references therein.
[25] N.R. Walker, R.R. Wright, P.E. Barran, J.N. Murrell, A.J. Stace, J. Am. Chem. Soc. 123 (2001) 4223.

[26] (a) All experimental ionization energies of atoms have been taken from www.webelements.com, where they are collated from J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed., HarperCollins, New York, USA, 1993;
(b) A.M. James, M.P. Lord, Macmillan's Chemical and Physical Data, Macmillan, London, UK, 1992.

[27] NIST Chemistry Webbook, http://webbook.nist.gov/chemistry/.

[28] For experimental evidence of similar decomposition processes of other acetonitrile metal ion solvates, see A.A. Shvartsburg, Chem. Phys. Lett. 360 (2002) 479.

[29] M. Beyer, E.R. Williams, V.E. Bondybey, J. Am. Chem. Soc. 121 (1999) 1565.