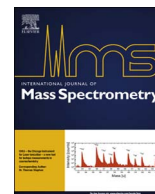




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Second-shell thermochemistry for hydration of strontium dications as determined by threshold collision-induced dissociation and computations[☆]

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ABSTRACT

This work reports a continuation of the guided ion beam tandem mass spectrometer (GIBMS) study of the threshold collision-induced dissociation of $\text{Sr}^{2+}(\text{H}_2\text{O})_x$. The present study measures 0 K hydration energies for $\text{Sr}^{2+}(\text{H}_2\text{O})_x$, where $x = 7-9$, which can be added to those previously measured for $x = 1-6$. The full range of these complexes is also examined theoretically employing B3LYP/SDD/def2-TZVP and B3LYP/DHF/def2-TZVPP geometry optimizations with additional B3LYP, B3P86, M06, and MP2(full) single point energy calculations performed with the larger SDD/def2-TZVPP and DHF/def2-TZVPP basis sets, respectively. The transition between first and second hydration shells is explored from both experimental and theoretical findings. Neither experimental nor theoretical results are completely consistent with a single coordination number for the first hydration shell at 298 K, but rather suggest mixed coordination numbers ranging from 6 to 8 water molecules.

1. Introduction

The delivery of metal cations to active biological sites as well as the removal of excess metals from aquifers makes the hydration of metal cations important both biologically and environmentally. The hydration of alkaline earth metals has been of interest and investigated experimentally a number of times over the last 35 years [1–18]. These works report fundamental thermochemistry as well as structural information for alkaline earth metal hydration. Such information is potentially useful in understanding details of the delivery of these metals to various biological binding sites, which must involve transfer through aqueous media followed by stripping the ligand shell away. One example involving the metal studied here is metal exchange in the skeletal structure, composed primarily of Ca. The radioactive ⁸⁹Sr isotope can replace the Ca and be directly incorporated into target sites of increased osteogenesis to help destroy cancerous cells [19]. A beneficial side effect of this replacement was bone pain reduction during incorporation of ⁸⁹Sr [19].

In the literature, a high pressure mass spectrometry (HPMS) study reported dissociation enthalpies, free energies, and entropies for water loss from $\text{M}^{2+}(\text{H}_2\text{O})_x$, where $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{and Ba}$, each with $x = 6-13$ or 14 [2,5]. These authors explicitly considered the size of the first hydration shell (commonly defined in terms of the coordination number, CN), the number of water molecules that bind directly to the

central metal atom. Results were consistent with a CN = 6 for Mg^{2+} and Ca^{2+} , and were less conclusive for Sr^{2+} and Ba^{2+} with CNs ≥ 6 suggested. For $\text{Ba}^{2+}(\text{H}_2\text{O})_x$, CNs of 8 or 9 were suggested on the basis of experimental results. For $\text{Sr}^{2+}(\text{H}_2\text{O})_x$, where $x = 6-13$, CNs of 6 and possibly 7 were reported, and it was concluded that a CN of 8 was unlikely on the basis of sequential entropy measurements [5].

Three studies from the Williams group are relevant to the current work. The first used blackbody infrared radiative dissociation (BIRD) to examine $\text{Sr}^{2+}(\text{H}_2\text{O})_x$, where $x = 5-7$ [7]. The BIRD kinetic data show that the $\text{Sr}^{2+}(\text{H}_2\text{O})_{5-7}$ complexes have behavior between $\text{Ca}^{2+}(\text{H}_2\text{O})_{5-7}$ and $\text{Ba}^{2+}(\text{H}_2\text{O})_{5-7}$ with $\text{Mg}^{2+}(\text{H}_2\text{O})_{5-7}$ showing different behavior because there is a mixing of 6 and 5-coordinate isomers predicted for the $\text{Mg}^{2+}(\text{H}_2\text{O})_6$ complex. The second study examined the transition between first and second hydration shells with action spectroscopy by investigating the $\text{Mg}^{2+}(\text{H}_2\text{O})_x$, $\text{Ca}^{2+}(\text{H}_2\text{O})_x$, and $\text{Ba}^{2+}(\text{H}_2\text{O})_x$ alkaline earth metal systems, but $\text{Sr}^{2+}(\text{H}_2\text{O})_x$ was not included [14]. The action spectroscopy results were consistent with the formation of a second shell directly related to the atomic radius of the metal. Results showed that hydrated Mg^{2+} and Ca^{2+} have a CN = 6, whereas the results for $\text{Ba}^{2+}(\text{H}_2\text{O})_x$ were more ambiguous, with CN = 6–8 possible. The final study of interest used action spectroscopy to investigate $\text{Ca}^{2+}(\text{H}_2\text{O})_x$ water complexes, where $x = 9-69$ [13]. Results were consistent with CN = 6 for $x = 6-9$; however, for larger complexes, spectral features were consistent with a mixture of CNs for $x = 10$ and 11 and at $x \geq 12$,

[☆] In honor of Terry McMahon and in thanks for his many notable contributions to ion thermodynamics and ion chemistry.

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the systems clearly shifted to CN = 8. In solution, X-ray absorption fine structure (EXAFS) [3,4,9], X-ray diffraction (XRD) [1], and anomalous X-ray diffraction (AXD) [11] studies of Sr^{2+} hydration have found CN values ranging from 7.3 to 10.3, although most values seem localized around CN = 8.

Theoretical calculations in the literature for larger $\text{Sr}^{2+}(\text{H}_2\text{O})_x$ complexes ($x > 6$) are sparse with Kerridge and Kaltsoyannis (KK) investigating $x = 2-8$ and 24 [20] and Boda et al. having studied $x = 1-13$, 16, and 24 [21]. In the former work, a CN = 6 was found for $x = 6-8$, whereas the latter work determined CN = 6 for $x = 6, 7$, and 9 water complexes, but $x = 8$ and 11–24 favored CN = 8. A potential oversight of these works was the failure to investigate any structures with CN = 5 by KK and CN = 7 by Boda et al.

Included among previous experimental and theoretical studies of the alkaline earth metal dications are guided ion beam tandem mass spectrometry (GIBMS) studies of the thermochemistry and structures of the $\text{M}^{2+}(\text{H}_2\text{O})_x$ water complexes where $\text{M} = \text{Mg}$ ($x = 2-10$) [17], Ca ($x = 1-9$) [12,16], Sr ($x = 1-6$) [15], and Ba ($x = 1-8$) [18]. Results for the 0 K bond dissociation energies (BDEs) follow the expected trend of decreasing BDEs as the atomic radii increase and as x increases. An interesting finding in the Ba study was that at thermal energies the $\text{Ba}^{2+}(\text{H}_2\text{O})_8$ water complex showed evidence for multiple isomer populations with CNs = 6–8 at 298 K. This range of CNs is quite different compared to that deduced for $\text{Ca}^{2+}(\text{H}_2\text{O})_x$ GIBMS studies [12,16], where the CN is clearly 6 water molecules on the basis of trends in the BDEs. For both of these systems, the ionic radii of the atoms, $\text{Ca}^{2+} = 1.05 \text{ \AA}$ and $\text{Ba}^{2+} = 1.38 \text{ \AA}$ [22], should play a strong role in determining the CN, with larger atomic radii leading to less steric hindrance among first shell water molecules. Sr^{2+} has an ionic radius of 1.18 Å placing it between Ca^{2+} and Ba^{2+} [22], such that its CN would be somewhere between these two alkaline earth metals. Whether it is more similar to Ca^{2+} or Ba^{2+} remains an interesting question.

$\text{Sr}^{2+}(\text{H}_2\text{O})_x$ complexes, where $x = 1-6$, have been previously studied by GIBMS as reported by Carl et al. [15] An electrospray ionization source (ESI) was utilized to form cluster sizes of $x = 6-9$, with an in-source fragmentation technique used to produce smaller water complex sizes [23]. Results for experimental BDEs agreed well with both experimental [2,5,7] and theoretical [24–28] values from literature; however, there is limited overlap with the other experimental techniques. The equilibrium measurements from HPMS studies [5] only overlap for the $x = 6$ water complex, while BIRD experimental results [7] overlap for $x = 5$ and 6.

In the present work, $\text{Sr}^{2+}(\text{H}_2\text{O})_{7-9}$ complexes are investigated using GIBMS techniques with both 0 and 298 K hydration enthalpies reported for these larger complexes. This expands upon the previous $\text{Sr}^{2+}(\text{H}_2\text{O})_{1-6}$ work [15], thereby improving the overlap between GIBMS experimental $\text{Sr}^{2+}(\text{H}_2\text{O})_x$ enthalpy values and those of HPMS [5] and BIRD [7]. Additionally, a thorough theoretical examination of low-lying isomers for $x = 5-9$ water complexes is conducted here with a larger number of isomers and increased range of CNs considered than in previous literature work [20,21]. The most stable geometries are explored for first and second shell hydration utilizing single point energies from four different levels of theory with two basis sets. Combining the experimental and theoretical information allows CNs for the first solvent shell to be evaluated.

2. Experimental and computational methods

2.1. Experimental methods

Threshold collision-induced dissociation (TCID) cross sections for the reaction of $\text{Sr}^{2+}(\text{H}_2\text{O})_x$ with Xe were measured with a GIBMS, well described in the literature [39,30]. Data collection pertaining to the current study was done in parallel to that of the previously published $\text{Sr}^{2+}(\text{H}_2\text{O})_{1-6}$ TCID paper under similar ESI source conditions [15]. Reactant ions entered the instrument through an inlet cap, offset by

~2 kV from the ESI needle, and a heated capillary (80 °C) and were passed into an ion funnel. The ion funnel was an 88-plate radio frequency (rf) ion funnel that collected and focused the reactant ions [31–33]. After passing through the ion funnel, ions entered a rf-only hexapole where thermalizing collisions ($> 10^4$) with ambient gas took place. The internal energy of the reactants can be characterized with a Maxwell-Boltzmann distribution at 300 K, as shown in past work [15,23,33–38]. The hexapole allowed transfer to a lower-pressure chamber where ions were extracted and focused into a magnetic momentum analyzer for reactant ion selection.

Reactant ions were then decelerated to a well-defined kinetic energy after which they entered an rf octopole ion guide [39,40]. The octopole passed through a collision cell that contained a controlled amount of Xe gas under near single collision conditions. Xe was used because of its efficient translational to internal energy transfer properties, as detailed elsewhere [41,42]. Upon exiting the octopole, reactant and product ions were passed through a quadrupole mass filter for mass analysis. Ion intensities were measured by a Daly detector capable of single ion counting [43].

Conversion of ion intensities to absolute cross sections is described elsewhere [30], with absolute uncertainties at 20%. Acceleration of ions in the octopole region occurs on the basis of the laboratory voltage, V_{Lab} , which is the dc bias between the source hexapole and the octopole. The doubly charged nature of the reactant ions means that the ion kinetic energy is $E_{\text{Lab}} = 2 \times V_{\text{Lab}}$. The energy available for reaction was found by converting E_{Lab} to the center-of-mass (CM) frame, $E_{\text{CM}} = E_{\text{Lab}} \times m/(m + M)$, where m and M represent the masses of the neutral collision gas and ionic reactant, respectively. The absolute zero of energy was measured using a retarding potential on the octopole [30], with the derivative of the transmission curve describing the kinetic energy distribution. Fitting the curve with a Gaussian distribution reveals a full width at half-maximum (FWHM) ranging from 0.10–0.15 eV, with uncertainties in the absolute zero estimated at 0.05 eV (V_{Lab}). Energies reported below are in the CM frame unless otherwise noted.

2.2. Thermochemical analysis

The kinetic energy dependence of the reaction cross sections for $\text{Sr}^{2+}(\text{H}_2\text{O})_{7-9}$ were modeled by an empirical threshold model, Eq. (1).

$$\sigma(E) = \left(\frac{n\sigma_0}{E} \right) \sum_i g_i \int_{E_0-E_i}^E P_{D1}(E - \epsilon)^{n-1} d\epsilon \quad (1)$$

Here, the magnitude of the cross section is controlled by the energy-independent scaling parameter σ_0 , the relative translational energy of the reactants is given by E , and n is an adjustable fitting parameter that describes the efficiency of energy transfer during the collision [31]. The 0 K reaction threshold is given by E_0 and the summation is over the rovibrational states of the reactant ions with excitation energies, E_i , and populations, g_i , where $\sum g_i = 1$. Molecular parameters for vibrational frequencies and rotational constants are taken from quantum chemical calculations, discussed below. Evaluation of the internal energy distribution at 300 K is performed with the Beyer-Swinehart-Stein-Rabinovich algorithm [35–38]. The energy deposited into the reactant upon collision with Xe is represented by ϵ such that the internal energy of the energized molecule (EM) is $E^* = \epsilon + E_i$. Eq. (1) accounts for lifetime effects in the dissociation [44] by including $P_{D1} = 1 - \exp[-k(E^*)\tau]$, the dissociation probability where τ is the time scale of the experiment ($\tau \approx 5 \times 10^{-4}$ s) and the RRKM unimolecular dissociation rate coefficient [38,45,46] is given by Eq. (2).

$$k(E^*) = sN_{vr}^{\ddagger}(E^* - E_0)/h\rho_{vr}(E^*) \quad (2)$$

Here, the reaction degeneracy, s , was calculated from the ratio of the rotational symmetry numbers of reactants and products, $N_{vr}^{\ddagger}(E^* - E_0)$ is the sum of rovibrational states of the transition state (TS) at an energy

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