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An ab Initio Investigation of Lithium Ion Hydration

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The structures, frequencies, and interaction energies of small lithium–water clusters, $\text{Li}(\text{H}_2\text{O})_n^+$, $n = 1-4$, were calculated by ab initio Hartree–Fock theory with small- and medium-sized basis sets (STO-3G, 3-21G, 6-31G*, 6-31G**, 6-31+G*, 6-31+G*(5d), 6-311G*). The interaction energies were corrected for basis set superposition error (BSSE) by Mayer's CHA/CE formalism. The CHA/CE/6-31+G**/HF/6-31+G* level gives an excellent description of the binding energy. The geometry and symmetric stretch frequency for $\text{Li}(\text{H}_2\text{O})_4^+$ of 248 cm^{-1} (255 cm^{-1} expt) are well described at the HF/6-31G* level. The choice of partition of the supermolecule was demonstrated to be of minor importance ($\pm 4\text{ kJ/mol}$). The binding energies were rationalized on crowding around the ion and a weakening Li–O interaction. The first ab initio calculation (STO-3G, 3-21G, 6-31G*, 6-31+G*) of a full second-solvation sphere of a metal cation is presented ($[\text{Li}(\text{H}_2\text{O})_4^+](\text{H}_2\text{O})_n$, $n = 4, 8$). The second solvation sphere of four waters raises the frequency of the Li–O vibration by 18 cm^{-1} (7%).

Introduction

Much effort has been spent in determining the hydration number of lithium cation in aqueous solution. Many different structural,^{1–6} physicochemical,^{7–12} and theoretical^{13–19} methods have been used to probe the structure and energetics of the hydrated ion. Whereas the main aim of our first study¹² was focused on determining the number of waters in the first hydration sphere, in this work our main concern is to clarify the role of the second hydration sphere on the spectroscopic behavior, in particular, the frequency of Li–O and O–H stretching and bending modes of aqueous lithium solutions.

Previous studies of the hydration of lithium ion^{13,14} have focused on the smaller $\text{Li}(\text{H}_2\text{O})_n^+$ clusters, with $n = 1-6$. The ab initio data were used to determine the gas-phase binding enthalpies of these clusters with respect to the ion and waters at infinite separation (the total binding energy) from which the incremental binding energies were determined. Both very large and moderately sized basis sets (6-31+G*) gave good agreement with the experimental mass spectrometric results. The aims of these papers were to derive converged values for the geometries and binding energies of these small clusters¹³ and to calibrate the HF/6-31+G* and MP2/6-31+G* methods for describing more complicated systems such as crown ethers.¹⁴ The lowest energy structures suggest that the hydration number of lithium in aqueous solution is four, since larger clusters with $n = 5, 6$ favored the additional waters in the second solvation shell. This is confirmed by our recent Raman and ab initio work, where we demonstrated unequivocally that the hydration number of lithium ion in dilute aqueous solution is indeed four.¹²

The experimental binding enthalpy for the lithium ion–water system may be regarded as a large electronic binding energy with smaller corrections for thermal and zero-point energy effects. Since these corrections have already been calculated by others,¹⁴ only the uncorrected results will be compared to demonstrate their validity. The electronic binding energy may be regarded as the sum of an interaction energy and a deformation energy. The interaction energy can be defined as

$$E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$$

where E_{int} is the interaction energy, E_{AB} is the total energy of the supermolecule, and E_{A} and E_{B} are the total energies of monomers A and B, respectively, at the supermolecule geometry. The deformation energy of a monomer is the amount of energy required to distort the monomer into its supermolecule geometry.

Any ab initio study of processes involving the thermodynamics of complex formation must address the problem of basis set superposition error (BSSE). BSSE results from the incompleteness of the basis set chosen to describe the system and generally results in the overestimation of the stability of the supermolecule. Mayer's chemical Hamiltonian approach with conventional energy (CHA/CE) formalism²¹ was chosen to address this problem, since this approach is both rigorous and practical and compares favorably with the Boys–Bernardi counterpoise correction scheme for neutral species.²² This is the first application of the CHA to a positively charged system.

With most BSSE correction schemes the supermolecule is partitioned into two fragments. For cases with more than two fragments the partitioning scheme is no longer unique. The study of the interaction energies pertinent to $\text{Li}(\text{H}_2\text{O})_n^+$ could be approached as a total solvation energy, which would suggest a $\text{Li}^+-(\text{H}_2\text{O})_n$ partition. Alternatively, the incremental solvation energies could be studied, for which a $\text{H}_2\text{O}-\text{Li}(\text{H}_2\text{O})_{n-1}^+$ partition is suggested. Therefore both schemes were used to correct for BSSE and then compared. Ideally, the supermolecule would be partitioned into as many subunits as there are fragments. The CHA method has recently been generalized to deal with this.²³

The remainder of the paper is organized as follows. First, the methods used to investigate this system are presented. Second, the results of our study of the first hydration sphere are presented, since any further description of the system requires this to be accurate. Finally, the study of the second solvation sphere is presented.

Method

Calculations were performed using the MUNGAUSS²⁴ program with a modified version²⁵ of the CHA routine.²⁶ The SCF interaction energies were computed with the STO-3G,²⁷ 3-21G,²⁸

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TABLE 1: Li–O Bond Lengths (Å)

Li(H ₂ O) _n , <i>n</i> = point group	<i>n</i>			
	1 <i>C</i> _{2v}	2 <i>D</i> _{2d}	3 <i>D</i> ₃	4 <i>S</i> ₄
6-31G*	1.8579	1.8841	1.9190	1.9715
6-31G**	1.8551	1.8788	1.9167	1.9701
6-311G*	1.8326	1.8601	1.8955	1.9495
6-31+G*	1.8502	1.8782	1.9156	1.9683
6-31+G*(5d)	1.8517	1.8767	1.9167	1.9700
expt ⁶				1.96 ± 0.02
Li–O Sym Stretch (cm ^{−1})				
6-31G*	564.4	292.1	272.1	248.0
expt ¹²				255

6-31G*,^{29–32} 6-31G**, 6-31+G*(5d), 6-31+G*,^{33,34} and 6-311G*³⁵ basis sets (the 6-31+G*(5d) basis set is equivalent to 6-31+G*, except for the use of a five-term pure d-function set of polarization functions as opposed to the conventional six-term Cartesian set). The CHA calculations were performed at the SCF geometries, which were optimized with the variable-metric gradient OC method.³⁶ Incompletely converged structures were further optimized using a version of the DIIS method³⁷ with a very tight root-mean-square (rms) convergence criterion for the gradient length of 5.0×10^{-5} . Frequency calculations were carried out at the optimized 3-21G and 6-31G* geometries with GAMESS-US³⁸ or Gaussian 92,³⁹ characterizing the structures as minima. The larger structures were optimized using both MUNGAUSS and Gaussian 92.

Primary Hydration Sphere

Our initial interest in the solvated lithium ion was in the assignment of the mode observed at 255 cm^{−1} and thus the characterization of the species giving rise to this totally symmetric vibration.¹² The Li–O bond lengths and calculated Li–O symmetric stretch frequencies are thus given in Table 1. The STO-3G and 3-21G basis sets fail to describe accurately the lithium–oxygen distance and binding energies and will not be discussed further. The geometry has already been shown to be rather insensitive to correlation, at least for the split valence basis sets, and somewhat more sensitive for the triple-ζ valence basis set.¹³ All extensions of the 6-31G* basis set (6-31G**, 6-31+G*, 6-31+G*(5d)) for the tetraaquo species reproduce the neutron diffraction Li–O distance of 1.96 ± 0.02 Å,⁶ and thus any possibility of the mono-, di-, and triaqualithium species existing in solution to any great extent can be ruled out. The calculations indicate that the Li–O “bond” lengthens nonlinearly with hydration number. The difference between the Li–O bond lengths of the mono- and *n*-aquo species increases almost as the square of the hydration number and is nearly independent of basis set. No minima were found for directly bound *C*₂ pentaquo or *T_h* hexaquo species at the 6-31G* level, as was noted previously¹⁴ at the 6-31+G* level. The unscaled 6-31G* frequency (248 cm^{−1}) of the Li–O symmetric stretching vibration is in good agreement with the experimental result of 255 cm^{−1}, which also is evidence for a tetraaqualithium species in solution.

Table 2 demonstrates that the interaction energy is rather sensitive to the presence of sp-diffuse functions on oxygen.⁴⁰ The CHA/CE correction ($E_{\text{bsse}}^{\text{inc}}$), as shown in Table 3, decreases the incremental interaction energy ($E_{\text{int}}^{\text{inc}}$) by about 8 kJ/mol for both the 6-31G* and 6-31+G* basis sets. This suggests that correction of BSSE is still important for basis sets containing diffuse functions, but more detailed systematic studies of diffuse functions and BSSE with CHA/CE are needed.⁴¹ The total binding energies, without ZPE or thermal corrections but with BSSE corrections ($E_{\text{int}}^{\text{tot}}$), are reasonably close to previously calculated¹⁴ binding energies and are consistently slightly closer

TABLE 2: SCF Binding Energies (kJ/mol)

	Li ⁺ + <i>n</i> H ₂ O → Li(H ₂ O) _n ⁺			
	<i>n</i>			
	1	2	3	4
6-31G*	−165.5	−312.0	−426.3	−509.2
6-31G**	−165.7	−312.2	−426.7	−509.5
6-311G*	−174.1	−326.8	−445.3	−530.2
6-31+G*	−153.6	−289.0	−392.0	−465.7
6-31+G*(5d)	−153.2	−288.8	−391.7	−465.5
	Li(H ₂ O) _{<i>n</i>−1} ⁺ + H ₂ O → Li(H ₂ O) _{<i>n</i>} ⁺			
	<i>n</i>			
	2	3	4	
6-31G*	−146.5	−114.3	−82.9	
6-31G**	−146.5	−114.5	−82.8	
6-311G*	−152.7	−118.5	−84.9	
6-31+G*	−135.5	−102.9	−73.7	
6-31+G*(5d)	−135.6	−102.9	−73.6	

TABLE 3: CHA Interaction Energies (kJ/mol)

	<i>n</i>			
	1	2	3	4
6-31G*				
$E_{\text{int}}^{\text{tot}}$	−157.7	−296.9		−477.1
$E_{\text{bsse}}^{\text{tot}}$	7.8	15.1		32.1
$E_{\text{int}}^{\text{inc}}$	−157.7	−138.5	−106.2	
$E_{\text{bsse}}^{\text{inc}}$	7.8	7.9	8.1	
$E_{\text{int}}^{\text{inc} \rightarrow \text{tot}}$	−157.7	−296.2	−402.4	
$E_{\text{def}}^{\text{nH}_2\text{O}, (\text{H}_2\text{O})_n}$	0.35	9.2	31.0	62.5
$E_{\text{def}}^{\text{H}_2\text{O}, \text{Li}(\text{H}_2\text{O})_n^+}$	0.35	0.28	0.23	0.19
$E_{\text{def}}^{\text{Li}(\text{H}_2\text{O})_{n-1}, \text{Li}(\text{H}_2\text{O})_n^+}$	0.0	0.2	6.4	12.9
$E_{\text{int}}^{\text{tot, SCF}}$	−165.9	−321.2	−457.3	−571.7
$E_{\text{int}}^{\text{tot, SCF}} - nE_{\text{int}, 1}^{\text{SCF}}$	0.0	10.6	40.4	91.9
6-31+G*				
$E_{\text{int}}^{\text{tot}}$	−146.1		−371.8	
$E_{\text{bsse}}^{\text{tot}}$	7.5		20.2	
$E_{\text{int}}^{\text{inc}}$	−146.1	−126.8	−95.0	
$E_{\text{bsse}}^{\text{inc}}$	7.5	8.6	7.9	
$E_{\text{int}}^{\text{inc} \rightarrow \text{tot}}$	−146.1	−272.9	−367.9	

to experiment once corrected for ZPE and thermal effects. The binding energies are also reasonably close to the early MESQUAC results of Rode.⁴³ In the case where total interaction energies were not available,⁴⁴ they could be successfully estimated ($E_{\text{int}}^{\text{inc} \rightarrow \text{tot}}$) by adding the incremental interaction energies calculated via the incremental partitioning scheme.

Table 3 also presents the deformation energies associated with lithium aquo complex formation ($E_{\text{def}}^{\text{x,y}}$ represents the difference in energy between *X* in its most stable shape and of *X* as part of the larger complex *Y*). The energy associated with adding a water molecule around a lithium ion would have a significant repulsive component as the hydrate grows in size, but the distortion of the individual water molecules plays no role in this process. About 20% of the strain is associated with distorting the Li(H₂O)_{*n*−1}⁺ complex into its “proper” shape for addition of another water molecule, and the remainder is essentially the interaction of the additional water with the existing cluster. Qualitative information such as this is useful in rationalizing the chemical basis of the decrease in successive binding energies. The interaction energies ($E_{\text{int}}^{\text{tot, SCF}}$), found by subtracting the water cluster deformation energies from the computed total SCF binding energies, are lower than the number of Li–O bonds times the first interaction energy ($E_{\text{int}, 1}^{\text{SCF}}$), the

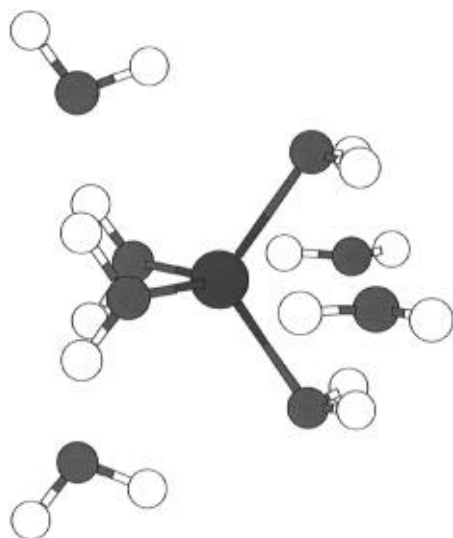


Figure 1. Structure of the octaaquolithium ion.

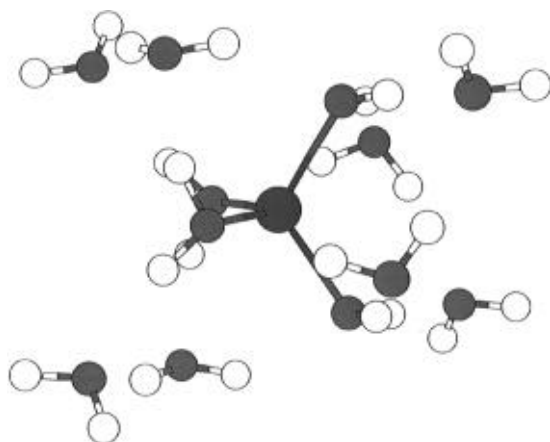


Figure 2. Structure of the dodecaaquolithium ion.

difference increasing as roughly the square of the hydration number. The weakening of the Li–O bond is of the same magnitude as the deformation energy of the waters around the lithium. The interaction energy changes can be rationalized both by crowding around the small lithium ion and by the resulting weakening of the Li–O bond.

Second Hydration Sphere

The evidence presented demonstrates that lithium cation is tetracoordinated. The addition of a second solvation sphere would be the next logical step in describing the solvated lithium ion. However, an *ab initio* search for the global minimum would be impractical, so only structures preserving the symmetry elements of the tetraaquo cluster were considered.

The octaaquo structure (6-31G*, 6-31+G*) consists of the tetraaquolithium species in the inner sphere and four water molecules in the second solvation sphere, denoted [4+4] (see Figure 1). Each water of the second solvation sphere is hydrogen-bonded to three waters of the inner sphere. Whereas the tetraaquolithium structure is of point group S_4 , this octaaquo structure is of higher symmetry (D_{2d}). The structure resembles a cubelike $(\text{H}_2\text{O})_8$ 4-31G structure found recently⁴⁶ which can be regarded as four water dimers hydrogen bonded to each other in a cycle. The “double donor” waters are coordinated to the central lithium ion resulting in a “tucking-in” of their oxygens toward the central lithium ion. If this structure persists in liquid water, then it can be seen that the lithium ion fits neatly in the center of this structure. The coordination to lithium results in

the introduction of significant nonlinearity to the hydrogen-bonds and a distortion of the tetramer rhombi. The Li–O distance in the [4+4] species is 1.968 Å at the 6-31G* level and 1.962 Å at the 6-31+G* levels, compared with 1.971 and 1.968 Å, respectively, for the tetraaquo complex. The distance to the oxygen of the second sphere waters is 2.941 and 2.975 Å at the 6-31G* and 6-31+G* levels, respectively. The average uncorrected SCF binding energy per water of the outer sphere to the inner sphere is -54.9^{47} and -46.3 kJ/mol, respectively. The 6-31+G* value is fairly close in magnitude to the enthalpy of vaporization of water extrapolated to 0 K (about 47 kJ/mol⁴⁸), and thus the second hydration sphere is only weakly associated with the ion.

A frequency analysis proved the octaaquolithium structure to be a minimum and gave a Li–O symmetric stretch frequency of 266 and 257 cm^{-1} at the 6-31G* and 6-31+G* levels, respectively, compared to 248 cm^{-1} (6-31G*) for the single hydration sphere case. The octaaquo 6-31+G* symmetric stretch frequency is very close to the experimental value of 255 cm^{-1} . A larger basis set (aug-cc-pVDZ, similar to 6-31+G**) gave a frequency of 239 cm^{-1} ⁴⁹ for the tetraaquo complex. The octaaquo symmetric stretching mode does not couple with the librational modes of the inner sphere waters, unlike the tetraaquo species.

By including the second solvation shell the frequency of the Li–O symmetric stretching mode is raised by 18 cm^{-1} (7%). The usual empirical HF scale factor of about 0.9 may not be applicable to these low-frequency modes. The agreement between *ab initio* gas-phase frequencies of the primary hydration sphere and experimental solution frequencies worsens upon extending the basis set (see the 6-31G* and aug-cc-pVDZ result). This would suggest that the disagreement is due to a deficiency not of the theory but of the model used to describe the solvated lithium ion. The second solvation shell plays an important role in modifying the symmetric Li–O stretch. For more highly charged cations, a greater effect is expected, since the hydrogens of the inner sphere would be more polarized, resulting in stronger hydrogen bonds between the first and second sphere. Indeed, scale factors greater than 1.0 are found for the symmetric stretching vibrations of primary hydrates of other well-characterized ions (Be^{2+} , Mg^{2+} , Al^{3+} , Sc^{3+} , In^{3+} , Ga^{3+} , Cd^{2+}).²⁰ The possibility for defining new scale factors to predict Raman frequencies in aqueous solution based on clusters with only one solvation shell is being investigated.

The vibrational modes for the [4+0] and [4+4] species are shown in Tables 4 and 5, respectively. The isotropic Raman spectrum should contain only bands due to totally symmetric vibrations, i.e., for our octaaquolithium model, those modes possessing A_1 symmetry. The calculated frequencies associated with motions of the outermost sphere cannot be expected to be accurate since they neglect hydrogen bonding to bulk water. The presence of the anion in the second shell does not change the measured frequency of the Li–O symmetric stretch (see ref 12).

The OH stretching region clearly consists of groups of modes that can be described as symmetric and asymmetric with respect to each water, separated by about 100 cm^{-1} . Comparisons between the tetra- and octaaquo species should reflect environmental differences for $\text{Li}(\text{H}_2\text{O})_4^+$ between in vacuo and in aquo. Hydrogen bonding to the inner sphere reduces the frequency of the symmetric and asymmetric groups by 80 and 90 cm^{-1} respectively and separates the E modes from previously coincidental A and B modes. The average downshift of 85 cm^{-1} is in fair agreement with a previous result of 101 cm^{-1} ,⁵⁰ although considering a hexaaquo complex for lithium ion as a

TABLE 4: Unscaled 6-31G* Frequencies (cm⁻¹) of Aqueous Lithium Cluster [4+0] $\Gamma_{\text{vib}} = 8A + 9B + 8E$

6-31G*	sym	mode
48.1	A	LiAq ₄ scissor + water twist
52.4	B	LiAq ₄ twisting
52.9	E	LiAq ₄ rock/wag + water twist
108.5	B	LiAq ₄ scissor
132.1	A	water twist
140.8	E	water twist
228.9	B	water twist
248.3	A	Li-O stretch + water wag
263.2	E	water wag
270.4	A	water wag
328.1	B	water wag
381.0	E	water rock
408.6	B	LiAq ₄ scissor + water rock
423.2	A	water rock
550.1	B	water rock + Li-O stretch
554.3	E	Li-O stretch + water rock
1824.6	B	HOH bend
1827.0	E	HOH bend
1830.9	A	HOH bend
4058.9	E	HO sym stretch
4059.1	B	HO sym stretch
4063.5	A	HO sym stretch
4157.1	A	HO asym stretch
4157.5	E	HO asym stretch
4158.0	B	HO asym stretch

first hydration sphere model is not appropriate.¹²⁻¹⁴ A scaled (0.89) frequency of 3546 cm⁻¹ is predicted, compared with an observed broad peak centered at 3400 cm⁻¹. It is possible that a predicted Fermi resonance with $2\nu_2 = 3260$ results in an apparent peak at the average of these two, or that the anion can play an important role in modifying the frequency, or that some coupling between different ion spheres lowers the symmetric mode frequency. This mode would be expected to be very dependent on the model used and would probably best be treated dynamically.

In the OH bending region, the E-mode is predicted to separate from the A and B modes upon addition of a second solvation sphere but the average position of the bands remains the same. This band should change little upon dilution but may be obscured by the OH bending of bulk water (1625 cm⁻¹). The scaled (0.89) A mode is predicted to be at 1630 cm⁻¹, in very close agreement with our experimental value of 1640 cm⁻¹.

A dodecaaquolithium species of S_4 symmetry, designated [4+8], was also obtained, with a long Li-O distance of 1.989 Å. In this structure the lithium ion is bound to oxygens of two hexamers of water. These hexamers resemble the boat structure of cyclohexane and are hydrogen-bonded to each other at the base of the twisted boat. Four of these waters are in the first hydration sphere. The waters in the second hydration sphere may be split into two groups. The waters closer to the lithium ion are hydrogen-bonded twice to the inner shell and reside about 3.15 Å from the lithium ion, whereas the other subset are hydrogen-bonded once to the inner shell and once to the second sphere and reside about 4.18 Å from the lithium ion. The A mode corresponding to the Li-O stretch couples strongly with a librational twisting of the distant second-sphere waters, giving frequencies of 248.8 and 273.4 cm⁻¹. This coupling is an artifact of the calculation since the outer sphere waters in this model are not hydrogen-bonded to external waters, whereas in solution they would be. In addition, the local structure of water, which likely resembles the octa cluster, would be destroyed. This second hydration sphere model of lithium cation should thus be expected to be rather poor. For the lithium cation, a model of the second solvation sphere containing only four waters seems to be closer to reality.

TABLE 5: Unscaled 6-31G* Frequencies (cm⁻¹) of Aqueous Lithium Cluster [4+4] $\Gamma_{\text{vib}} = 11A_1 + 6A_2 + 7B_1 + 11B_2 + 17E$

freq	sym	mode
58.2	B1	2nd-sph trans
71.0	A1	2nd-sph trans
76.8	E	2nd-sph trans
84.1	B2	2nd-sph trans + LiAq ₄ scissor
92.2	A2	2nd-sph trans
105.2	E	LiAq ₄ rock/wag
109.9	B2	2nd-sph trans + LiAq ₄ scissor
115.7	B1	LiAq ₄ twisting
119.7	A1	2nd-sph trans + LiAq ₄ scissor
136.4	E	2nd-sph trans + LiAq ₄ rock/wag
179.8	A1	2nd-sph trans + LiAq ₄ scissor
187.8	B2	2nd-sph trans + LiAq ₄ scissor
188.9	E	2nd-sph trans + LiAq ₄ rock/wag
266.1	A1	Li-O stretch
331.8	E	2nd-sph rocking
342.9	A2	2nd-sph twisting
343.7	B1	2nd-sph twisting
348.8	E	2nd-sph twisting
365.3	B1	1st-sph rock + 2nd-sph wag
374.1	B2	2nd-sph rock
388.5	A1	2nd-sph rock
447.0	A2	1st-sph rock + 2nd-sph wag
451.6	E	Li-O stretch
460.5	E	1st-sph rock + 2nd-sph wag
472.4	B2	Li-O stretch + 1st-sph wag
515.2	A2	1st-sph rock + 2nd-sph wag
577.2	E	1st-sph rock
602.7	B1	1st-sph twist
605.9	A2	1st-sph twist
611.3	E	1st-sph wag
707.9	B1	1st-sph twist
713.5	A1	1st-sph wag
751.2	E	1st-sph twist
752.6	B2	1st-sph wag
1810.7	B2	HOH bend 2nd sph
1812.5	E	HOH bend 1st sph
1820.3	A1	HOH bend 2nd sph
1829.8	E	HOH bend 2nd sph
1846.8	A1	HOH bend 1st sph
1851.4	B2	HOH bend 1st sph
3977.3	E	HO stretch 1st sph sym
3984.3	A1	HO stretch 1st sph sym
3984.9	B2	HO stretch 1st sph sym
4026.0	E	HO stretch 2nd sph sym
4030.9	A1	HO stretch 2nd sph sym
4031.8	B2	HO stretch 2nd sph sym
4068.7	A2	HO stretch 1st sph asym
4069.0	B1	HO stretch 1st sph asym
4083.0	E	HO stretch 1st sph asym
4141.9	E	HO stretch 2nd sph asym
4142.3	B2	HO stretch 2nd sph asym
4142.6	A1	HO stretch 2nd sph asym

Conclusions

The structures and vibrational frequencies of small lithium ion-water clusters have been calculated with several basis sets. The CHA interaction energies are nearly independent of the choice of fragment partitioning. The first ab initio calculation of a full second solvation sphere of a metal cation is presented and is shown to significantly modify the vibrational spectra of aqueous metal ions. The [4+4] octaaquolithium structure is shown to afford an excellent description of the Raman spectra of lithium ion in water.

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