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# Formation, acidity and charge reduction of the hydrates of doubly charged ions $M^{2+}$ ( $Be^{2+}$ , $Mg^{2+}$ , $Ca^{2+}$ , $Zn^{2+}$ )

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## Abstract

There are two methods for producing in the gas phase doubly charged metal ion hydrates,  $M(H_2O)_n^{2+}$  (or other ion ligand  $L ML_n^{2+}$  complexes). In the clustering method, one starts with the naked ion  $M^{2+}$ , and in the presence of a third (bath) gas and water vapor, the ion hydrates form by ion-molecule clustering reactions. The second method is based on electrospray with which a spray of aqueous solutions containing the dissolved salts  $M^{2+} + 2X^-$ , leads to gas phase  $M(H_2O)_n^{2+}$  with a distribution around  $n \approx 8$ . For  $M$ , which has a high second ionization energy,  $IE(M^{2+})$ , both methods can fail to produce a full range of hydrates with a given  $n$ , because of the interference of a charge reduction reaction which involves intramolecular proton transfer. This reaction becomes possible at  $n = 2$ ;  $(M(H_2O)_2^{2+})^* = MOH^+ + H_3O^+$ , and competes with the simple ligand loss:  $(M(H_2O)_2^{2+})^* = M(H_2O)^{2+} + H_2O$ . The thermally excited  $(M(H_2O)_2^{2+})^*$  results in the clustering method by the exothermicity of the forward clustering reaction and in the electrospray method by the thermal declustering required to produce lower  $n$  ions. Ab initio calculations are presented for the energies of the above reactions and transition states for  $Mg^{2+}$  and  $Ca^{2+}$ . These show that the transition state for the charge reduction reaction is much lower than that for the simple ligand loss at  $n = 2$ . However, as  $n$  increases, the two transition states move closer together and above a given  $n = r$ , simple ligand loss becomes dominant. The capabilities and limitations of the two methods to produce hydrates of a given  $n$  is discussed. Experimental results illustrate competing charge reduction and simple  $H_2O$  loss for  $Be(H_2O)_n^{2+}$  under thermal equilibrium conditions at  $n \approx 9$ . Charge reduction reactions when occurring in the forward clustering direction can be viewed as proton transfer reactions to the incoming  $H_2O$  molecule. These can be generalized by examining the proton affinities of the  $MOH(H_2O)_n^+$  ions, which are obtained by ab initio calculations. Proton transfer from  $M(OH)_2^{2+}$  can be induced not only by  $H_2O$  but also by other bases  $B$ . Experimental results for the deprotonation of  $Zn(OH)_2^{2+}$ ,  $n = 8$  or  $9$ , by  $NH_3$  are presented. The charge reduction reactions by which a deprotonated ligand attached to  $M$  is formed, can have synthetic utility. Examples are given for the production of methylthiolate complexes which may be useful for modeling ion complexes in which one of the ligands is the deprotonated amino acid residue cysteine. (Int J Mass Spectrom 185/186/187 (1999) 685–699) © 1999 Elsevier Science B.V.

**Keywords:** Acidity of metal ion hydrates  $M(H_2O)^{2+}$ ; Hydration of metal ions  $M^{2+}$ ; Metal ion hydrates, preparation, and stabilities; Proton transfer, intramolecular, in metal ion hydrates

## 1. Introduction

We reported recently the energies of hydration of the doubly charged ions:  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$  [1]

and  $Zn^{2+}$  [2]. These were obtained from determinations of the gas-phase equilibria, Eq. (1)



The measurements were performed in a reaction chamber attached to a mass spectrometer [3]. Determinations of the equilibrium constants,  $K_{n-1,n}$  at

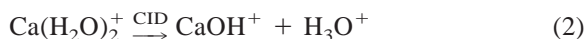
\* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

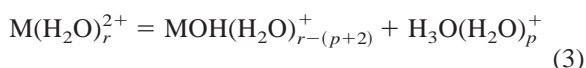
different temperatures led via van't Hoff plots to:  $\Delta G_{n-1,n}^\circ$ ,  $\Delta H_{n-1,n}^\circ$  and  $\Delta S_{n-1,n}^\circ$ . The doubly charged ions were obtained by electrospray [4] of dissolved salts,  $\text{MX}_2$ , in aqueous solution. The electrospray method leads to a transfer of ions from solution to the gas phase [4,5] such that with the above salts the  $\text{M}(\text{H}_2\text{O})_n^{2+}$  ions can be obtained in the gas phase. With the apparatus available [3], only temperatures below 240 °C were accessible and therefore the strongly bonded hydrates  $n < 5$ , whose hydrate dissociation enthalpies,  $\Delta H_{n,n-1}^\circ$ , are bigger than  $\sim 26$  kcal/mol, could not be determined. On the other hand, the higher hydrates from  $n = 5$  to  $n \approx 16$  were accessible. Fortunately, relatively good theoretically calculated energies are now available [6] for the low hydrates. Therefore the theoretical [6] and experimental results are complementary and provide a good quantitative description of the hydration and coordinative thermochemistry of these ions in the gas phase. The gas phase results were found to provide good relative values for the total hydration energies in aqueous solution [1,7]. The solvation and the coordinative behavior towards water and other ligands of doubly charged ions like  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  has become of special interest lately [6,8] because of the importance of these ions in ion-protein complexes such as metallo enzymes.

Even though good theoretical accounts of the bonding and structure of the low  $n$  hydrates are provided by theoretical calculations, it is still desirable to obtain also good experimental values. Such results would in principle be accessible, either by equilibrium measurements with apparatus designed for high temperature or by the collision induced dissociation (CID) threshold technique (guided ion beam mass spectrometry) developed by Armentrout and co-workers [9]. However for certain ions  $\text{M}^{2+}$  like  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  measurements for all ligand numbers  $n$  are expected not to be possible because of the occurrence of an important competing reaction which leads to a reduction of the charge of the ion. Thus, for example, qualitative experiments involving CID of  $\text{Ca}(\text{H}_2\text{O})_n^{2+}$  [10], produced by electrospray, led to simple  $\text{H}_2\text{O}$  dissociation

down to  $n = 2$ . However, CID of the dihydrate led almost exclusively to the reaction



There are many  $\text{M}^{2+}$  ions whose second ionization energies  $\text{IE}(\text{M}^+)$  are higher than that of Ca, such as ( $\text{M} = \text{Be}, \text{Mg}, \text{Mn}, \text{Co}, \text{Zn}$ ), and for these, the charge reduction on CID occurs earlier [10,11], i.e. at a higher hydrate number  $r$



Thus the ( $r$ ) values at which CID occurred were: Mg (3), Ca (2), Sr (2), Ba (0), Mn (3), Co (4), Zn (5). These correlated with  $\text{IE}(\text{M}^+)$ . The intervention of the charge reduction reaction is expected to make measurements of the hydration energies for  $\text{M}(\text{H}_2\text{O})_n^{2+}$  very difficult or impossible for  $n < r$ .

Another method to obtain the hydrates is to start with the naked  $\text{M}^{2+}$ , which in general is not too difficult to produce, and then execute the consecutive hydration reactions in the presence of a third gas and water vapor. However, this method also does not work for the above ions. This was discovered by Spears and Fehsenfeld [12] who produced  $\text{Ca}^{2+}$  in a flowing afterglow apparatus. In the presence of  $\text{H}_2\text{O}$  vapor they observed the first hydrate,  $\text{Ca}(\text{H}_2\text{O})^{2+}$ , but the second hydration led exclusively to the reaction



which they considered to be an “unusual” reaction.

Obviously reactions in Eqs. (2) and (4) are closely related. In Eq. (2) one supplies enough energy to dissociate a water molecule but instead one induces charge reduction, while in Eq. (4), the incoming second water molecule on bonding to  $\text{Ca}(\text{H}_2\text{O})^{2+}$  causes release of the exothermicity of the bond formation which is sufficient to lead to the charge reduction, in the absence of rapid third body collisional cooling. In fact, it was the expectation of processes of this type that led us some time ago to initiate the production of multiply charged ion ligand

complexes by electrospray [10,11]. The occurrence of the charge reduction, Eq. (4), on hydration of the naked ions  $M^{2+}$  is expected to occur at  $r = 2$  for all the  $M^{2+}$  ions such as:  $Be^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ , which on dehydration by CID undergo charge reduction at  $r \geq 2$ . Therefore, if one intended to prepare the  $M^{2+}$  hydrates by hydrations of the naked ions, one would be able to determine only the energy for the first hydration (0, 1). On the other hand, starting with electrospray produced hydrates one will be able to determine the energies for all hydrates with  $n > r$ .

The hydration equilibria measurements [1] for  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  involved values of  $n > 5$ , so that no problems with charge reduction were encountered in these measurements. However the first member of the alkaline earth series,  $Be^{2+}$ , was an exception. For this ion, charge reduction occurs already at much higher values than five, and this process interfered with the equilibria measurements. The partial equilibria data obtained are given in the present work. Results demonstrating the occurrence of charge reduction under thermal conditions and at third gas pressures of 10 Torr for this ion are also presented.

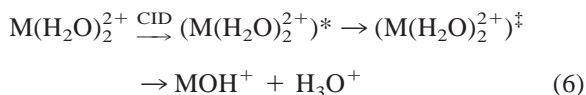
Occurrence of charge reduction reactions was observed [10,11] also with other protic solvent molecules such as methanol and ammonia. Charge reduction was fostered by these molecules, which have higher gas phase basicities than water. On the other hand, nonprotic solvents such as dimethylsulfoxide (DMSO) and acetonitrile (AN), increased the stability of the ion ligand complexes  $ML_n^{2+}$  with regard to charge reduction. The charge reduction for these ligands when it occurred, involved not intramolecular proton transfer but electron transfer such as:



In the present work, which involves both theoretical computation and experimental work, we address the following topics:

(a) The mechanism of the intramolecular proton

transfer and the energy of the transition state for the charge reduction reactions:



These are determined by computation for  $Mg^{2+}$ ,  $Ca^{2+}$ . The enthalpy changes for the thermal reactions, Eq. (6), was also obtained by computation for the above ions and  $Be^{2+}$  and  $Zn^{2+}$ . These results provide useful insights on the competition between charge reduction and simple  $H_2O$  dissociation.

(b) Formally, the forward clustering reaction that leads to charge reduction, can be considered as a proton transfer reaction,



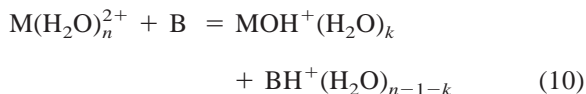
where  $M(H_2O)^{2+}$  is the acid and  $H_2O$  the base. These acid-base reactions can be generalized to other bases, B



Similarly, one can consider also  $MOH^+$  as an acid and examine its deprotonation to the neutral oxide MO.



Finally, the proton transfer reaction Eq. (8) can be generalized to all higher hydrates



Eqs. (7)–(9) will be examined on the basis of computational and experimental results obtained with added gas phase bases.

(c) Proton transfer reactions, like those in Eqs. (8) and (10), can have also a gas phase synthetic utility, allowing one to prepare certain desired ion-ligand complexes. Some examples will be given.

## 2. Experimental and computational

### 2.1. Experimental

The equilibrium determinations and proton transfer observations were performed with the ion-reaction chamber previously described [3]. Briefly, the ions were produced by electrospray of aqueous solutions of the  $\text{MX}_2$  salts at concentrations  $10^{-4} - 10^{-3}$  mol/L at flow rates of less than  $0.5 \mu\text{L}/\text{min}$ . Atmospheric air and the ions produced were introduced through a capillary into a forechamber, containing 10 Torr  $\text{N}_2$  gas. An imposed electric field caused the ions to drift into the reaction chamber which contained nitrogen gas at 10 Torr and known partial pressures of water vapor,  $p(\text{H}_2\text{O})$ , in the 1–100 mTorr range for the equilibria determinations or other reagent gases B, for the proton transfer determinations. The reaction chamber was sampled by letting gas and ions escape through an orifice leading to an evacuated chamber and a triple quadrupole mass spectrometer. A very weak drift field, 6 V/cm, was present in the reaction chamber. For the equilibria determinations, the observed ion intensity ratio:  $I(\text{M}(\text{H}_2\text{O})_n^{2+})/I(\text{M}(\text{H}_2\text{O})_{n-1}^{2+}) = I_p/I_r$ , remained constant for drift fields below 12 V/cm, confirming the expectation [3] that ions at such low drift fields have thermal internal energies. The ratio  $I_p/I_r$  was determined at several water partial pressures and plots of  $I_p/I_r$  versus  $p(\text{H}_2\text{O})$  led to straight lines as required by the equilibrium expression

$$\frac{I_p}{I_r} = K_{\text{eq}} p(\text{H}_2\text{O}) \quad (11)$$

where the assumption is made that the ion intensity ratio is equal to the ion concentration ratio near the sampling orifice in the reaction chamber.

### 2.2. Computational details

All calculations were performed using GAUSSIAN<sup>94</sup> [13] with the B3LYP hybrid density functionals as the method of choice [14]. The basis set employed for all

optimizations and frequency calculations was the 6-311++G(d, p) set except for Ca systems. For Ca, the valence triple- $\zeta$  basis set by Ahlrich [15] supplemented with two contracted  $d$  polarization functions, was used, and the 6-311++G( $d$ ,  $p$ ) set for oxygen and hydrogen was retained. The parameters for the polarization functions were optimized analogous to the method employed by Garmer [16], by minimizing the interaction energy for  $\text{Ca}^{2+}$  and the hydroxyl anion. As Garmer has pointed out, the parameters for the polarization functions do not vary much from system to system. The interaction energies using the parameters from Garmer ( $0.41 d(1.78) + 1.0 d(0.38)$ ) change by less than 1 kcal/mol from the energies using the newly optimized parameters ( $0.43 d(1.97) + 1.0 d(0.40)$ ). However, inclusion of the polarization functions is essential, because in at least one reaction ( $\text{Ca}(\text{OH}^+) \rightarrow \text{Ca}^{2+} + \text{OH}^-$ ) the resulting difference is approximately 30 kcal/mol.

The frequencies were used unscaled, because the various scaling factors for ZPE,  $S_{\text{vib}}(T)$ , and  $\Delta H_{\text{vib}}(T)$  are essentially 1 [17].

To locate the transition state for the reactions  $\text{M}(\text{H}_2\text{O})_2^{2+} \rightarrow \text{M}(\text{OH})^+ + \text{H}_3\text{O}^+$  ( $\text{M} = \text{Ca}, \text{Mg}$ ) a pseudoreaction coordinate, the angle O–M–O, was varied while the other degrees of freedom were optimized, see Figs. 1 and 2. The structure with the highest energy was then reoptimized as a transition state.

A few notes need to be made with respect to  $\text{M}(\text{H}_2\text{O})_2^{2+}$  ( $\text{M} = \text{Be}, \text{Mg}, \text{Ca}, \text{Zn}$ ). The initially expected structures for these dehydrates would be linear, with both waters at opposite sides of the metal cation center with a  $D_{2d}$  point group. However, as already pointed out by Bauschlicher et al. [18] in a study involving Mg, Ca, and Sr, the linear conformation occurs for the smaller dications (Mg) while the larger dications favor a bent structure (Ca, Sr). Bauschlicher attributed that difference to the larger polarizabilities of Ca and Sr with respect to Mg that creates a favorable core polarization on the metal center offsetting the repulsion of the two water molecules. The same behavior was reproduced in our study where Be, Mg, and Zn exhibit linear structures for the dihydrates while Ca shows a bent structure with an angle of approximately  $118^\circ$ , compared to  $126^\circ$  in

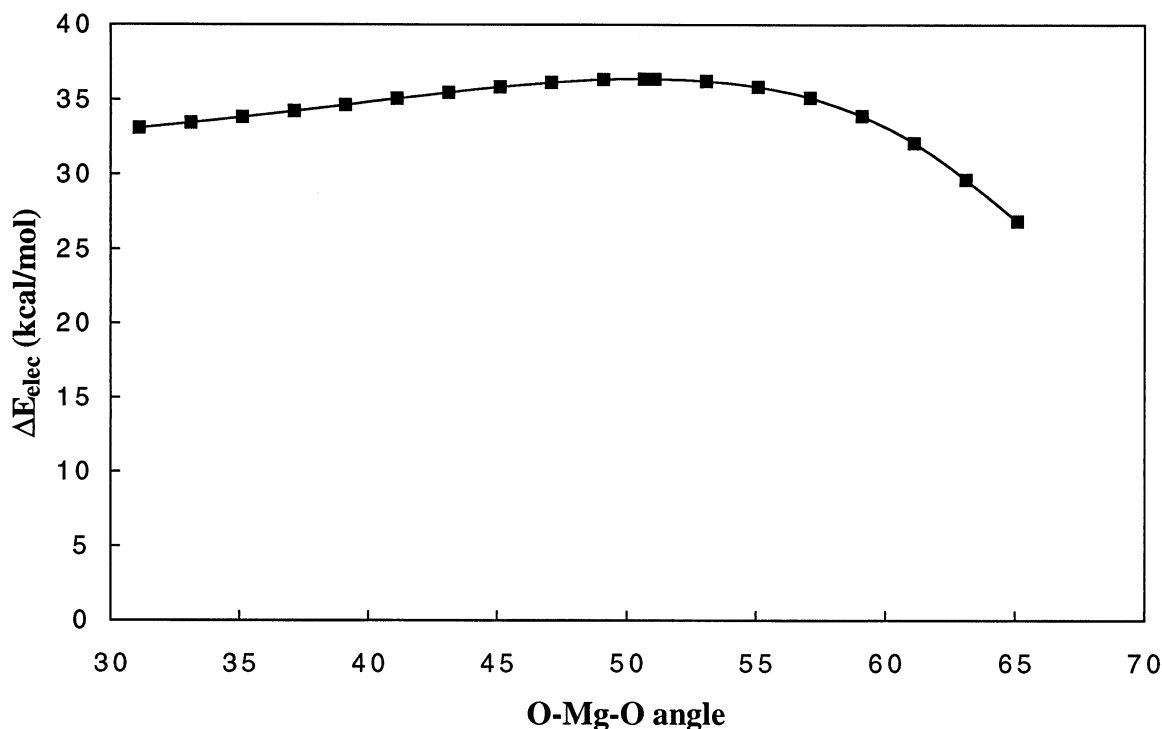


Fig. 1. Computed changes of energy for transition state for reaction  $\text{Mg}(\text{H}_2\text{O})_2^{2+} = \text{MgOH}^+ + \text{H}_3\text{O}^+$  in function of the angle between  $\text{Mg}^{2+}$  and the oxygens of the two water molecules. The geometry was optimized for each change of angle. For some important bond distances and energies, see Scheme 1 and Table 1.

Bauschlicher et al.'s study [18]. However, the energy difference to the  $D_{2d}$  structure for Ca so far obtained is 0.7 kcal/mol, in good agreement with Bauschlicher et al.'s value of 0.3 kcal/mol. In other words, the potential energy surface (PES) of  $\text{Ca}(\text{H}_2\text{O})_2^{2+}$  along the O–Ca–O coordinate is exceedingly flat for over  $120^\circ$ . However, as already pointed out in several other studies [19], the linearity barrier is in the same range as the zero-point energy and the equilibrium geometry of the molecule in most experimental situations can be regarded as quasilinear.

In general, the energies of all hydrate and dihydrate systems are in excellent agreement with published values as shown in Table 1. The structural parameters also agree well with literature. For example, for  $\text{Ca}(\text{H}_2\text{O})_2^{2+}$ , the M–O bond distance is 2.250 Å while that by Bauschlicher [18] is 2.275 and by Pavlov et al. [6] is 2.26. For the dihydrate the M–O distances are 2.287 Å and 2.283 Å compared to 2.310 by Bauschli-

cher et al. [18] and 2.28 Å by Pavlov et al. [6]. Similarly good agreement has been obtained for the M–O distances of Be, Mg, Zn hydrates and dihydrates [20] when compared with Pavlov et al.'s and Bauschlicher et al.'s (Mg only) values.

### 3. Results and discussion

*3.1. Energy changes and transition states for the charge reduction reaction:  $M(\text{H}_2\text{O})_2^{2+} = \text{MOH}^{2+} + \text{H}_3\text{O}^{2+}$ . Charge reduction for  $M(\text{H}_2\text{O})_n^{2+}$  hydrates, where  $n > 2$*

The results from the theoretical calculations for Be, Mg, Ca, Zn, are given in Table 1. Evaluation of the transition state were performed only for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The changes of energy with the angle O–M–O on the way to the transition state are shown in Fig. 1 (Mg) and Fig. 2 (Ca). To reach the transition state, the

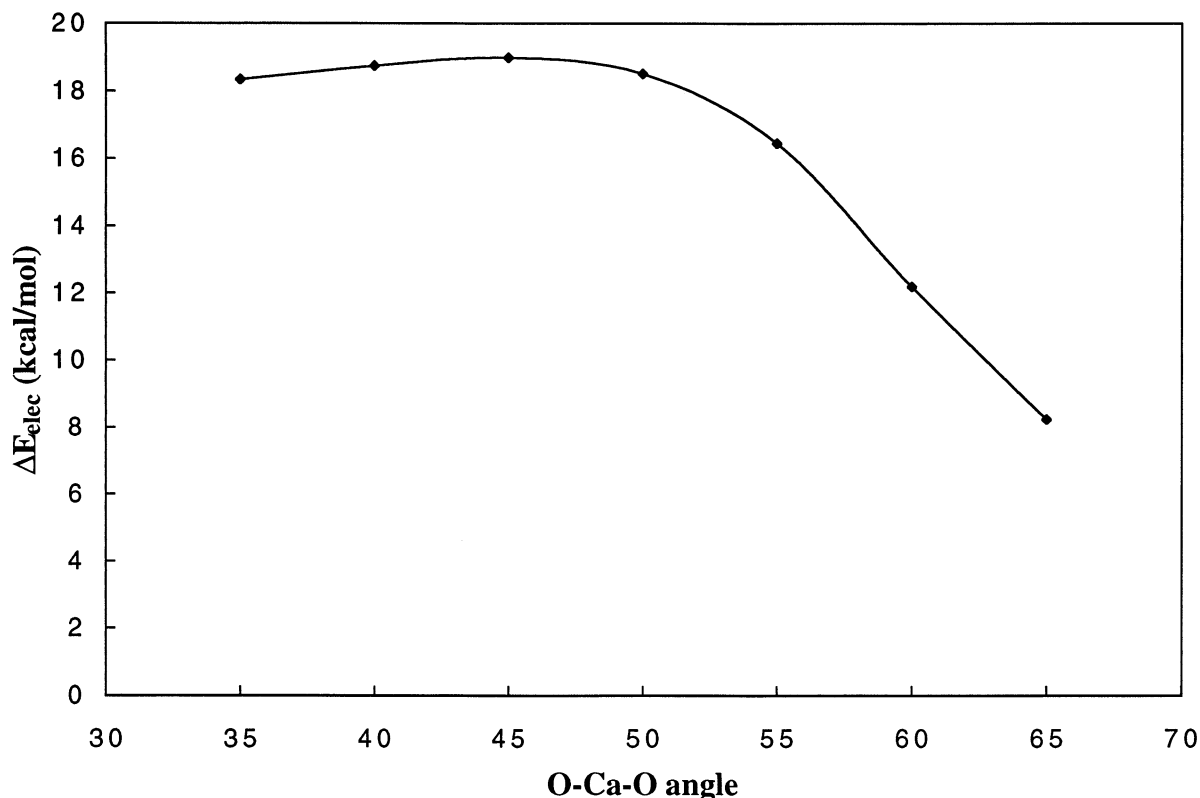
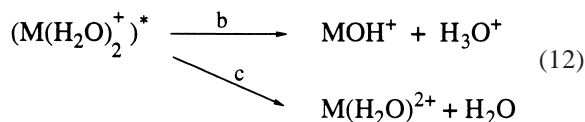


Fig. 2. Same as in Fig. 1 but for reaction involving  $\text{Ca}(\text{H}_2\text{O})_2^{2+}$ , see Scheme 2 and Table 1.

water molecule that “leaves” must increase its distance from M and the O–M–O angle must decrease. The major energy increase should be associated with increase of the O–M distance of the leaving molecule. For Mg, the Mg–O distance increases from 1.96 Å in  $\text{Mg}(\text{H}_2\text{O})_2^{2+}$  to 3.2 Å in the transition state. At the transition state the O–M distance of the  $\text{OH}_2$  that “stays” has decreased somewhat and the O–H bond which is involved in proton transfer has increased, see Scheme 1, (Mg) and Scheme 2, (Ca). The transition state energy  $\Delta H_b$  (Mg) = 36.3 kcal/mol is considerably larger than  $\Delta H_b$  (Ca) = 19.3 kcal/mol, see Schemes 1, 2 and Table 1.

The higher value for Mg is in line with the expected bigger energy required to increase the M–O distance for the leaving molecule. For comparison, one can consider the total energy for one molecule to leave the dihydrate, which are, Table 1,  $\Delta H_c^\circ$  (Mg) = 72.0 kcal/mol versus  $\Delta H_c^\circ$  (Ca) = 48.5 kcal/mol.

The differences between the energy for one molecule to leave the dihydrate  $\Delta H_c$ , and the transition state energy  $\Delta H_b$  are of interest because they reveal the excess energy that will be available to drive the charge reduction reaction when one has provided sufficient excitation to the dihydrate to dissociate it.



The bigger the difference,  $\Delta H_c - \Delta H_b$ , the larger will be the yield of charge reduced product. These differences for both Mg  $\approx 71.5 - 36.3 = 35.2$  kcal/mol; Ca  $\approx 48.1 - 19.2 = 28.9$ , are very big and indicate very low yields for the doubly charged monohydrate for both Mg and Ca. Notably, the yields

Table 1

Calculated energies for hydration reactions of doubly charged ions  $M^{2+}$ 

| Reactions <sup>a</sup>                                  | Be                            |                               |                               | Mg   |                  |                  | Ca   |                  |                  | Zn                            |                  |                  |
|---|-------------------------------|-------------------------------|-------------------------------|--|------------------|------------------|--|------------------|------------------|-------------------------------|------------------|------------------|
|   | $\Delta H_0$ <sup>b</sup>     | $\Delta H^\circ$ <sup>c</sup> | $\Delta S^\circ$ <sup>d</sup> | $\Delta H_0$                                       | $\Delta H^\circ$ | $\Delta S^\circ$ | $\Delta H_0$                                       | $\Delta H^\circ$ | $\Delta S^\circ$ | $\Delta H_0$                  | $\Delta H^\circ$ | $\Delta S^\circ$ |
| (a) $M(H_2O)_2^{2+} = M(OH)^+ + H_3O^+$                 | -24.2                         | -23.7                         | 31.1                          | -5.2   | -4.7             | 29.5             | -7.8   | -7.6             | 17.8             | -19.9                         | -19.5            | 32.1             |
| (b) $M(H_2O)_2^{2+} = M(H_2O)_2^{2+} (TS)$ <sup>e</sup> |                               |                               |                               | 36.3   | 35.3             | -4.7             | 19.3   | 18.0             | -12.6            |                               |                  |                  |
| (c) $M(H_2O)_2^{2+} = M(H_2O)^{2+} + H_2O$              | 118.0<br>(118.4) <sup>f</sup> | 119.0                         | 33.0                          | 71.5<br>(70.9) <sup>f</sup><br>(73.8) <sup>g</sup> | 72.0             | 28.9             | 48.1<br>(47.5) <sup>f</sup><br>(48.9) <sup>g</sup> | 48.5             | 20.8             | 87.4<br>(86.6) <sup>f</sup>   | 88.0             | 32.0             |
| (d) $M(H_2O)^{2+} = M^{2+} + H_2O$                      | 145.2<br>(146.1) <sup>f</sup> | 146.2                         | 25.2                          | 80.6<br>(81.5) <sup>f</sup><br>(81.9) <sup>g</sup> | 81.8             | 24.2             | 55.4<br>(56.9) <sup>f</sup><br>(55.0) <sup>g</sup> | 56.5             | 23.4             | 102.0<br>(101.9) <sup>f</sup> | 103.1            | 24.0             |
| (e) $M(H_2O)^{2+} = M(OH)^+ + H^+$                      | 20.8                          | 20.8                          | 22.9                          | 86.3   | 86.8             | 25.4             | 107.1  | 107.4            | 21.8             | 55.7                          | 56.0             | 24.9             |
| (f) $M(OH)^+ = MO + H^+$                                | 224.6                         | 225.3                         | 23.9                          | 257.8  | 257.9            | 21.1             | 299.3  | 299.6            | 24.0             | 224.7                         | 224.9            | 21.1             |
| (g) $M(OH)^+ = M^{2+} + OH^-$                           | 512.4                         | 514.1                         | 24.4                          | 382.4  | 383.3            | 20.8             | 336.3  | 337.4            | 23.6             | 434.3                         | 345.4            | 21.1             |

<sup>a</sup> Reaction equations where M = Be, Mg, Ca, or Zn. The coordinates for any of the structures are mailed to anyone interested, upon request.

<sup>b</sup> Reaction enthalpies at 0 K, include zero-point energy corrections. Units are in kcal/mol.

<sup>c</sup> Standard reaction enthalpies at 298 K using calculated thermal corrections. Units are in kcal/mol.

<sup>d</sup> Units in cal/mol K, at 298 K.

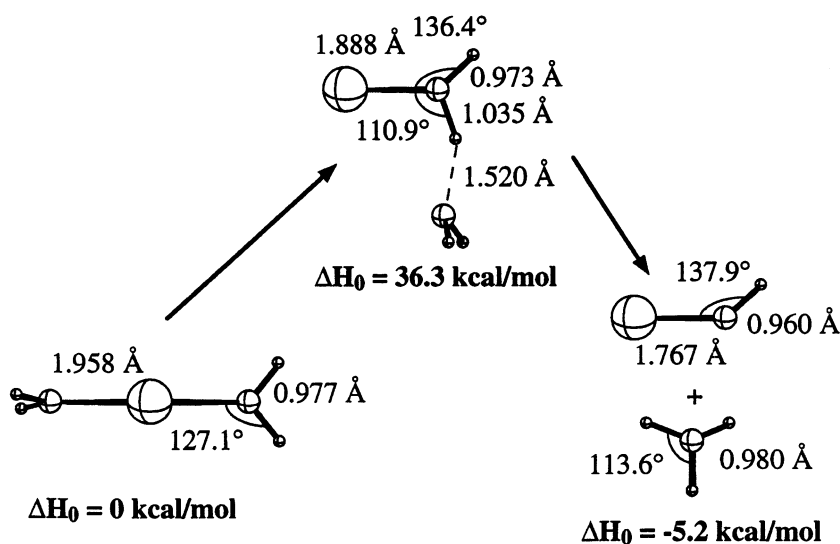
<sup>e</sup> Transition state (TS) for reaction  $M(H_2O)_2^{2+} = M(OH)^+ + H_3O^+$ .

<sup>f</sup> [6].

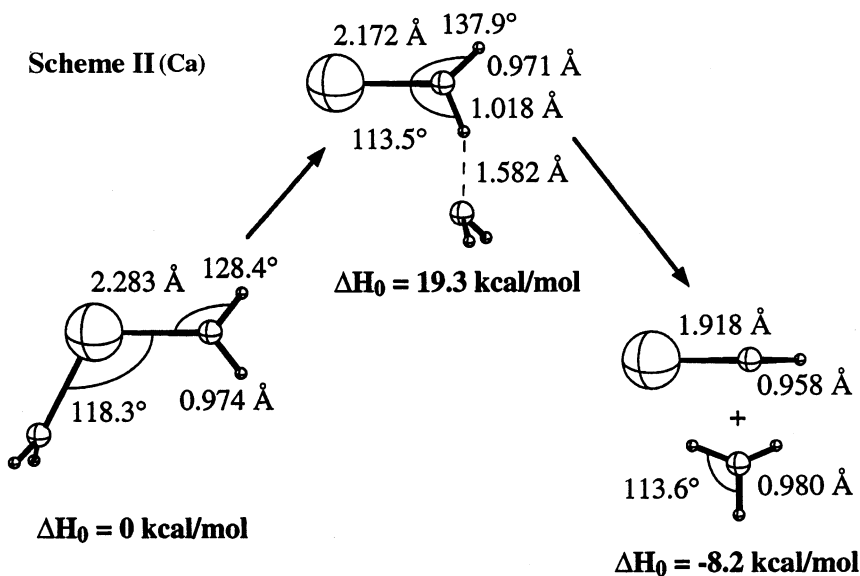
<sup>g</sup> [18].

will be lower for Mg relative to Ca. The above differences are also of interest in experiments where one attempts to build up the hydrates  $M(H_2O)_2^{2+}$  and  $M(H_2O)_n^{2+}$  starting with the naked ion, as attempted by Spears and Fehsenfeld [12], with  $Ca^{2+}$ . The  $Ca(H_2O)_2^+$  hydrate, on formation from  $Ca(H_2O)^{2+}$  and

$H_2O$ , will be energized by  $\sim 48.1$  kcal/mol, but requires only  $\sim 19.2$  kcal/mol to undergo charge reduction. The charge reduction will be extremely rapid and very high pressures of third gas will be required to achieve collisional quenching that leads to significant yields of the thermalized dihydrate. It is not surprising that



Scheme 1.



Scheme 2.

these authors, working at less than 1 Torr of He, observed only charge reduction and zero yield of  $\text{Ca}(\text{H}_2\text{O})_2^{2+}$ .

The changes of the relative rates for the charge reduction (12a) and hydrate dissociation (12b), with increase of hydration number  $n$ , are of interest. Previous results [10,11] from CID of hydrates  $\text{M}(\text{H}_2\text{O})_n^{2+}$ , and the equilibria measurements [1,2] do indicate that for an increase of  $n$ , the rates of the charge reduction decrease relative to the  $\text{H}_2\text{O}$  dissociation reaction, because above some  $n$  only the  $\text{H}_2\text{O}$  dissociation is observed. This indicates that the nature of the transition state for the charge reduction reaction changes significantly. While the increase of the distance between M and the O of the leaving  $\text{H}_2\text{O}$  molecule was the most important term for the dihydrate, the importance of this term decreases with increase of  $n$ . On the other hand the endothermicity of the intracuster proton transfer from one to the other water molecule increases significantly in the presence of other  $\text{H}_2\text{O}$  ligands. A decrease of the protic character of the hydrogen atoms  $\text{M}(\text{H}_2\text{O})_n^{2+}$  is expected when many water molecules are present. This is illustrated by the deprotonation reactions



for which the enthalpy changes were obtained by ab initio calculations, for  $n = 1, 2, 3$ , see Table 2. These show that the enthalpy change for deprotonation of  $\text{Mg}(\text{H}_2\text{O})_n^{2+}$  increases rapidly from 86.8 kcal/mol ( $n = 1$ ) to 107.8 kcal/mol ( $n = 2$ ) to 126.4 kcal/mol ( $n = 3$ ). Another important factor increasing the transition state energy for charge reduction, as  $n$  is increased, is the need to redistribute the remaining water molecules over the two incipient singly charged ions  $\text{MOH}^+$  and  $\text{H}_3\text{O}^+$ . The separation of charge is analogous to charge delocalization which is known to lead to decreased solvation exoergicity.

Table 2  
Calculated deprotonation energies of  $\text{Mg}(\text{H}_2\text{O})_n^{2+}$

| Reactions  | $\Delta H_0^a$ | $\Delta H^\circ^b$ | $\Delta S^\circ^c$ |
|--|----------------|--------------------|--------------------|
| $\text{Mg}(\text{H}_2\text{O})_3^{2+} = \text{Mg}(\text{H}_2\text{O})_2(\text{OH})^+ + \text{H}^+$ | 125.9          | 126.4              | 23.7               |
| $\text{Mg}(\text{H}_2\text{O})_2^{2+} = \text{Mg}(\text{H}_2\text{O})(\text{OH})^+ + \text{H}^+$   | 107.3          | 107.8              | 25.3               |
| $\text{Mg}(\text{H}_2\text{O})^{2+} = \text{Mg}(\text{OH})^+ + \text{H}^+$                         | 86.3           | 86.8               | 25.4               |

<sup>a</sup> Zero-point energies included. Units in kcal/mol.

<sup>b</sup> Using calculated thermal corrections to 298 K. Units in kcal/mol.

<sup>c</sup> Units in cal/mol K.



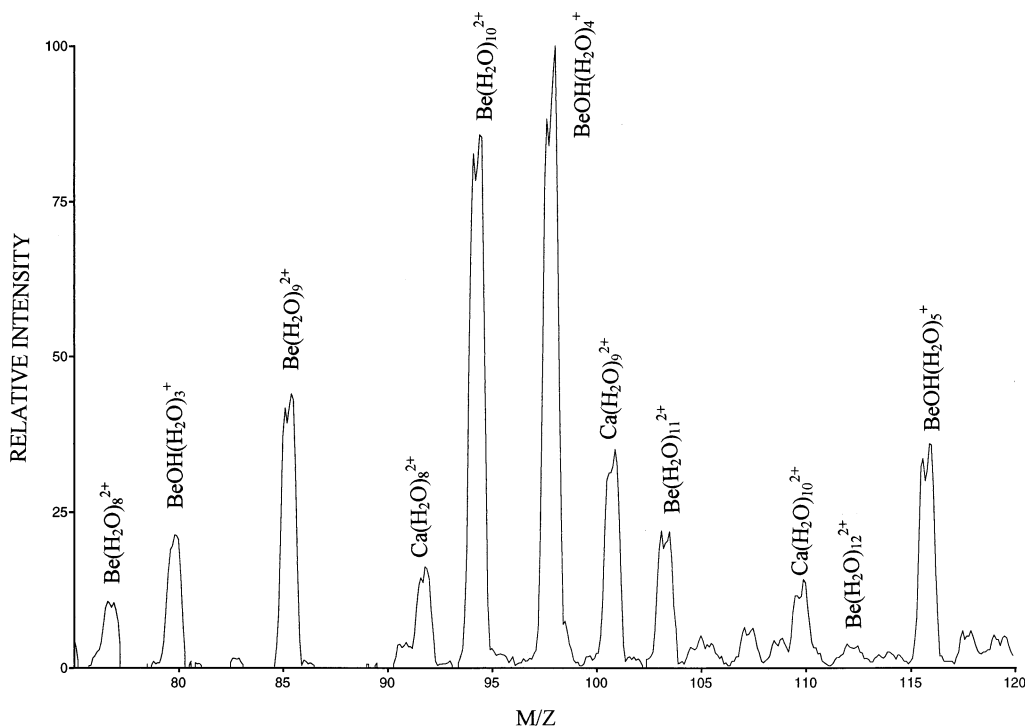


Fig. 3. Major ions observed at 25 °C, 10 Torr  $N_2$  bath gas and 0.6 mTorr  $H_2O$ . The initial  $Be(H_2O)_n^{2+}$  ions introduced into the reaction chamber were produced by electrospray. The hydration reactions  $Be(H_2O)_{n-1}^{2+} + H_2O = Be(H_2O)_n^{2+}$  are close to equilibrium. Intramolecular proton transfer leads to charge reduced  $BeOH(H_2O)_n^+$  ions. Some  $Ca(H_2O)_n^{2+}$  ions are also observed. These are because some  $CaX_2$  impurities in the solution used.

For hydrates where  $n$  is close to  $r$ , the rates of dissociation of  $H_2O$  molecules and charge reduction will be similar and thermochemical data for both processes could be obtained by threshold CID. The precursor ions can be prepared by electrospray. However a preparation by a modification of the naked ion clustering method may also be possible. Spears and Fehsenfeld [12], after failing to produce  $Ca(H_2O)_n^{2+}$ ,  $n > 1$ , observed that they could obtain very good yields of  $Ca(CO_2)_n^{2+}$  via thermomolecular clustering of  $Ca^{2+}$  and  $CO_2$  where  $Ca(CO_2)_6^{2+}$  was the major ion. Exposing this ion to  $H_2O$  vapor in the flow tube, they obtained  $Ca(H_2O)_n^{2+}$  with  $n \geq 1$ . They considered this process a simple ligand switching reaction but probably more than one  $CO_2$  was exchanged for one  $H_2O$ , achieving thus an “evaporative” cooling of the high exothermicity water– $M^{2+}$  interactions. This method could be of special utility also in producing

$M(H_2O)_n^{2+}$  ions where  $n < r$  for physical measurements such as optical spectroscopy.

### 3.2. Charge reduction interference with hydration equilibria measurements. Hydration of $Be^{2+}$

The hydration equilibria, Eq. (1), for  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Zn^{2+}$ , could be determined [1,2] between  $n = 5$  and  $n = 15$  without interference from charge reduction because charge reduction for these ion hydrates occurs at lower  $n$  ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ) or not at all ( $Ba^{2+}$ ). However, for  $Be(H_2O)_n^{2+}$ , interference from charge reduction was experienced, as illustrated by the mass spectra shown in Figs. 3 and 4. At a temperature of 24 °C only some 45% of the ion intensity was because  $Be(H_2O)_n^{2+}$ , and 55% because  $BeOH(H_2O)_n^+$ , Fig. 3. At 46 °C, the  $Be(H_2O)_n^{2+}$  intensity decreased to only 5–10%, Fig. 4. The charge

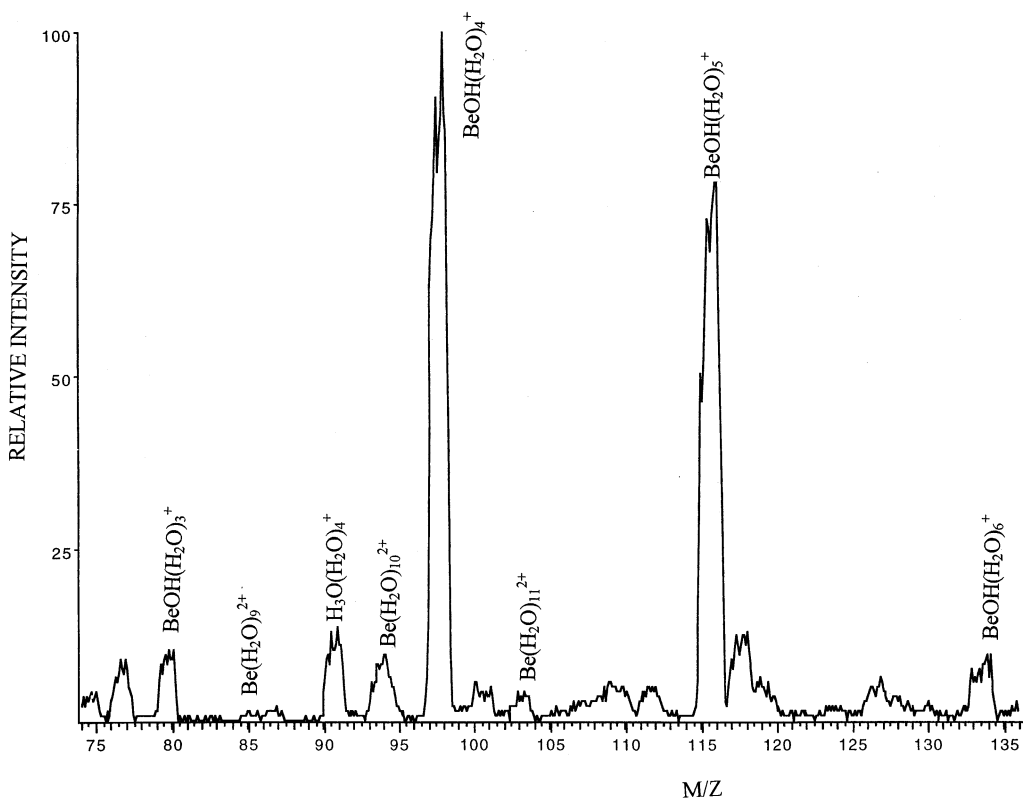


Fig. 4. Major ions observed at 46 °C, 10 Torr N<sub>2</sub> bath gas and 12 mTorr H<sub>2</sub>O. Because of increased rate for charge reduction at this higher temperature most of the Be(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup> ions have been converted to BeOH(H<sub>2</sub>O)<sub>n</sub><sup>+</sup>.

reduction probably occurs mostly from the  $n = 8$  and  $n = 9$  Be<sup>2+</sup> hydrate.

Qualitative CID experiments with Be(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup> precursor ions showed that the  $n = 9$  hydrate led to some 80% yield of charge reduced product BeOH(H<sub>2</sub>O)<sub>n</sub><sup>+</sup> with  $n = 4$  and 3 and only 20% H<sub>2</sub>O dissociation to Be(H<sub>2</sub>O)<sub>8</sub><sup>2+</sup>, see Fig. 5. For the precursor ion with  $n = 8$ , essentially only charge reduction was observed and the major charge reduced BeOH(H<sub>2</sub>O)<sub>n</sub><sup>+</sup> ions had  $n = 3$  and 4. On the other hand, the CID of the higher hydrate Be(H<sub>2</sub>O)<sub>10</sub><sup>2+</sup>, led to approximately 50% loss of H<sub>2</sub>O and 50% charge reduction to BeOH(H<sub>2</sub>O)<sub>n</sub><sup>+</sup> with  $n = 4$  being the major product. The gradual increase of H<sub>2</sub>O dissociation versus charge reduction, as  $n$  of the precursor ions Be(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup> is increased, follows the predictions made in the preceding section.

The thermal charge reduction illustrated by the

data in Figs. 3 and 4 occurs even though 10 Torr bath gas (N<sub>2</sub>) is present in these experiments. Under the reaction conditions of these experiments, the forward and reverse rates of the hydration reaction, Eq. (1), are in equilibrium. This means that Be(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup> ions are continuously thermally activated to decompose to the lower Be(H<sub>2</sub>O)<sub>n-1</sub><sup>2+</sup> hydrate. Collisional deactivation by the bath gas, which in principle can suppress charge reduction in the forward hydration reaction, cannot be expected to suppress charge reduction in the reverse, i.e. H<sub>2</sub>O dissociation reaction as long as the transition state free energy for this reaction is higher than that for the charge reduction.

The hydration equilibria for the Be(H<sub>2</sub>O)<sub>n</sub><sup>2+</sup> hydrates  $n > 9$  could be determined at 25 °C. The resulting free energies  $\Delta G_{n-1,n}^\circ$  are given in Table 3. The Be<sup>2+</sup> free energies are compared with those for Mg<sup>2+</sup> and Ca<sup>2+</sup> in Fig. 6. The exoergicities for Be<sup>2+</sup>

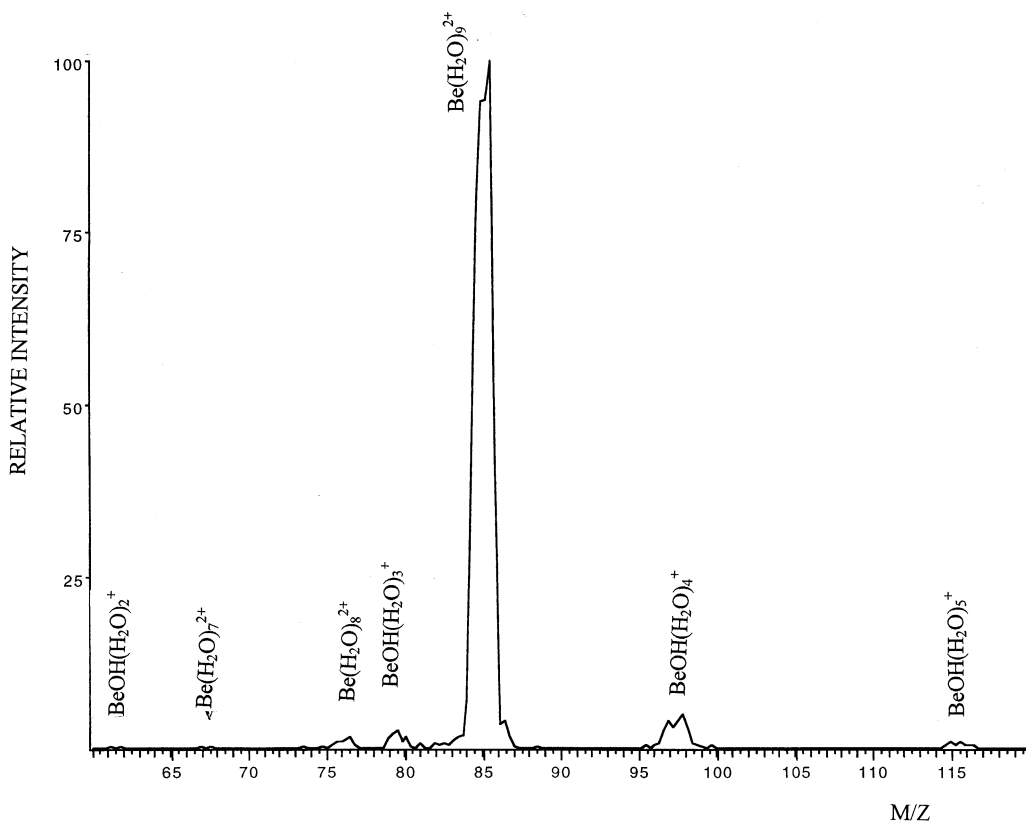


Fig. 5. Qualitative results for collision induced dissociation (CID) of  $\text{Be}(\text{H}_2\text{O})_9^{2+}$  precursor ion. Both charge reduction to  $\text{BeOH}(\text{H}_2\text{O})_n$ ,  $n = 2, 3, 4, 5$ , and dehydration to  $\text{Be}(\text{H}_2\text{O})_8^{2+}$  occur, however the charge reduced ions are more abundant.

are only slightly higher than those for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in this high hydrate range. The exothermicity of the hydration of Be is very much higher at low  $n$  as indicated by the data for the enthalpy changes in Table 1. The hydration exothermicities and exoergicities at high  $n$  become almost the same for all the above  $\text{M}^{2+}$  because charge transfer from the  $\text{H}_2\text{O}$  to the core ion at low  $n$  is more pronounced for the small ions, i.e.  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ . For more details, see [1,2].

Table 3  
Free energies<sup>a</sup> of hydration of  $\text{Be}^{2+}$

| $n$                                  | 10  | 11  | 12  | 13  | 14  |
|--------------------------------------|-----|-----|-----|-----|-----|
| $-\Delta G_{n-1,n}^\circ$ (kcal/mol) | 8.6 | 7.4 | 6.4 | 5.6 | 5.1 |

<sup>a</sup> Values for 298 K. Standard state, 1 atm.

### 3.3. Acidities and proton transfer from doubly charged $\text{ML}_n^{2+}$ , where $L = \text{H}_2\text{O}$ and other ligands

It was pointed out in the Introduction that the forward clustering reaction which becomes a charge reduction can be viewed as a proton transfer reaction



The proton affinity of  $\text{MOH}^+$  is given in Table 1, reaction (e). For Ca,  $\Delta H_e = \text{PA}(\text{CaOH}^+) = 108$  kcal/mol. As discussed above, water whose  $\text{PA}(\text{H}_2\text{O}) = 165$  kcal/mol [21], is able to deprotonate  $\text{Ca}(\text{H}_2\text{O})^{2+}$ . Because of the large release of kinetic energy associated with the coulombic repulsion between the two positively charged product ions of the proton transfer reaction, only bases B whose proton

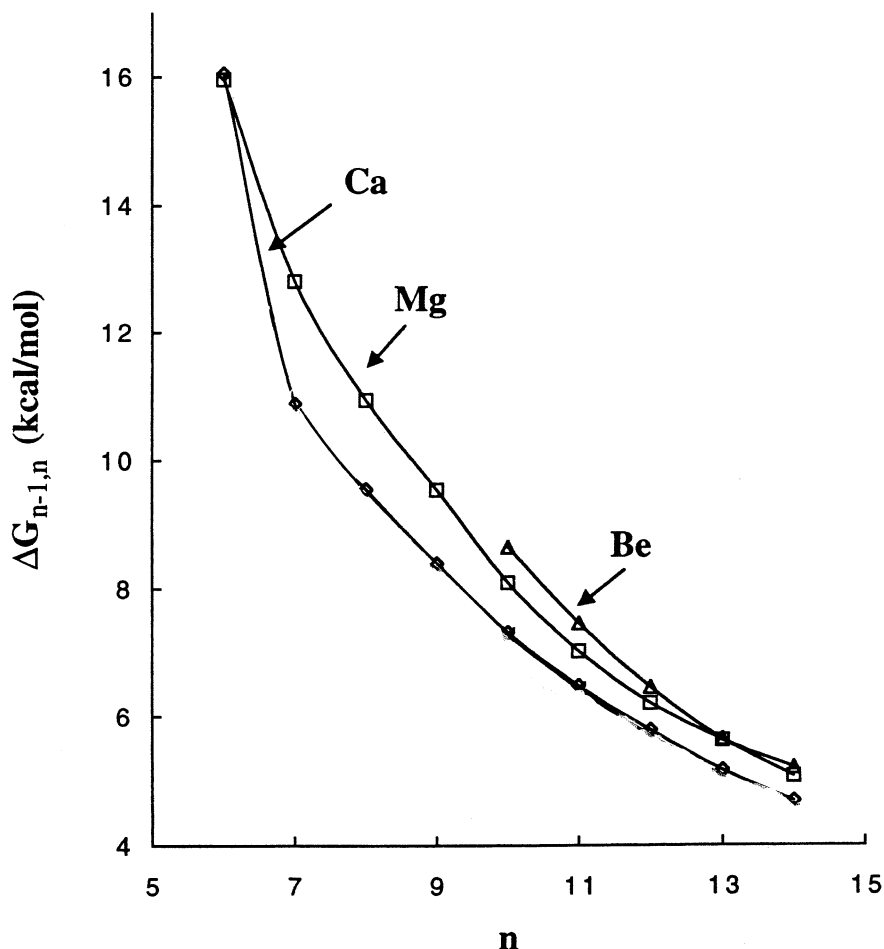


Fig. 6. Free energies  $\Delta G_{n-1,n}^\circ$  for reaction:  $\text{Be}(\text{H}_2\text{O})_{n-1}^{2+} + \text{H}_2\text{O} = \text{Be}(\text{H}_2\text{O})_n^{2+}$ , determined from measurement of the equilibria at 298 K. Because of interference of charge reduction, see Figs. 4 and 5, only these high  $n$  free energies could be determined. Comparison with data [1] for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  shows that for high values of  $n$ , the free energies are almost the same, even though very large differences are present for  $n < 5$ .

affinity is higher by  $\sim 30$  kcal or more than the  $\text{PA}(\text{CaOH}^+) = 108$  kcal/mol, will be able to induce proton transfer. For a recent discussion of proton transfer from doubly charged ions and the associated activation barrier, see Gronert [22]. The Spears and Fehsenfeld [12] experiments discussed in Sec. 3.1. are consistent with the presence of a significant barrier. These authors successfully used  $\text{CO}_2$  as intermediate clustering gas for the production of  $\text{Ca}(\text{H}_2\text{O})_n^{2+}$  with  $n \geq 1$ . Because  $\text{PA}(\text{CO}_2) = 129$  kcal/mol is much higher than  $\text{PA}(\text{CaOH}^+) =$

108 kcal/mol, deprotonation of the  $\text{Ca}(\text{H}_2\text{O})^+$  did not occur, only because of the presence of an activation barrier.

The  $\text{M}(\text{H}_2\text{O})_n^{2+}$  hydrates, with higher  $n$  are expected to have lower acidities, i.e. the hydrate hydroxides  $\text{M}(\text{H}_2\text{O})_n\text{OH}^+$  have higher proton affinities as discussed in Sec. 3.1. and illustrated in Table 2 for  $\text{Mg}(\text{H}_2\text{O})_n^{2+}$  on the basis of ab initio calculations. For much higher  $n$  hydrates, calculations of the corresponding proton affinities might not be practical. For these hydrates approximate basicities could be deter-

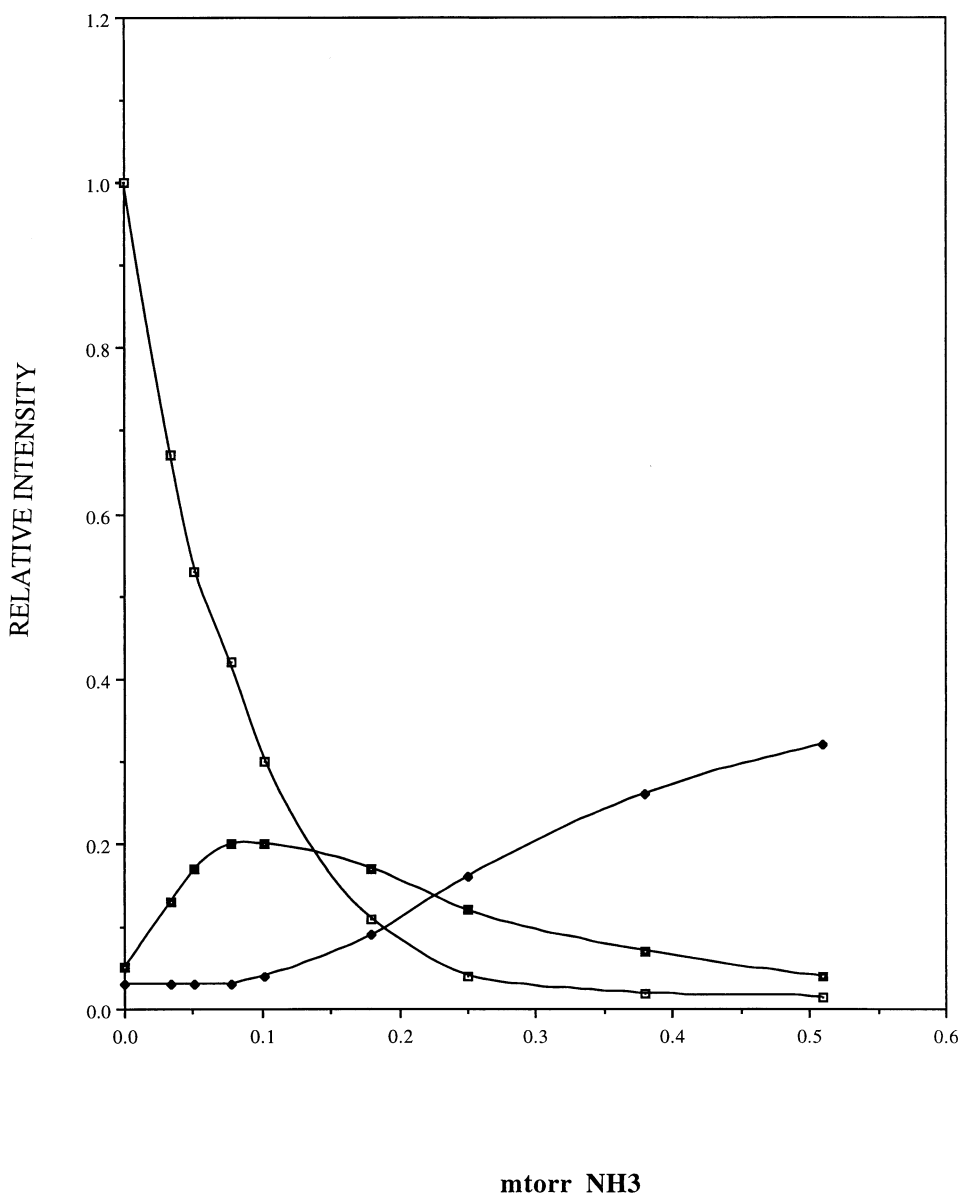


Fig. 7. Ion intensity changes observed when vapor of the base  $\text{NH}_3$  is added to the reaction chamber which contains  $\text{Zn}(\text{H}_2\text{O})_n^{2+}$  ions with  $n = 8, 9$  being the major species. Deprotonation of these ions by the base leads to  $\text{ZnOH}(\text{H}_2\text{O})_n^+$ . Exchange of the ligands  $\text{H}_2\text{O}$  for  $\text{NH}_3$  occurs at higher  $\text{NH}_3$  pressures. (Open square) Sum of major  $\text{Zn}(\text{H}_2\text{O})_n^{2+}$ ,  $n = 8, 9$ . (Filled square) Intensity of  $\text{ZnOH}(\text{H}_2\text{O})_4^+$ , one of the major  $\text{ZnOH}(\text{H}_2\text{O})_n^+$  ions. (Filled diamond) Intensity of  $\text{ZnOH}(\text{NH}_3)_3^+$  one of the major  $\text{ZnOH}(\text{NH}_3)_n^+$  ions. Mixed ligand ions  $\text{ZnOH}(\text{H}_2\text{O})_x(\text{NH}_3)_y^+$  were also observed but are not given in the figure.

mined experimentally by kinetic bracketing followed by corrections for the Coulombic barrier [22]. In exploratory work we exposed  $\text{Zn}(\text{H}_2\text{O})_n^{2+}$ , where  $n = 8, 9$  were the dominant hydrates, to  $\text{NH}_3$  reagent gas

in our reaction chamber. Representative ion intensities in function of  $\text{NH}_3$  pressure are shown in Fig. 7. The  $\text{Zn}(\text{H}_2\text{O})_n^{2+}$  ions are seen to be rapidly replaced by  $\text{ZnOH}(\text{H}_2\text{O})_n^+$ , with major ions at  $n = 4$ , which

shows that proton transfer to  $\text{NH}_3$  occurs. The  $\text{ZnOH}(\text{H}_2\text{O})_n^+$  ions are then replaced by  $\text{ZnOH}(\text{NH}_3)_n^+$  via ligand exchange reactions.

Very strong bases B might be able to charge reduce the product ion  $\text{MOH}^+$  of Eq. (7) to the neutral oxide MO. Calculated deprotonation energies  $\Delta H_f^\circ$  for  $\text{MOH}^+$  (M = Be, Mg, Ca, Zn) are given in Table 1.  $\text{BeOH}^+$  has the lowest deprotonation energy,  $\Delta H_f^\circ = 225$  kcal/mol. Because of the presence of a large barrier of more than 30 kcal/mol for the proton transfer reaction, only bases B with extremely high proton affinities,  $\text{PA}(\text{B}) > 260$  kcal/mol can be expected to achieve deprotonation.

As mentioned in the Introduction, charge reduction by proton transfer to a stronger base can have also a synthetic utility. Thus, the reactions already discussed



represent methods for obtaining the hydroxide ligand. Of special interest are reactions involving deprotonation of ligands other than water. For example, determinations of binding energies between metal ions and ligands which are analogs of amino acid residues can provide useful insights into metallo-enzyme ion-ligand thermochemistry [2]. In this connection it is desirable to prepare ion-ligand complexes with a variety of ligands including the methylthiolate negative ion  $\text{CH}_3\text{S}^-$ , which may be used to model the deprotonated cysteine residue. This residue is very often present in metallo-enzyme ion-ligand complexes of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and other  $\text{M}^{2+}$ . The method that can be envisaged, is to attach  $\text{CH}_3\text{SH}$  to the desired ion-ligand group and then deprotonate the methylthiol by a suitable base B. We have only very recently attempted such reactions, initially with  $\text{H}_2\text{S}$  rather than  $\text{CH}_3\text{SH}$ . We were able to deprotonate this ligand obtaining thus the  $\text{HS}^-$  ion complexed to  $\text{Zn}^{2+}$ . We hope soon to be able to report also the preparation of transition metal ions complexed to one or more methylthiolate ligands.

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