



Heavy water reactions with alkaline-earth metal dications in the gas phase: Kinetics at room temperature

Stefan Feil, Greg K. Koyanagi, Diethard K. Bohme*

Department of Chemistry, Centre for Research in Mass Spectrometry and Centre for Research in Earth and Space Science, York University, 4700 Keele Street, Toronto, Ontario, Canada M3J 1P3

ARTICLE INFO

Article history:

Received 12 May 2008

Received in revised form 15 July 2008

Accepted 23 July 2008

Available online 3 August 2008

Dedicated to Zdenek Herman on the occasion of his 75th birthday.

Keywords:

Alkaline-earth dication

Heavy water

Kinetics of reaction

Charge separation

Hydration

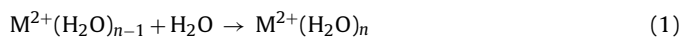
ABSTRACT

Room temperature rate coefficients and product distributions are reported for the reactions initiated in D₂O with dications of the alkaline-earth metals Mg, Ca, Sr and Ba. The measurements were performed with a selected-ion flow tube (SIFT) tandem mass spectrometer and electrospray ionization (ESI). Mg²⁺ reacts with water by a fast electron transfer leading to charge separation with a rate coefficient of $1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Ca²⁺ reacts with D₂O in a first step to form the adduct Ca²⁺(D₂O), with an effective bimolecular rate coefficient of $2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which then undergoes rapid charge separation by deuterium transfer to form CaOD⁺ and D₃O⁺ in a second step with $k = 7.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The CaOD⁺ ion reacts further by clustering up to five more D₂O molecules. Sr²⁺ clusters up to eight D₂O molecules and Ba²⁺ up to seven D₂O molecules, with the first addition of D₂O being rate determining in each case and the last addition being distinctly slower, as might be expected from a transition in the occupation of the added water molecules from an inner to an outer hydration shell.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

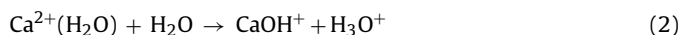
The thermodynamics of the gas-phase hydration of the alkaline earth metal dications Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ has been well characterized in the literature, both experimentally and theoretically. In 1998 Kebarle's group [1] determined the enthalpies, free energies, and entropies for the sequential hydration reaction (1) for M = Mg, Ca, Sr, and Ba, and $n = 6\text{--}14$, in the gas phase.



The ion hydrates in these experiments were produced by electrospray ionization, and hydration equilibrium constants were measured over a range of temperature in a reaction chamber attached to a mass spectrometer. An inflection was observed in the thermodynamic trends consistent with a transition between an inner and outer hydration shell. Also in 1998, Pavlov et al. [2] provided a thorough theoretical treatment of trends in binding energies for hydrates of Be²⁺, Mg²⁺ and Ca²⁺ with a view to the transition between the first and second hydration shells. Interest in the thermodynamics of hydration of the alkaline-earth dications is

ongoing. For example, just last year in 2007, Armentrout's group [3] applied guided-ion beam mass spectrometry and collision-induced dissociation (CID) to the measurement of the sequential bond energies in electrosprayed hydrates Ca²⁺(H₂O)_n with $n = 5\text{--}9$.

In contrast to hydration thermodynamics, the kinetics of hydration of these Group 2 dications has received much less attention and is poorly known. Early interests in ionospheric chemistry and fundamental aspects of the role of charge in termolecular association reactions prompted Spears and Fehsenfeld [4] to investigate the addition of H₂O to Ca²⁺ and Ba²⁺ in a flowing afterglow apparatus at 296 K. Double ionization of Ca and Ba was achieved by exposing the vapour of these two metals to 100 eV electrons. Termolecular rate coefficients of $\sim 5 \times 10^{-28}$ and $1.1 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ were reported for Ca²⁺ and Ba²⁺, respectively. Also, these authors reported the observation (without a rate coefficient measurement) of an unusual fast bimolecular "proton transfer" reaction of type (2) that leads to charge separation at near the collision rate and precludes the further hydration of Ca²⁺(H₂O).



Spears et al. also reported the observation of electron transfer from H₂O to Mg²⁺ but were not able to measure a rate coefficient for this process [5].

* Corresponding author. Tel.: +1 416 736 2100x66188; fax: +1 416 736 5936.
E-mail address: dkbohme@yorku.ca (D.K. Bohme).

Here we report the results of kinetic measurements of the reactions of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} produced by ESI with heavy water molecules and the higher-order chemistry initiated by these reactions at room temperature in a helium bath gas at 0.35 Torr (D_2O was chosen instead of H_2O in order to relax the resolution requirements in the downstream mass spectrometer).

The chosen sequence of Group 2 metal dications affords a systematic exploration of their reactivity with one water molecule and the role of the electron recombination energy in determining this reactivity. There has been a certain fascination expressed in the literature for the stability and possible formation of adducts of doubly charged atomic ions with one water molecule [6,7]. So it is of interest to see directly what happens in the interaction of M^{2+} with one D_2O molecule as $\text{IE}(\text{M}^+)$ drops systematically from a fairly high value of 15.0 eV for $\text{IE}(\text{Mg}^+)$ down the Group 2 elements to 10.0 eV for $\text{IE}(\text{Ba}^+)$. Furthermore, our recent systematic studies of the room temperature kinetics of reactions of D_2O with singly charged Group 2 cations [8] also allows a quantitative assessment of the role of charge state in reactions with the first water molecule.

2. Experimental

The experiments were performed with a multi-sector selected-ion flow tube tandem mass spectrometer fitted with an electrospray ion source, symbolized as ESI/qQ/SIFT/QqQ, developed in the Ion Chemistry Laboratory at York University [9,10].

Dications of Mg, Ca, Sr, and Ba were generated with ESI from 30 μM solutions of magnesium nitrate in water/methanol (80/20), calcium acetate in water/methanol (80/20), strontium acetate in water/methanol (80/20), and barium chloride in water/methanol (80/20). A declustering potential of 200 V was applied to remove the heavy water from the hydrated ions that emerge from the solution.

The bare dications emerging from the ESI source are mass selected and injected through a Venturi type aspirator into the flow tube that is flushed with helium at 0.35 ± 0.01 Torr. Before reaching the reaction region, the ions undergo multiple collisions with helium ($\sim 4 \times 10^5$) to ensure thermalization. The large number of collisions with the helium buffer gas atoms ensures that the atomic ions reach a translational temperature equal to the tube temperature of 292 ± 2 K prior to entering the reaction region. The ions are allowed to react with D_2O vapour added into the reaction region and then they are sampled along with product ions and analyzed in a triple quadrupole mass spectrometer. The reactant and product ion signals are monitored as a function of the flow of D_2O . The D_2O was introduced into the reaction region of the SIFT as a dilute mixture in helium ($\sim 2.5\%$) and obtained commercially with high purity (Aldrich, isotopic purity $>99.75\%$). Primary rate coefficients with an absolute accuracy estimated to be $\pm 30\%$ are determined from the observed semi-logarithmic decay of the primary reactant ion intensity in the usual manner using pseudo first order kinetics [11,12].

3. Results and discussion

3.1. Mg^{2+}

Mg^{2+} dications were difficult to produce in large quantities; signals were low and required a 2 min acquisition time per data point. Nevertheless the semi-logarithmic decay was observed to be linear for more than 1 decade with $k = 1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Fig. 1). The mass spectra at each flow were accumulated for more than 5 min and clearly demonstrated the occurrence of the electron transfer reaction (3) that leads to charge separation.

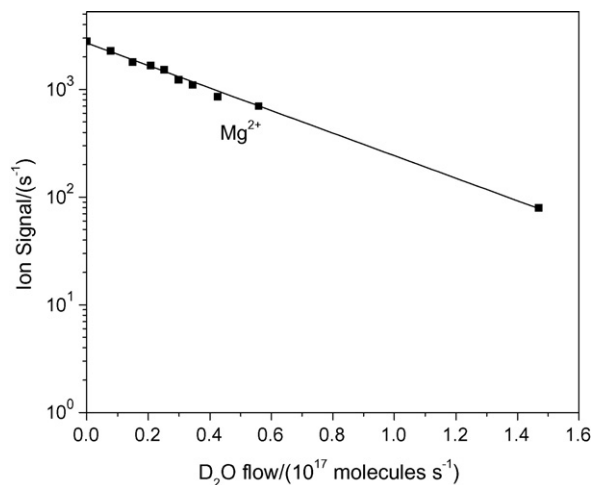


Fig. 1. The Mg^{2+} ion profile measured for the reaction with D_2O . The ion signal was acquired for 2 min per data point. $P_{\text{He}} = 0.35$ Torr and $T = 292$ K.

Reaction (3) is quite exothermic since $\text{IE}(\text{Mg}^+) = 15.0 \text{ eV} \gg \text{IE}(\text{D}_2\text{O}) = 12.6 \text{ eV}$ [11]. The analogous reactions with Ca^{2+} ($\text{IE}(\text{Ca}^+) = 11.9 \text{ eV}$), Sr^{2+} ($\text{IE}(\text{Sr}^+) = 11.0 \text{ eV}$) and Ba^{2+} ($\text{IE}(\text{Ba}^+) = 10.0 \text{ eV}$) [13], all of which have $\text{IE}(\text{M}^+) < \text{IE}(\text{D}_2\text{O})$, are endothermic. Mg^{2+} reacts further with D_2O to produce MgOD^+ and the well-known secondary formation of D_3O^+ from D_2O^+ and then $\text{D}_3\text{O}^+(\text{D}_2\text{O})$ by addition of D_2O also was recorded. The occurrence of reaction (3) has been reported previously by Spears et al. [5], but a rate coefficient was not. Our measurement of $k = 1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ indicates that the electron is transferred from D_2O to Mg^{2+} in about 1 out of 4 collisions. A collision or capture rate coefficient of $5.52 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ can be computed using the algorithm of the modified variational transition-state classical trajectory theory developed by Su and Chesnavich [14] with $\alpha(\text{D}_2\text{O}) = 1.26 \times 10^{-24} \text{ cm}^3$ [15] and $\mu_{\text{D}}(\text{D}_2\text{O}) = 1.8545 \text{ D}$ [16].

3.2. Ca^{2+}

In the case of Ca^{2+} we saw the formation of a first cluster of the dication with one water molecule according to reaction (4), with an effective bimolecular rate coefficient of $2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, followed by a fast “deuteron transfer”, charge separation reaction with the formation of the singly charged hydroxide CaOD^+ and D_3O^+ according to reaction (2) with $k = 7.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Fig. 2).



Our value for k_4 is slightly lower than the value of $\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ that can be deduced from the very approximate termolecular rate coefficient of $\sim 5 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ reported by Spears and Fehsenfeld for similar experimental conditions (He third body, $T = 296 \text{ K}$) [4].

Our high value for k_2 is consistent with the result of Spears and Fehsenfeld [4] who indicated a rate for this reaction close to the collision rate (but did not measure k_2). Direct formation of CaOD^+ by charge separation according to reaction (5) is energetically unfavourable; reaction (5) is endothermic by 51 kcal mol^{-1} . Reaction (2) is thermodynamically more favourable by $\text{PA}(\text{H}_2\text{O}) - \text{D}(\text{Ca}^{2+} - \text{H}_2\text{O}) = 166$ [17] $- 60$ [2] or $106 \text{ kcal mol}^{-1}$ and so is exothermic by 55 kcal mol^{-1} .



Also, for Sr and Ba the increase in $\text{D}(\text{M}^+ - \text{OH})$ [8] is offset by the decrease in $\text{RE}(\text{M}^+)$ and reaction (5) will remain endothermic and

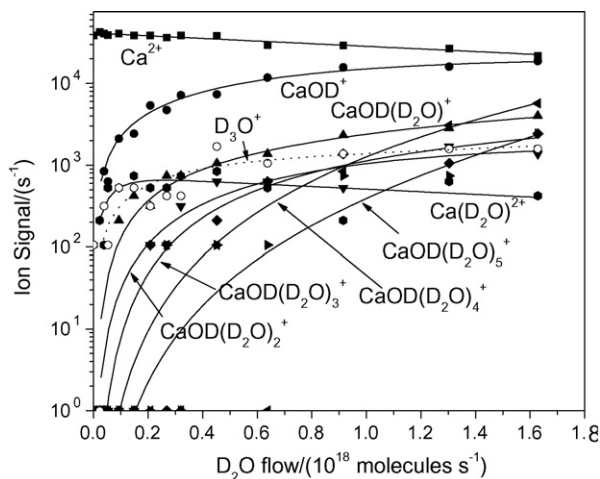
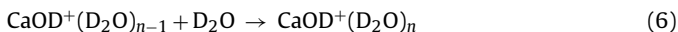


Fig. 2. Ion signals recorded for the reaction of selected Ca^{2+} cations derived by ESI with added heavy water vapour. $P_{\text{He}} = 0.35$ Torr and $T = 292$ K.

may stay so with increasing hydration or become insufficiently exothermic to overcome the Coulombic barrier associated with charge separation.

The CaOD^+ formed in reaction (5) reacts further by the sequential addition of at least five water molecules according to reaction (6).



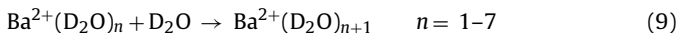
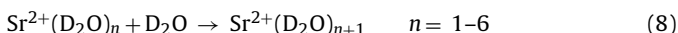
Interesting to note is that the attachment of the first D_2O to doubly charged Ca^{2+} is about $10\times$ faster than the attachment to the singly charged Ca^+ , reaction (7), under similar experimental conditions, for which we recently have reported an effective bimolecular rate coefficient $k = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8]. Formation of $\text{CaOD}^+ + \text{D}$ in reaction (7) is endothermic by $18.5 \text{ kcal mol}^{-1}$.



Of further interest is that our effective bimolecular rate coefficient for reaction (7) with D_2O is significantly larger than the value of $0.47 \pm 0.58 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported very recently by Broadley et al. [18] at 301 K and 1.2 Torr He. This apparently large isotope effect is in line with expectations based on, for example, the isotope effect observed by Mitchell for the low-pressure association of Ni and C_2H_4 (C_2D_4) [19]. The latter was attributed to the higher density of vibrational states of the deuterated intermediate adduct (with lower vibrational frequencies) and so a longer lifetime (and thus probability of stabilization). The magnitude of the isotope effect also was predicted to depend on the binding energy of the adduct that is formed.

3.3. Sr^{2+} and Ba^{2+}

No charge separation reactions were observed in the D_2O chemistry initiated by Sr^{2+} and Ba^{2+} . Both systems are characterized by a slow first addition of D_2O followed by faster higher-order additions according to reactions (8) and (9).



The increase in the rate of hydration is evidenced by the lower intensity rate-limited ion profiles for $\text{M}^{2+}(\text{D}_2\text{O})_{2-5}$ in Figs. 3 and 4. The effective bimolecular rate coefficient for the addition of the first D_2O to Sr^{2+} was immeasurably small, $k_{\text{obs}} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and that for Ba^{2+} was only $6.7 \times 10^{-12} \text{ cm}^3$

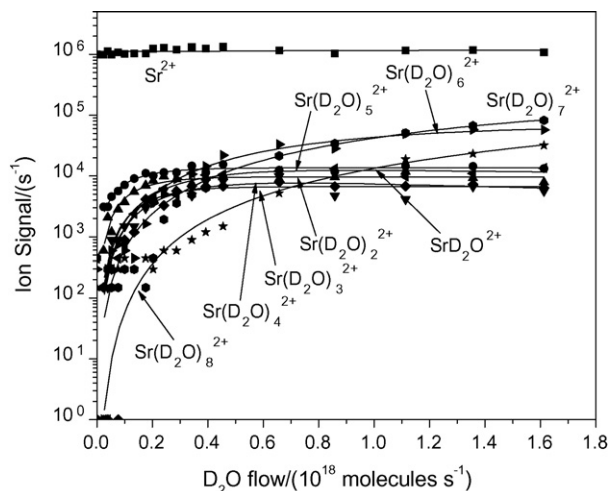


Fig. 3. Ion signals recorded for the reaction of selected Sr^{2+} cations derived by ESI with added heavy water vapour. $P_{\text{He}} = 0.35$ Torr and $T = 292$ K.

$\text{molecule}^{-1} \text{ s}^{-1}$. We are not aware of a previous observation of the reaction of Sr^{2+} with water. Our value for k_0 (for reaction (9) with $n=0$) is somewhat lower than the value of $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ that can be deduced from the termolecular rate coefficient of $1.1 \times 10^{-28} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ reported by Spears and Fehsenfeld for similar experimental conditions (He third body, $T = 296$ K) [4].

The increased rate of addition of the second D_2O molecule is expected from the increased lifetime of the intermediate that is anticipated from the substantial fractional increase in the number of degrees of freedom. This fractional increase decreases with higher additions of D_2O and is compensated by a systematic decrease in the binding energy of the added water molecule with increasing numbers of water molecules.

The data in Figs. 3 and 4 also exhibit interesting discontinuities in the kinetics of hydration as manifested by a substantial change in the rate of rise in the hydrated ion signal. Thus the rate of rise in $\text{Sr}^{2+}(\text{D}_2\text{O})_8$ and in $\text{Ba}^{2+}(\text{D}_2\text{O})_7$ with the flow of D_2O appears much slower than the rate of rise in their immediate precursors. Such a transition in the rate of addition is expected from a sudden decrease in stability, viz. the enthalpy of hydration. Such discontinuities in thermodynamics have been reported for $\Delta(\Delta G^\circ)$, $\Delta(\Delta H^\circ)$ and

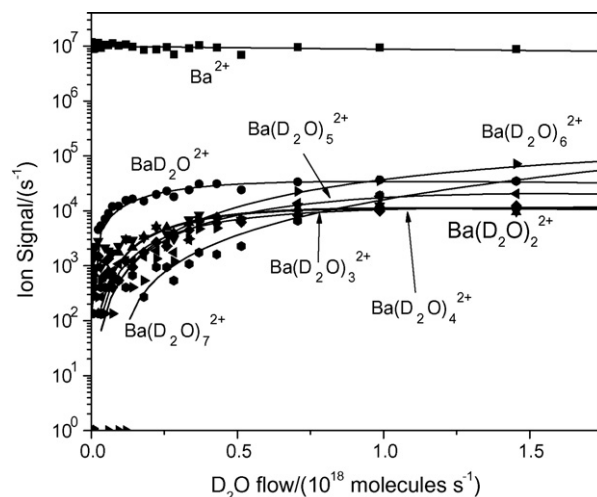


Fig. 4. Ion signals recorded for the reaction of selected Ba^{2+} cations derived by ESI with added heavy water vapour. $P_{\text{He}} = 0.35$ Torr and $T = 292$ K.

Table 1

Rate coefficients and ion products for reactions of alkaline-earth metal dications and some higher-order dications with D₂O proceeding in He at 0.35 Torr and 292 ± 2 K

Ion	RE (eV ^a)	Products	k ^b	Higher-order products
Mg ²⁺	15.0	Mg ⁺ + D ₂ O ⁺	1.4 × 10 ⁻⁹	MgOD ⁺ , D ₃ O ⁺
Ca ²⁺	11.9	Ca ²⁺ (D ₂ O)	2.3 × 10 ⁻¹¹	
Ca ²⁺ (D ₂ O)		CaOD ⁺ + D ₃ O ⁺	7.9 × 10 ⁻¹⁰	CaOD ⁺ (D ₂ O) _{1–5}
Sr ²⁺	11.0	Sr ²⁺ (D ₂ O)	<1 × 10 ⁻¹³	Sr ²⁺ (D ₂ O) _{1–6}
Ba ²⁺	10.0	Ba ²⁺ (D ₂ O)	6.7 × 10 ⁻¹²	Ba ²⁺ (D ₂ O) _{1–7}
Sr ²⁺ (D ₂ O)		Sr ²⁺ (D ₂ O) ₂	≥ × 10 ⁻¹⁰	
Sr ²⁺ (D ₂ O) ₂		Sr ²⁺ (D ₂ O) ₃	≥ × 10 ⁻¹⁰	
Ba ²⁺ (D ₂ O)		Ba ²⁺ (D ₂ O) ₂	≥ × 10 ⁻¹⁰	
Ba ²⁺ (D ₂ O) ₂		Ba ²⁺ (D ₂ O) ₃	≥ × 10 ⁻¹⁰	

^a RE = electron recombination energy taken from Ref. [13]. IE(D₂O) = 12.6 eV.

^b Effective bimolecular reaction rate coefficient measured in helium at 0.35 Torr and 292 K. The uncertainties are estimated to be 30% for the primary reactions and 50% for the higher-order reactions. Ions were generated by electrospray ionization (ESI).

Δ(ΔS^o), all for hydration at 298 K. The changes become small after 7 additions of D₂O for Sr²⁺ and after 6 for Ba²⁺ [1] as a new (outer) shell of hydration begins to become occupied. Quite remarkably, the results in Figs. 3 and 4 also show a break in the kinetics of hydration after 7 in the case of Sr²⁺ and possibly 6 in the case of Ba²⁺, judging from the slower rise in the formation of Sr²⁺(D₂O)₈ and Ba²⁺(D₂O)₇, respectively. Even higher clusters were observed at still higher flows of D₂O, but only in trace amounts and so apparently these are of lower stability.

The comparison with the reactions of the singly charged alkaline-earth cations with D₂O is again interesting. Our previous measurements taken under similar operating conditions [8] have shown that the reaction of Sr⁺ exhibits a bimolecular channel forming SrOD⁺ + D as well as an addition channel that makes Sr⁺(D₂O) in a 1:1 ratio ($k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) while Ba⁺ forms exclusively BaOD⁺ at the same rate. So curiously, hydroxide formation is increasingly favoured in the reactions with singly charged alkaline-earth cations with increasing mass while the opposite is true for the reaction of the doubly charged dications with D₂O (in which the accompanying production of deuterium atomic ions makes the production of the hydroxide cations endothermic).

4. Conclusions

We have shown that ESI is useful for the generation of atomic alkaline-earth dications and effective in the measurement of the kinetics of their reactions with heavy water molecules when coupled to our flow-tube mass spectrometer. The kinetics of the

interaction of these cations with a single water molecule has been quantified and are summarized in Table 1. The results of the measurements indicate that the hydration of alkaline-earth dications is pre-empted by electron transfer when IE(M⁺) > IE(H₂O). This is the case for Mg²⁺ and likely also for Be²⁺. Also, although delayed by one molecule, hydration of Ca²⁺ is pre-empted by hydroxide formation according to reaction (2). The trend in the ΔH of reaction (2) for the Group 2 dications will follow trends in IE(M⁺) and D(M⁺–OH) and will favour high values of both. So the experiments indicate that ΔH changes sign between M = Ca (for which it is negative) and M = Sr. A remarkable break occurs in the kinetics of sequential hydration of Sr²⁺ and Ba²⁺ (after 7 in the case of Sr²⁺ and possibly 6 in the case of Ba²⁺) that is consistent with a similar break previously established by others in the thermodynamic of hydration.

Acknowledgments

Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatly appreciated. Also, we acknowledge support from the National Research Council, the Natural Science and Engineering Research Council and MDS SCIEX in the form of a Research Partnership grant. As holder of a Canada Research Chair in Physical Chemistry, Diethard K. Bohme thanks the contributions of the Canada Research Chair Program to this research.

References

- [1] M. Peschke, A.T. Blades, P. Kebarle, J. Phys. Chem. A 102 (1998) 9978.
- [2] M. Pavlov, P.E.M. Siegbahn, M. Sandström, J. Phys. Chem. A 102 (1998) 219.
- [3] D.R. Carl, R.M. Moision, P.B. Armentrout, Int. J. Mass Spectrom. 265 (2007) 308.
- [4] K.G. Spears, F.C. Fehsenfeld, J. Chem. Phys. 56 (1972) 5698.
- [5] K.G. Spears, F.C. Fehsenfeld, M. McFarland, E.E. Ferguson, J. Chem. Phys. 56 (1972) 2562.
- [6] A.A. Shvartsburg, K.W.M. Siu, J. Am. Chem. Soc. 123 (2001) 10071.
- [7] T. Shi, G. Orlova, J. Guo, D.K. Bohme, A.C. Hopkinson, K.W.M. Siu, J. Am. Chem. Soc. 126 (2004) 7975.
- [8] P. Cheng, G.K. Koyanagi, D.K. Bohme, J. Phys. Chem. A 111 (2007) 8561.
- [9] G.K. Koyanagi, V.I. Baranov, S.D. Tanner, J. Anichina, M.J.Y. Jarvis, S. Feil, D.K. Bohme, Int. J. Mass Spectrom. 265 (2007) 295.
- [10] S. Feil, G.K. Koyanagi, A.A. Viggiano, D.K. Bohme, J. Phys. Chem. A 111 (2007) 13397.
- [11] G.I. Mackay, G.D. Vlachos, D.K. Bohme, H.I. Schiff, Int. J. Mass Spectrom. Ion Phys. 36 (1980) 259.
- [12] A.B. Raksit, D.K. Bohme, Int. J. Mass Spectrom. Ion Process. 55 (1983/1984) 69.
- [13] NIST data base: <http://webbook.nist.gov/chemistry>.
- [14] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
- [15] A.A. Maryott, F. Buckley, Natl. Bu. Stand. Circ. (U.S.) (1953) 29.
- [16] T.R. Dyke, J.S. Muentzer, J. Chem. Phys. 59 (1973) 3125.
- [17] S.G. Lias, J.F. Liebman, R.D. Levin, J. Phys. Chem. Ref. Data 13 (1984) 695.
- [18] S.L. Broadley, T. Vondrak, M.C. Plane, Phys. Chem. Chem. Phys. 9 (2007) 4357.
- [19] S.A. Mitchell, Int. J. Chem. Kin. 26 (1994) 97.