

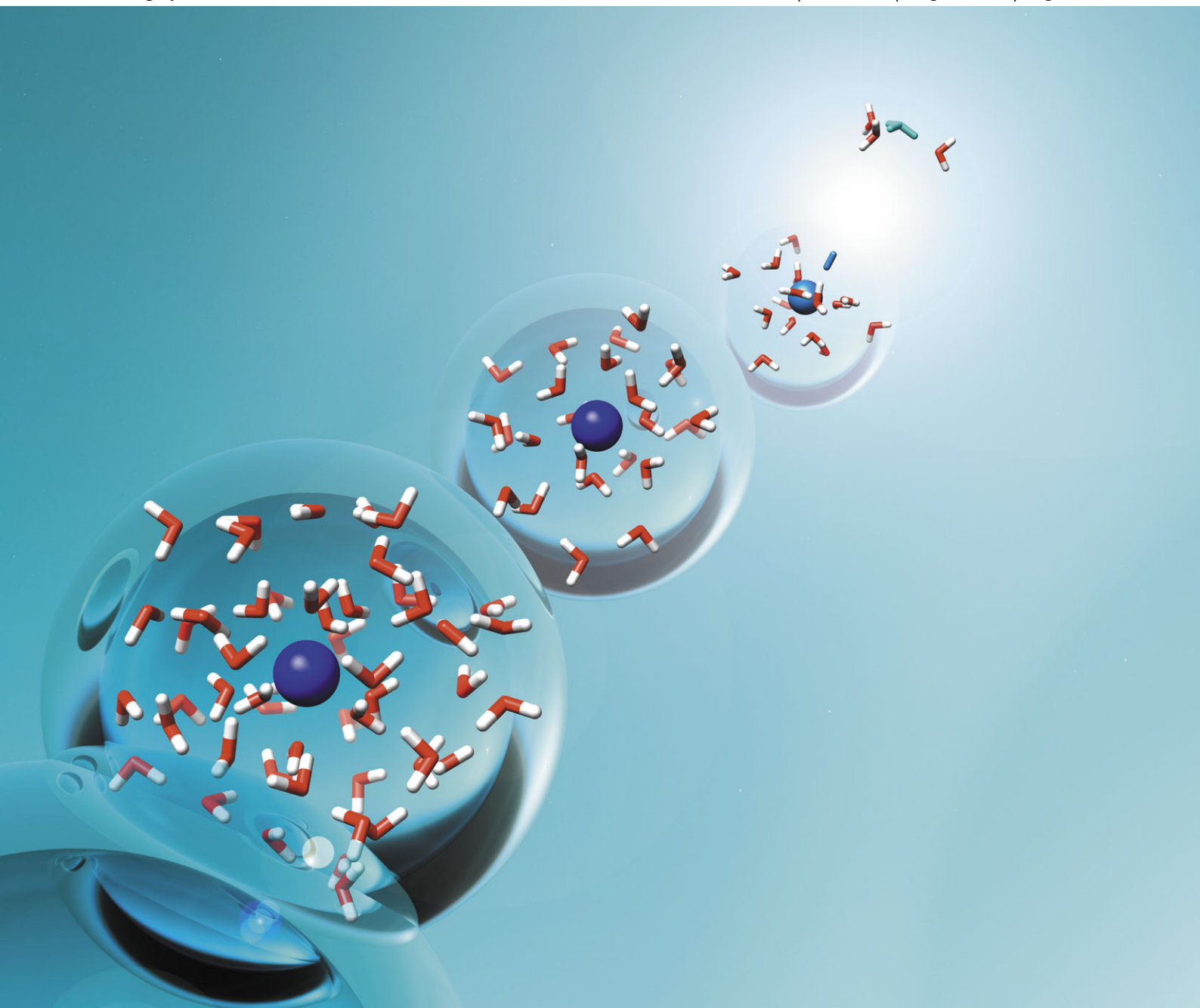
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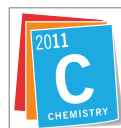
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PAPER

# Blurring the line between solution and the gas phase: collision-induced dissociation of hypersolvated lanthanide trications provides insights into solution acidity

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Lanthanide ions provide a classic example of the distortion of speciation that sometimes occurs during the electrospray ionization (ESI) process. Under normal conditions,  $M^{3+}$  ions are not observed as such from aqueous solution; rather, they appear as charge-reduced species such as  $[M(OH)]^{2+}$  or even  $[MO]^+$  ions. However, source conditions can be tuned to a “cold-flooding” mode such that  $[M(H_2O)_n]^{3+}$  ions can be readily obtained, thus providing spectra that are much more representative of the solution speciation. Examination of heavily hydrated trications by MS/MS enables the step-by-step progression of a small droplet to a solvated ion and eventually to a solvent-free ion to be examined in detail, and the point at which charge reduction occurs can be established. We find a strong correlation between the solution acidity of each lanthanide ion and the number of water molecules at which charge reduction occurs under MS/MS conditions. Examination of previously published data on a range of dications supports this conclusion. So not only can ESI-MS provide an accurate picture of the solution speciation, it can also provide insights into chemical behavior in solution.

The lanthanide elements, La through Yb (and often including Lu and sometimes even Y; collectively abbreviated as Ln), all have a stable +3 oxidation state in aqueous solution, and the non-involvement of the contracted f orbitals in bonding means that all 15 ions tend to behave rather like closed-shell ions.<sup>1</sup> Famously, the elements exhibit the “lanthanide contraction”, a steady reduction in size across the period as the additional f electrons fail to screen the outermost electrons completely from the increasing nuclear charge.  $La^{3+}$  at 130.0 pm (8 coordinate) is therefore considerably larger than  $Lu^{3+}$  at 111.7 pm (8 coordinate), with the sizes of the intervening 13 ions monotonously decreasing between these two.<sup>2</sup> The lanthanides therefore offer an opportunity, unique in the periodic table, to study a collection of ions whose properties change incrementally rather than abruptly across an extended series. Even one of the more notable phenomena that involves the lanthanides, the “gadolinium break”, is rather subtle.<sup>3–6</sup> Laing summarizes the gadolinium break as “the value of the physical property for a  $Gd^{3+}$  species is displaced from the smooth curve joining  $La^{3+}$  and  $Lu^{3+}$  in the direction of larger ionic radius, weaker bonding or lower stability of the complex”.<sup>7</sup> A common explanation for the effect is that the solution coordination number changes from 9 to 8 near Gd.<sup>8,9</sup> However, more recent work has cast some doubt on this

hypothesis, with Persson *et al.* describing the gadolinium break as a “myth”,<sup>10</sup> by using EXAFS to compare solid samples of crystallographically characterized  $[Ln(H_2O)_n](CF_3SO_3)_3$  with their aqueous solutions. All consisted of tricapped trigonal prisms with varying degrees of water deficiency in a capping site ( $n = 8.2$  to 9), and no abrupt change in the coordination number was observed at any point.

The lanthanide ions, while relatively large (compare  $Sc^{3+}$ , 101.0 pm, 8-coordinate), remain hard by virtue of their high charge and correspondingly favor hard ligands (*i.e.* the affinity of lanthanides for hard bases is mainly ionic in nature).<sup>11</sup> They are highly water soluble, and in aqueous solution water outcompetes all other monodentate ligands and occupies all coordination sites.  $Ln^{3+}$  ions are extraordinarily labile, and water molecules in the first coordination shell exchange at close to the diffusion rate.<sup>12</sup> Aquated lanthanide ions are weakly acidic, by virtue of eqn (1) (where  $\beta_1^*(M)$  = first hydrolysis constant of M):



The concentrations of  $Ln^{3+}$  and  $Ln(OH)^{2+}$  are equal at the pH value corresponding to the  $pK_a$  (about 7 to 9 for the lanthanides). So even in neutral solution, we would expect to observe some charge-reduced species present.

Electrospray ionization mass spectrometry (ESI-MS)<sup>13</sup> is a powerful tool for the analysis of ions dissolved in polar solvents, and it generally does a fine job of representing the

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solution speciation of such species.<sup>14</sup> However, for some time, small, highly charged ions were notable failures for the technique.<sup>15</sup> Rather than observing the multiply charged ions, *only* charge-reduced species such as solvated  $[M(OH)]^+$  ions would be seen.<sup>16–19</sup> This situation is particularly acute for the triply-charged lanthanides in water, and the ESI-MS spectrum of  $M^{3+}$  ions generally consists only of hydrated  $[M(OH)]^{2+}$ ,  $[M(OH)_2]^+$  and  $[M(O)]^+$  ions.<sup>20</sup> This behaviour contrasted sharply with what is observed in solvents other than water: acetonitrile,<sup>21</sup> diacetone alcohol,<sup>22</sup> acetonitrile,<sup>23</sup> peptides,<sup>24</sup> dimethylsulfoxide and hexamethylphosphoramide,<sup>25</sup> and various sugars<sup>26</sup> all allow observation of  $[M(\text{molecule})_n]^{3+}$  ions. The Williams group was the first to show that  $[M(H_2O)_n]^{3+}$  ions could be readily produced in the gas phase, provided that there are sufficient water molecules present ( $n > 15$ ).<sup>27</sup> They used a custom-made nano-ESI source that included a heated copper block coupled to a Fourier transform ion cyclotron resonance instrument (FTICR-MS), and obtained highly hydrated ions, with  $n$  in the hundreds. The smallest  $n$  observed depended on the particular lanthanide ion:  $n$  was largest for smaller, more acidic lanthanides, and less for the larger lanthanides. They subsequently extended their investigation of the lanthanides to the full series (with the exception of radioactive promethium), lutetium and yttrium (the related Group 3 metals).<sup>28</sup> They trapped the smallest observable  $[M(H_2O)_n]^{3+}$  ions at 220 K and allowed them to dissociate slowly through BIRD (blackbody infrared dissociation). From these data, they established a non-integer turnover size, the effective cluster size at which the loss of water and charge-separation reaction rates become equal. Their findings included a relationship between the turnover size and the solution acidity and a change in slope in the plot which they attributed to a gadolinium break, a lack of correspondence between the turnover size and the third ionization energy, and an unusually low signal intensity for ytterbium, the smallest of the lanthanides (though larger than lutetium, which was successfully observed).

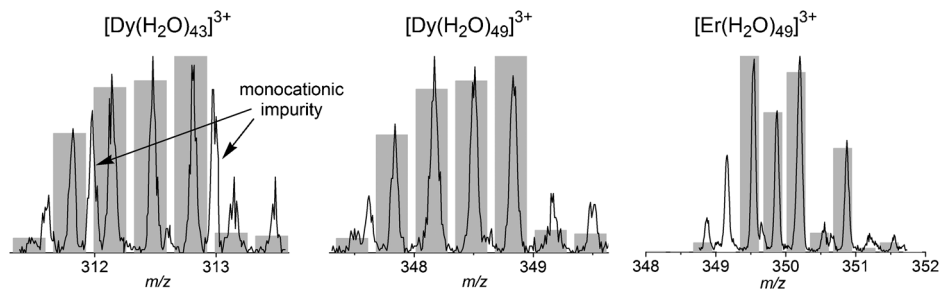
We obtain super-hydrated cations using a commercial hybrid quadrupole/time-of-flight instrument, by setting up the unmodified Micromass Z-spray source under “cold-flooding” conditions: high flow rates (20–50  $\mu\text{L min}^{-1}$ ) and ambient temperatures being key to success.<sup>29</sup> This approach works for a variety of ions, including  $\text{H}^+$ ,<sup>30</sup>  $\text{Pb}^{2+}$ ,<sup>31</sup> and variously methylated guanidinium ions.<sup>32</sup> Selection of  $[M(H_2O)_n]^{3+}$  ( $n \approx 50$ ) ions in the quadrupole and collision-induced dissociation (CID) stripped off water molecules through

multiple collisions to the point at which proton transfer occurred, and evaporation of a solvated proton as the Eigen cation,  $[\text{H}(\text{H}_2\text{O})_4]^+$ ,<sup>33</sup> was directly observed—the first such observation of a solvated ion evaporating from a droplet.<sup>29</sup> We have found the minimum value of  $n$  for CID studies,  $n_{\text{min}}$ , to be consistently lower than values found through other techniques—for example,  $n_{\text{min}}$  for  $\text{Pb}^{2+}$  is 8, but when studied using MIKES (mass analyzed ion kinetic energy spectra), 11 water molecules were required to stabilize the complex against proton transfer.<sup>31</sup> The difference is likely to be related to the fact that while  $[\text{Pb}(\text{H}_2\text{O})_{11}]^{2+}$  is indefinitely stable,  $[\text{Pb}(\text{H}_2\text{O})_n]^{2+}$  ( $n = 8, 9, 10$ ) are metastable sufficiently so that mass analysis can be completed before proton transfer can completely occur. Here, we extend our CID investigations to examine all the weakly acidic  $M^{3+}$  ions, the tricationic ions from the lanthanide series La–Yb (excluding Pm) and the Group 3 metals Y and Lu.

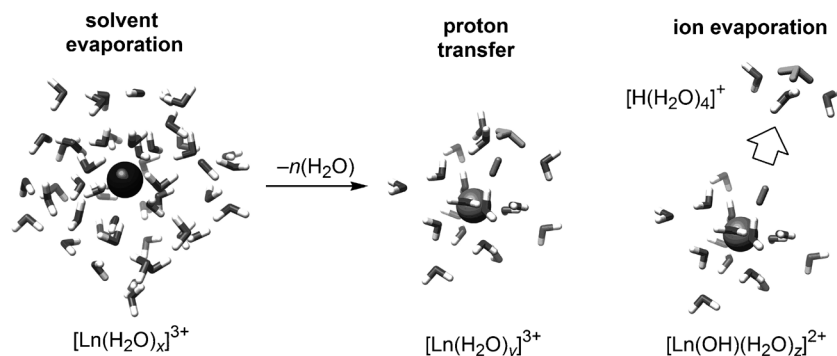
## Results and discussion

The mass spectrometer was set up in a “cold-flooding” mode, whereby the flow rate is high and the source and desolvation temperatures were low (see Experimental section for details). Under these conditions, the source becomes visually saturated with water, with droplets forming on the baffle leading to the exhaust. Desolvation is much reduced, but strong signals are attained through the use of high cone voltage (in-source collision-induced dissociation). All  $M^{3+}$  ions studied provided strong series of peaks attributable to  $[M(H_2O)_n]^{3+}$ , though the signal-to-noise ratio was significantly better for those elements with odd atomic numbers (one or two isotopes) compared to those with even atomic numbers (many isotopes), because in the former case the signal is concentrated at one or two values of  $m/z$  rather than distributed over many. Nonetheless, signals were sufficiently strong in all cases that a peak could be selected from the numerous choices at around  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$  ( $n \approx 50$ ) that provided good MS/MS data with no isobaric interferences (Fig. 1), and the minimum cluster size,  $n_{\text{min}}$ , for all 15 elements was established. Ytterbium provided the most difficulty, as it has seven isotopes and is the second-smallest ion investigated (and hence has a large  $n_{\text{min}}$ ), but an extended collection time addressed these issues.

We have already published the data for  $\text{La}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Lu}^{3+}$ ,<sup>29</sup> and the other 12 elements were investigated under identical conditions. Selection of  $[M(H_2O)_n]^{3+}$  in the quadrupole was followed by collision-induced dissociation (CID) of



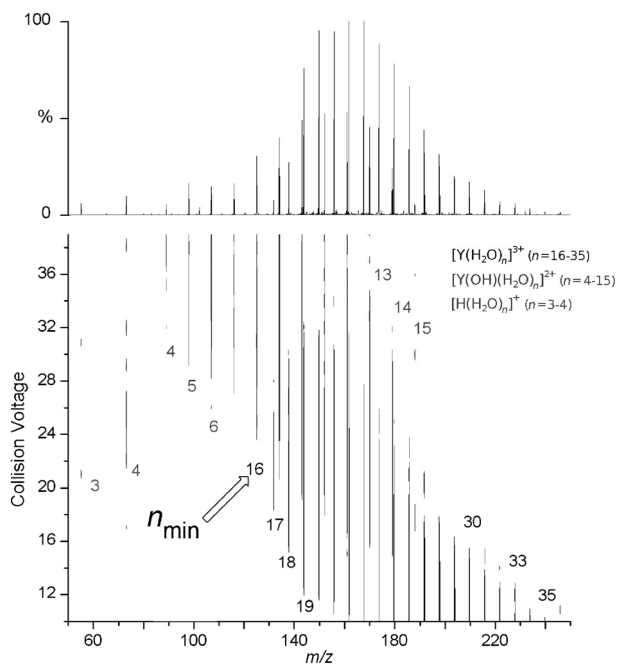
**Fig. 1** Representative experimental (line) and calculated (histogram) isotope patterns. The  $[\text{Dy}(\text{H}_2\text{O})_{43}]^{3+}$  ion was rejected in favour of the  $[\text{Dy}(\text{H}_2\text{O})_{49}]^{3+}$  ion due to the presence of overlap with a monocationic impurity at the same mass.



**Fig. 2** The process of solvent and ion evaporation through collision-induced dissociation (CID).

the ions with argon atoms in the collision cell (pressure  $2.2 \pm 0.1 \times 10^{-5}$  mbar), which has the effect of stripping off water molecules. This process continues, through increasing the collision voltage and hence the energy of the atom-ion interactions, until a number of water molecules remain,  $n_{\min}$ , at which point no higher charge density can be tolerated so charge reduction occurs through proton transfer from an inner-sphere water ligand to another water molecule and the solvated ion  $[\text{H}(\text{H}_2\text{O})_{\geq 3}]^+$  evaporates from the droplet (Fig. 2).

An example of the data collected is presented in Fig. 3, in an energy-dependent format (EDESI-MS/MS).<sup>34–37</sup> In this method of data presentation, multiple spectra are combined



**Fig. 3** EDESI-MS/MS for  $[\text{Y}(\text{H}_2\text{O})_5]^{3+}$ . The precursor ion at 335.9  $m/z$  is selected in the quadrupole mass analyzer, and subjected to CID at different collision voltages (10–39 V,  $y$ -axis). The 30 spectra are presented in the form of a contour map, with intensity being the third dimension. The spectrum at the top is the summation of all MS used to generate the map. This approach is a compact way of displaying all the information from a full CID experiment.  $n_{\min}$  represents the lowest value of  $n$  observed for a product ion of the type  $[\text{Y}(\text{H}_2\text{O})_n]^{3+}$ , in this case  $n = 16$ .

into a matrix and plotted as a contour map of collision voltage *vs.*  $m/z$ , where intensity is represented as the third variable. A summation of all the spectra used to generate the map is presented in the conventional format in the spectrum above the map. The map made it easy for us to focus on the particular collision voltage(s) at which  $n_{\min}$  was most likely to be found (for the example shown, 22 V). The value of  $n_{\min}$  was recorded for each  $[\text{M}(\text{H}_2\text{O})_n]^{3+}$ , as the smallest value of  $n$  observed in *any* of the MS/MS product ion spectra collected (where  $n \approx 50$  for the corresponding precursor ion). We chose a criterion for selection of the  $n_{\min}$  ion with a signal-to-noise ratio of at least three (any higher threw up many false negatives for the least intense spectra, and any lower produced many false positives, including at implausibly low values of  $n$ , for all spectra). All data are summarized in Table 1.

When  $n_{\min}$  is plotted against the first hydrolysis constant (Fig. 4a)<sup>39</sup> and the ionic radius (Fig. 4b), linear trends are obtained. Smaller and more acidic lanthanide ions have higher  $n_{\min}$ . The value was quite reproducible, but is necessarily an integer value and so the error in  $n_{\min}$  can be regarded as  $\pm 1$ . It is reasonable to expect both the ionic size and first hydrolysis constant to be related to  $n_{\min}$ . The first hydrolysis constant measures the same process as we observe in the gas phase as in solution—the Brønsted acidity of the hydrated metal ion (*i.e.* its propensity to release a proton), the only difference being the size of the solvation sphere (effectively infinite in solution, tightly circumscribed in the gas phase). For cations of a given charge, the smallest most effectively drain electron density from the oxygen of the bound water molecules, and hence from the hydrogen, thus increasing the propensity of a proton to transfer to a nearby water molecule (from which it can receive more electron density).

The minimum  $n$  value appears to relate slightly more closely to the first hydrolysis constant ( $R^2 = 0.92$ ) than to the ionic radius ( $R^2 = 0.86$ ), most obviously when considering yttrium. This element is an outlier in the ionic size plot (the agreement improves to  $R^2 = 0.93$  when Y is excluded) but falls near the line in the hydrolysis constant plot. Given that the resolution in  $n_{\min}$  has been limited to integer values, the correspondence to a straight line is similarly good in both cases, and it is not possible for us to say with confidence which tracks better. An empirical approximation of the relationship between acidity and ionic size is given by eqn (2).<sup>41</sup>

$$\text{p}K_a = 15.14 - 88.16[\text{Z}^2/r + 0.096(\chi_P - 1.50)] \quad (2)$$



**Table 1** Key parameters.  $^X\text{M}$  = the element and isotope selected for MS/MS studies;  $r_{\text{M}^{3+}}$  = 8-coordinate ionic radius;<sup>38</sup>  $\log^0\beta_1^*(\text{M})$  = first hydrolysis constant;<sup>39</sup> IE3 = 3rd ionization energy;<sup>40</sup> precursor  $m/z$  is the mass-to-charge ratio selected (choice defined by intensity and lack of isobaric interference);  $n_{\text{precursor}}$  defines the corresponding hydrated precursor ion,  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$ ;  $n_{\text{min}}$  defines the smallest value of  $n$  observed from the CID process for an ion of the type  $[\text{Ln}(\text{H}_2\text{O})_n]^{3+}$

M	Atomic number	# Stable isotopes	$r_{\text{M}^{3+}}/\text{pm}$	$\log^0\beta_1^*(\text{M})$	IE3/eV	Precursor $m/z$	$n_{\text{precursor}}$	$n_{\text{min}}$
<sup>89</sup> Y	39	1	115.9	-7.80	20.52	335.9	51	16
<sup>139</sup> La	57	2	130.0	-8.81	19.18	334.5	48	14
<sup>140</sup> Ce	58	4	128.3	-8.34	20.20	340.9	49	15
<sup>141</sup> Pr	59	1	126.6	-8.32	21.62	347.2	50	15
<sup>142</sup> Nd	60	7	124.9	-8.18	22.1	353.5	51	16
*Pm	61	0	—	—	—	—	—	—
<sup>152</sup> Sm	62	7	121.9	-7.84	23.4	356.9	51	16
<sup>153</sup> Eu	63	2	120.6	-7.76	24.92	357.1	51	16
<sup>158</sup> Gd	64	7	119.3	-7.83	20.63	358.9	51	17
<sup>159</sup> Tb	65	1	118.0	-7.64	21.91	335.1	47	17
<sup>164</sup> Dy	66	7	116.7	-7.59	22.8	348.8	49	17
<sup>165</sup> Ho	67	1	115.5	-7.56	22.84	355.0	50	17
<sup>166</sup> Er	68	6	114.4	-7.52	22.74	373.5	53	17
<sup>169</sup> Tm	69	1	113.4	-7.39	23.68	356.5	50	18
<sup>174</sup> Yb	70	7	112.5	-7.24	25.05	364.2	51	18
<sup>175</sup> Lu	71	2	111.7	-7.27	20.96	346.4	48	18

However, because the Pauling electronegativity ( $\chi_{\text{P}}$ ) of all the elements in this study is  $<1.3$  and the modified ratio is used only when the electronegativity of the metal exceeds 1.50, to a good approximation the acidity ( $\text{p}K_{\text{a}}$ ) is inversely proportional to the radius of the ion for ions of like charge, and our observations are in agreement with this rule of thumb. There is no correspondence between the data and the third ionization energy of the lanthanides (Fig. 4c), a reasonable result given that there is no change in the oxidation state during the charge reduction process, which is a proton transfer reaction that involves no redox chemistry.

Unlike Bush *et al.*,<sup>28</sup> we did not observe any evidence for a gadolinium break.<sup>42,43</sup> Given the subtleties of typical gadolinium break effects, the resolution of our data is unlikely to be sufficient to detect the sorts of features observed in formation constant plots. The appearance of a more dramatic gadolinium break in the data of Bush *et al.* is not strictly comparable to our results—CID is a higher-energy process than BIRD, as manifested by appreciably lower  $n_{\text{min}}$  values in our investigation of 14–18 compared to their turnover numbers of 19–21. Kinetic shift is an issue here, because the CID experiment captures short-lived ions.

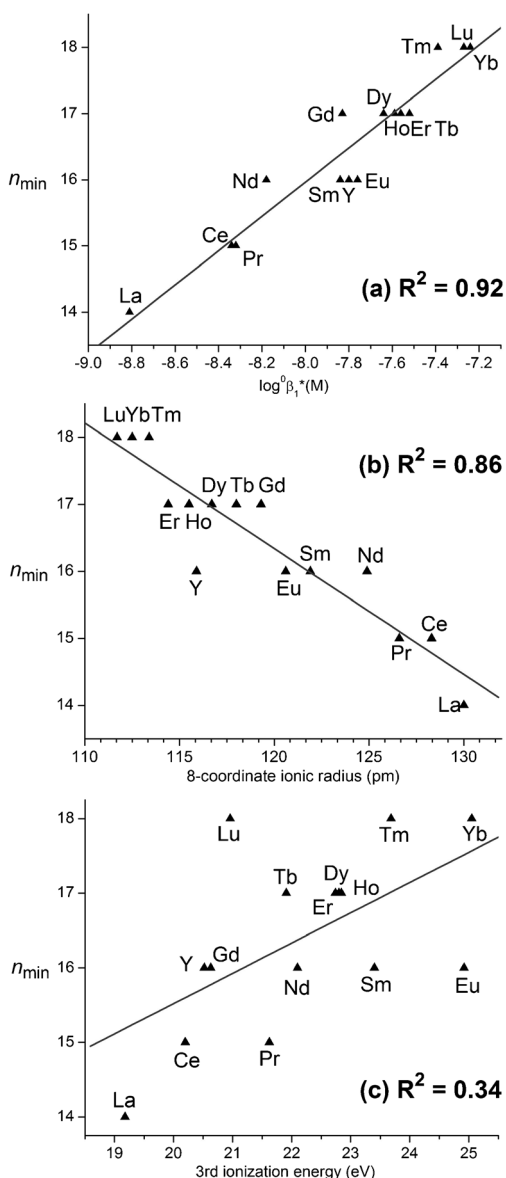
Having established a strong correlation between acidity (and a strong inverse correlation with ionic radius) and  $n_{\text{min}}$  for these large  $\text{M}^{3+}$  ions, how well does the trend hold up for the rest of the periodic table and other metal cations? As eqn (2) indicates, the most acidic cations are those that have a high charge and are small. Correspondingly, Group 1 metal ions are essentially non-acidic with  $\text{p}K_{\text{a}} \approx 14$  (and being monocationic, do not charge-reduce in the gas phase), and the Group 2 dications are feebly acidic. Using the same conditions and criteria as reported herein for  $n_{\text{min}}$ , we have looked at  $\text{Sr}^{2+}$  ( $\text{p}K_{\text{a}}$  13.3) and  $\text{Pb}^{2+}$  ( $\text{p}K_{\text{a}}$  7.7), and obtained  $n_{\text{min}}$  values of 0 and 8 for these two ions. These values are in keeping with the general trend that the higher the acidity of an ion, the greater the number of water molecules needed. These data would be outliers on the plot shown in Fig. 5, so while the linearity holds true for trications in the size range of  $\sim 120 \pm 10$  pm, it does not appear to carry through to

dications (we would expect  $n_{\text{min}}$  for  $\text{Pb}^{2+}$  to be  $\sim 17$ , based on our data).

Transition metal trications such as  $\text{Sc}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and  $\text{Cr}^{3+}$  can all be thought of as “moderately acidic” ( $\text{p}K_{\text{a}} \approx 4$ ) rather than “weakly acidic” ( $\text{p}K_{\text{a}} \approx 8$ ). Indeed, to keep the hydroxides of transition metal trications dissolved, solutions of these ions are typically kept highly acidic. Accordingly, when neutral solutions of these metal ions are analyzed by ESI-MS using the same conditions as for the lanthanides (as nitrates or chlorides), we observed no tricationic species, only charge-reduced 2+ and 1+ ions. Similarly, the moderately acidic tetracationic actinide  $\text{Th}^{4+}$  ( $\text{p}K_{\text{a}}$  3.2) provided only 1+ and 2+ ions, and no 3+ or 4+ ions are observed. Based on these results, we did not even attempt to investigate any *strongly* acidic cations (*e.g.*  $\text{Ti}^{4+}$ ,  $\text{Au}^{3+}$ , both of which have negative  $\text{p}K_{\text{a}}$ ).

While our values of  $n_{\text{min}}$  are not the same as (they are always lower than) the more usually reported  $n_{\text{crit}}$ , examining published values of  $n_{\text{crit}}$  and comparing them to the acidity of the ions are illustrative. Shvartsburg and Siu have previously determined the  $n_{\text{crit}}$  values for a wide range of dications,<sup>44</sup> ranging from the small  $\text{Be}^{2+}$  to the much larger  $\text{Sr}^{2+}$ , and including a variety of transition metals. These data were first collected by Kebarle *et al.*<sup>17,18,45</sup> and have been further developed in work by Stace *et al.*<sup>46–48</sup> and Armentrout *et al.*<sup>49–52</sup> The first hydrolysis constant of these ions has been long-established.<sup>53</sup> The result from these published studies is another good straight line (Fig. 5). The fit with the first hydrolysis constant is better than with either ionic radius or with second ionization energy. The correlation between ionization energy and  $n_{\text{crit}}$  is reasonable, but it notably fails for  $\text{Be}^{2+}/\text{Zn}^{2+}/\text{Ni}^{2+}$ , which have very similar ionization energies but very different  $n_{\text{crit}}$  values.

Given that both our own data on trications and reinterpretation of previously published data on dications both produce good linear fits, and superior in both cases to plots against ionization energies, we are in agreement with the suggestion of Williams and co-workers that it is proton transfer rather than electron transfer, which is the key step in the charge separation

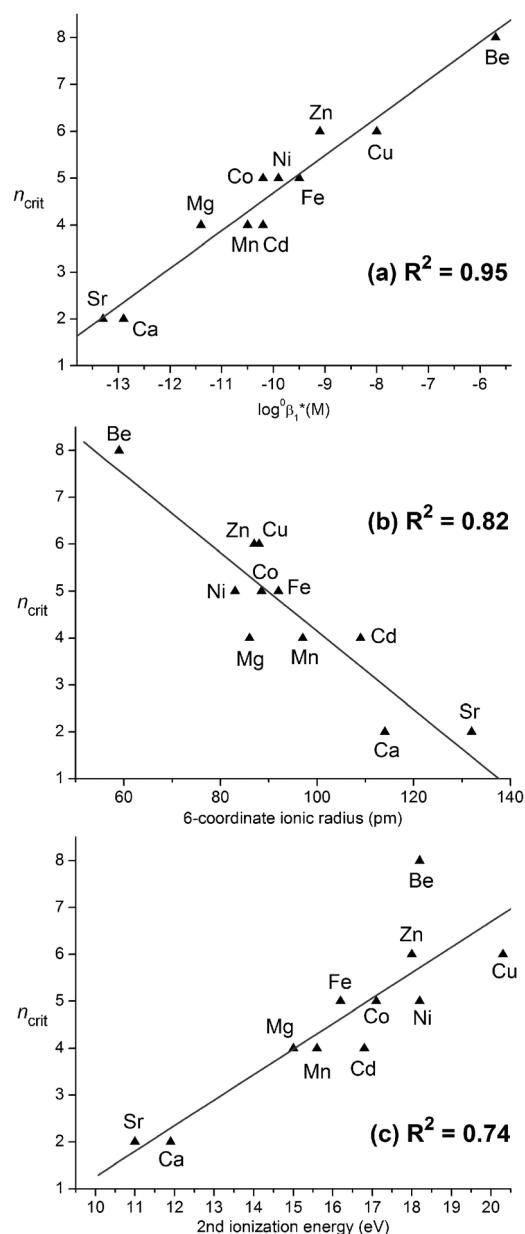


**Fig. 4** Plot of  $n_{\min}$  (minimum  $n$  for a detectable  $[M(H_2O)_n]^{3+}$  product ion in MS/MS) vs. (a) the first hydrolysis constant; (b) the eight-coordinate ionic radius; and (c) the 3rd ionization energy for  $M^{3+}$  ions. Linear regressions are (a)  $y = 36.7 + 2.59x$ ; (b)  $y = 38.8 - 0.187x$ ; (c)  $y = 7.40 + 0.406x$ .

process.<sup>54</sup> The strong inverse correlation between ionic radius and  $n_{\min}$  (or  $n_{\text{crit}}$ ) values is as expected, given the strong inverse relationship between ionic radius and acidity.

## Conclusions

The hydrated tricationic metal ions  $[M(H_2O)_n]^{3+}$  ( $M = Y, La-Nd, Sm-Lu$ ) decompose by proton transfer to form  $[M(OH)(H_2O)_{n-(x+1)}]^{2+}$  and  $[H(H_2O)_x]^+$  ( $x = 3, 4, \dots$ ) when  $n$  is reduced below a point that correlates well to the solution acidity of the ion in question. The minimum value of  $n$  can be established by performing collision-induced dissociation of  $[M(H_2O)_n]^{3+}$  ( $n \approx 50$ ) in the collision cell of a tandem mass spectrometer, and the resulting  $n_{\min}$  values were found to



**Fig. 5** Plot of  $n_{\text{crit}}$  vs. (a) the first hydrolysis constant; (b) the six-coordinate ionic radius; and (c) the 2nd ionization energy for  $M^{2+}$  ions. Linear regressions are (a)  $y = 13.5 + 0.893x$ ; (b)  $y = 12.5 - 0.0836x$ ; (c)  $y = -4.18 + 0.544x$ .

range from 14 for  $La^{3+}$ , the least acidic ion, to 18 for  $Yb^{3+}$ , the most acidic. ESI-MS proves to not only accurately represent solution speciation for multiply-charged metal ions if the right source conditions are selected, but it can also provide insights into the solution behavior through MS/MS investigations.

## Experimental

Metal ions were investigated as nitrates except for La, Pr, Eu, Tb, Ho, Tm and Lu (chlorides) and were purchased from Aldrich. Experimental data were collected on an unmodified Micromass Q-ToF *micro*<sup>TM</sup> with a Z-spray source. Voltage settings ranged from 180 V to 200 V for the cone voltage

and 2600 to 2900 V for the capillary. The cone and desolvation gas flows were 0 L h<sup>-1</sup> and 100 L h<sup>-1</sup>, respectively, while desolvation and source temperatures were maintained at 20 °C and 60 °C. Resolution settings and scan times were varied based on the quality of the signal obtained. Typical values for the low and high mass resolutions were 12.0 and 2 min for the scan time. The ion energy was kept constant at 1 V and adjustment of other instrumental parameters showed minimal impact. Aqueous solutions were 5 to 15 mM and flow rates of 20 to 50 μL min<sup>-1</sup> were used. EDESI experiments were carried out by performing MS/MS on a selected peak and increasing the collision voltage from one-volt increments across the energy range of interest (typically 10–40 V). Spectra were collected for 2–5 min at each collision voltage to obtain a reasonable ion count. Automation of the mass spectrometer software (MassLynx<sup>®</sup>) to carry out the EDESI experiments (ramping of the collision voltage) was achieved using the program Autohotkey (freely available from <http://www.autohotkey.com/>).

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