

An *Ab Initio* Investigation of Lithium Ion Hydration III. *Revisiting Hydration and the Halide Ion Pair†

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Abstract

Tetraaqualithium(I) has been examined using a wide variety of basis sets at the HF and MP2 levels. Various models for a second hydration sphere of four additional water molecules have also been examined and new structures have been found. The ONIOM model has also been employed. Hydrated lithium halide ion pairs have also been re-examined, and some anomalous features of the hydrated lithium bromide have been corrected.

Keywords: lithium, hydration, *ab initio*, ion pair

Résumé

Nous avons examiné le tétraaqualithium (I) en se servant d'une grande variété de bases de données aux niveaux HF et MP2. Nous avons aussi examiné les différents modèles pour la seconde sphère d'hydratation des quatre molécules d'eau additionnelles et nous avons trouvé de nouvelles structures. Le modèle ONIOM a aussi été utilisé. Nous avons re-examiné les paires ioniques halogénées hydratées du lithium et corrigé certaines anomalies de structure du bromure de lithium hydraté.

Introduction

The coordination number of lithium in aqueous solution is four (1-3). Except for the most concentrated solutions, lithium appears to exist as the tetraaqua ion (2). For a salt to water ratio greater than 1:4, chloride or bromide enters the inner coordination sphere to form a contact ion pair (1, 2).

Much insight into the thermodynamics of lithium ion hydration has been provided by mass spectrometry

(4). The subject continues to be of much interest as new methods such as collision-induced dissociation (5), electrospray (6), and flame sampling (7) are employed. These gas-phase clusters serve as a bridge between gas-phase calculations and experimental solution measurements.

Ab initio calculations on lithium ion-water interactions have been carried out for at least three decades (8). Some computational literature prior to our previous papers has been summarized there (1, 3). We now summarize subsequent papers relating to the hydration of lithium ion and various ion pairs. Density functional theory has been employed to study the aqualithium series at the BLYP/6-31+G** (9), B3LYP/6-311+G(d,p) (10), B3LYP/6-31++G** (11), and B3LYP/aug-cc-pVDZ levels (12). The aqua complexes have also been useful in testing energy decomposition schemes (13). The hydrated lithium chloride ion pair was studied by Bacelo (14), who used Monte Carlo simulated annealing at the B3LYP/6-31G* level, followed by B3LYP- and MP2/6-311++G(2d,2p) geometry optimizations and QCISD(T) single point calculations. Their results agreed with ours (1), with the exception that our chlorotriaqualithium structure is slightly higher in energy than their lowest energy structure. The hydrated lithium fluoride ion pair has been examined at the B3LYP and MP2/6-31+G** levels (15), and there are some similarities with our one- and six-water structures (1). The hydrates of lithium hydroxide have also been investigated (16). Because of its use in high energy-density batteries, the ion pairs of lithium with triflate-derived anions have also been studied (17). A joint ATR-FTIR and QM study (18) examined several salts, including lithium chloride, especially in the OH stretching region, but the authors appear not to be aware of the extensive QM literature available. The effective fragment potential method has also been applied to lithium hydration(19), as has molecular dynamics simulation (20-28). Finally, an interesting application of computational chemistry is the estimation of separation factors for the isotopes of lithium, important in the

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nuclear industry (29-33).

In the past decade, Raman and ab initio studies of ions in aqueous solutions have been combined in an attempt to understand their structural and vibrational characteristics (34-38). Raman spectroscopy is a very sensitive probe of contact ion pairing, and *ab initio* theory can provide a useful supporting or interpretative role. Contact ion pairs can usually be distinguished from the free aqua ions, but it is generally much more difficult to detect solvent-shared or solvent-separated ion pairs from the free ions using Raman spectroscopy. Most physicochemical methods detect all ion pairs collectively, and thus Raman spectroscopy supported by ab initio calculations on the contact ion pair is a very useful combination.

Although *ab initio* calculations have proven to be useful, as more waters are added to lithium, MP2 calculations in particular become much more expensive. Practical means of reducing this cost without sacrificing accuracy would be beneficial. One way to potentially reduce costs is to alter the basis set and to use effective core potentials. As analytic frequency calculations of systems described by effective core potentials, and the use of the ONIOM technique, became possible in Gaussian 98 (37), we decided to pursue this, in conjunction with the octahedral magnesium ion already published (34).

In our previous work (1), we could not then carry out MP2 frequency calculations on some of these systems, as the systems were too large for our computers. We are pleased to be able to now show these results. In addition, we solve a longstanding anomaly in the bromide results.

Experimental

All calculations were performed using Gaussian 98 (39), utilizing the 6-31G* (40) and 6-31+G* (41) basis sets. For Br and I, the Huzinaga (43321/4321/41*) and (433321/43321/431*) basis sets (42) were used in conjunction with the 6-31G* basis sets, augmented by diffuse functions as appropriate. The MP2 calculations utilize the frozen core approximation. No diffuse functions were used on lithium unless otherwise specified, since its cationic nature renders them unnecessary.

The geometries were optimized using a stepping stone approach, in which the geometries at the levels HF/STO-3G, HF/3-21G, HF/6-31G*, MP2/6-31G*, HF/6-31+G*, and MP2/6-31+G* were sequentially optimized. Default optimization specifications were normally used for the halide ion pairs, and "Tight" criteria used for the cations. After each level a frequency calculation

was performed and the resulting Hessian was used in the following optimization.

In some cases, an intermediate level was used when reasonable geometries were available from our earlier calculations (1, 2). Z-matrix coordinates constrained to the appropriate symmetry were used to speed up the optimizations. Since frequency calculations were done at each level, any problems with the Z-matrix coordinates would manifest themselves by giving imaginary frequencies corresponding to modes orthogonal to the spanned Zmatrix space. The Hessian was evaluated at the first geometry (opt=CalcFC) for the first level in a series in order to aid geometry convergence.

Results and Discussion

Lithium Cation models

For these calculations, diffuse functions on lithium were included where defined as part of the basis set.

Li[4+0]

The structure of the [4+0] cluster is given in Figure 1. The lithium-oxygen distances are given in Table 1. We make the assumption that the largest basis set (aug-cc-pVTZ) is best. The cc series of basis sets have been designed to converge smoothly to the basis-set limit. We can then classify the results based on how close the corresponding HF (or MP2) values are to the results using this basis set. Here, we see that the results for the SVP, SDDAll, D95+(d,p), cc-pVTZ, cc-pVDZ are always within 0.01 Å of aug-cc-pVTZ. Other accurate basis sets that are within 0.01 Å of either the best HF or MP2 result include aug-cc-pVDZ, HF/6-31G(d), HF/6-31+G(d), and D95(d,p). Basis sets that are within 0.01-0.02 Å of the best result include TZV and CEP-121G(d); within 0.02-0.05 Å of the best result, D95V(d,p). The 3-21G, CEP-4G, and CEP-31G(d) fall between 0.050-0.10 Å of the best result, and STO-3G falls outside of that range. The computational times for the most part reflect this accuracy, that is, the more accurate the calculation, the longer it takes. Calculations involving the D95V(d,p) and CEP-31G(d) basis sets are costly, but inaccurate. Calculations using the SDDAll basis set are inexpensive, but surprisingly accurate. We verify the (aug)-cc-pVDZ HF and MP2 results of Feller and co-workers (43) on the tetraaqualithium (I) ion and extend their results to the triple-zeta basis.

The ν_1 frequency of the [4+0] cluster are given in Table 2. We assume that our best result is that derived using the aug-cc-pVTZ basis set (HF = 239.2, MP2=234.3

cm^{-1}). The 6-31+G*, D95V(d,p), D95(D,p), D95+(d,p), CEP-121G*, aug-cc-pVDZ, and cc-pVTZ results are always within 10 cm^{-1} of the best result. The 6-31G*, TZV, and SDDAll results are sometimes within 10 cm^{-1} but always within 20 cm^{-1} of the best. The cc-pVDZ, CEP121G, and SVP results are between $10\text{-}20 \text{ cm}^{-1}$ of the best result, and the CEP-4G, CEP-31G, CEP-4G* can be expected to lie $20\text{-}50 \text{ cm}^{-1}$ from the best. The worst performers were CEP-31G*, 3-21G, and STO-3G.

Li[4+4]

The structures of the [4+4] clusters are given in Figure 1. We have examined four possible structures, two of symmetry S_4 and two of symmetry D_{2d} . The first S_4 structure features four dangling waters in the second hydration sphere accepting a hydrogen from the inner sphere (A). The second-sphere waters do not interact with one another. In the second S_4 structure the waters of the second hydration sphere cluster near each other near the symmetry axis. This structure always possesses an imaginary E mode, and was therefore not examined in as much depth as the others. The first D_{2d} structure is that examined previously (1, 3), in which the second-sphere waters are embedded in the dihedral planes, and the water molecules donate one (weak) hydrogen bond and accept two (DAA). The second D_{2d} structure places the oxygen of the second-sphere water molecules on the C_2 axes perpendicular to the main C_2 axis. For this structure, the second sphere waters are double acceptors of hydrogen bonds (AA). For some levels, the D_{2d} ascends in symmetry to D_{4h} to give a square-planar species. The S_4 #1 structure (and D_{2d} #1) were also found by Yanase (30).

If we compare the eight water structures to the four water structure, some clear trends exist. In the S_4 #1 structure, the lithium-oxygen distance is typically $0.01\text{-}0.02 \text{ \AA}$ shorter. For the D_{2d} #1 structure, the distance is usually within 0.005 \AA . For the D_{2d} #2 structure, it is typically $0.01\text{-}0.02 \text{ \AA}$ longer. The exceptions are typically the poorer performing basis sets determined for the tetraaqualithium.

A comparison between the ν_1 stretching frequency of the eight water structures to that of the four water structure can also be made. The D_{2d} #1 frequency is typically $10\text{-}30 \text{ cm}^{-1}$ higher, the D_{2d} #2 frequency is typically $15\text{-}50 \text{ cm}^{-1}$ higher, and the S_4 #1 is typically $30\text{-}70 \text{ cm}^{-1}$ higher.

The MP2 calculations on the lithium cluster with eight waters are very demanding computationally. The ONIOM technique was applied to the D_{2d} #1 cluster, in which the inner sphere was modeled using MP2, and

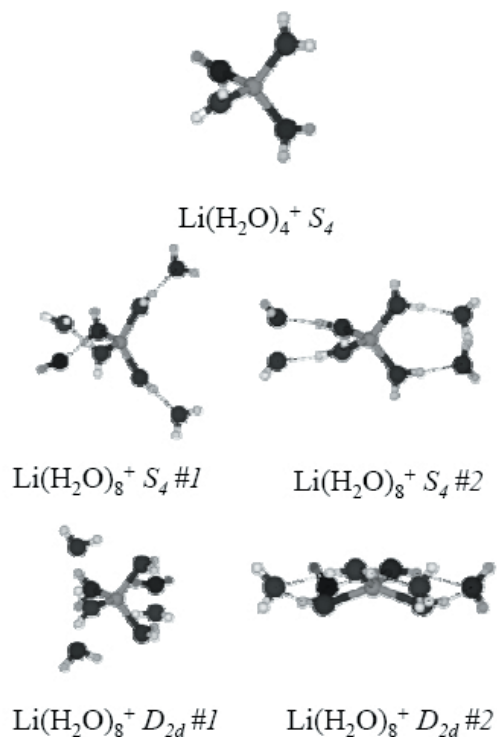


Figure 1: Structures examined in this study

the outer sphere using HF. When compared with the MP2 method on the entire cluster, the bond lengths were about 0.01 \AA larger, which was surprising as the MP2 and HF calculations were within $0.002\text{-}0.004 \text{ \AA}$ of each other. The ν_1 frequency, accordingly, is calculated to be about 10 cm^{-1} lower than the corresponding MP2 value. As might be expected, the level of the inner sphere is more important in determining the inner sphere Li-O distance and frequency than is the level of the outer sphere. Although the ONIOM calculations are about an order of magnitude less demanding, they do not seem to reflect what happens at the desired MP2 level for the entire cluster.

Lithium Halide Solution models

The frequency assignments for lithium halides with six water molecules are given in Table 3. Calculation of the MP2 frequencies of the bromide initially gave nonsensical results. We also note that the MP2 geometry and frequency results for $\text{LiBr}(\text{H}_2\text{O})_3$, and the geometry of $\text{LiBr}(\text{H}_2\text{O})_6$, were atypical. In order to understand the nature of the problem, the Hartree-Fock orbital energies of the constituents are presented in Table 4. We first note that if we compare the orbital energies of the water component, the presence of lithium cation lowers these significantly by about 0.25 eV . We surmise that

Table 1. Lithium-oxygen distances for a plethora of basis sets.

| Level | Li(H ₂ O) ₄ ⁺ | Li(H ₂ O) ₈ ⁺ | | | |
|-----------------|--|--|-------------------|--------------------|--------------------|
| | | S ₄ #1 | S ₄ #2 | D _{2d} #1 | D _{2d} #2 |
| HF/STO-3G | 1.7809 | 1.7793 | X | 1.8146 | 1.8061 |
| HF/3-21G | 1.8859 | 1.8777 | 1.8814 | 1.9069 | 1.8986 |
| HF/6-31G(d) | 1.9704 | 1.9583 | 1.9600 | 1.9682 | 1.9765 |
| HF/6-31+G(d) | 1.9687 | 1.9554 | 1.9567 | 1.9617 | 1.9837 |
| MP2/6-31G(d) | 1.9681 | NS | 1.9604 | 1.9664 | 1.9824 |
| MP2/6-31+G(d) | 1.9685 | 1.9547 | 1.9548 | 1.9562 | 1.9919 |
| HF/D95V(d,p) | 1.9821 | 1.9698 | X | 1.9801 | 1.9880 |
| HF/D95(d,p) | 1.9718 | 1.9594 | X | 1.9726 | 1.9785 |
| HF/D95+(d,p) | 1.9671 | 1.9553 | X | 1.9652 | 1.9788 |
| MP2/D95V(d,p) | 1.9829 | 1.9698 | X | 1.9822 | 1.9998 |
| MP2/D95(d,p) | 1.9669 | 1.9530 | X | 1.9681 | 1.9817 |
| MP2/D95+(d,p) | 1.9574 | 1.9438 | X | 1.9551 | 1.9779 |
| HF/CEP-4G | 2.0391 | 2.0267 | X | 2.0495 | 2.0358 |
| HF/CEP-31G(d) | 2.0301 | 1.9826 | 2.0019 | 2.0146 | 1.9928 |
| HF/CEP-121G(d) | 1.9431 | 1.9322 | X | 1.9437 | 1.9563 |
| MP2/CEP-31G(d) | 2.0321 | 1.9712 | X | 2.0158 | 1.9775 |
| MP2/CEP-121G(d) | 1.9364 | 1.9246 | X | 1.9349 | 1.9585 |
| HF/SVP | 1.9656 | 1.9538 | X | 1.9694 | 1.9707 |
| HF/TZV | 1.9459 | 1.9375 | X | 1.9491 | 1.9663 |
| HF/SDDAll | 1.9435 | 1.9279 | X | 1.9434 | 1.9731 |
| MP2/SVP | 1.9643 | NS | X | 1.9745 | 1.9777 |
| MP2/TZV | 1.9744 | 1.9633 | X | 1.9698 | 1.9843 |
| MP2/SDDAll | 1.9671 | 1.9495 | X | 1.9630 | 1.9922 |
| HF/cc-pVDZ | 1.9634 | 1.9486 | X | 1.9678 | 1.9689 |
| HF/aug-cc-pVDZ | 1.9670 | 1.9558 | X | 1.9671 | 1.9786 |
| HF/cc-pVTZ | 1.9573 | 1.9454 | X | 1.9617 | 1.9695 |
| HF/aug-cc-pVTZ | 1.9578 | 1.9467 | X | 1.9602 | 1.9682 |
| MP2/cc-pVDZ | 1.9610 | NS | X | 1.9731 | 1.9757 |
| MP2/aug-cc-pVDZ | 1.9708 | | X | 1.9718 | 1.9909 |
| MP2/cc-pVTZ | 1.9509 | | X | | |
| MP2/aug-cc-pVTZ | 1.9585 | | X | | |
| A/B | | | | ONIOM(MP2/A:HF/B) | |
| 6-31G*/6-31G* | | | | 1.9775 | |
| 6-31G*/6-31+G* | | | | 1.9766 | |
| 6-31+G*/6-31G* | | | | 1.9706 | |
| 6-31+G*/6-31+G* | | | | 1.9704 | |

NS - not stable, X - calculation not attempted

Table 2. ν_1 -(LiO₄) frequency (cm⁻¹) for a plethora of basis sets.

| Level | Li(H ₂ O) ₄ ⁺ | Li(H ₂ O) ₈ ⁺ | | | |
|-----------------|--|--|-------------------|--------------------|--------------------|
| | | S ₄ #1 | S ₄ #2 | D _{2d} #1 | D _{2d} #2 |
| HF/STO-3G | 379.1 | 498.9 | X | NS 2i | 368.9 |
| HF/3-21G | 292.8 | 357.3 | NS Ei | 319.9 | 315.8 |
| HF/6-31G(d) | 249.0 | 296.3 | NS Ei | 266.1 | av277 |
| HF/6-31+G(d) | 239.6 | 287.6 | NS Ei | 257.1 | 278.9 |
| MP2/6-31G(d) | 251.1 | NS | NS Ei | 273.5 | 266.3 |
| MP2/6-31+G(d) | 236.3 | 298.8 | NS Ei | 263.6 | 285.4 |
| HF/D95V(d,p) | 239.0 | 279.5 | X | 254.3 | 277.3 |
| HF/D95(d,p) | 240.2 | 281.7 | X | 254.2 | 278.4 |
| HF/D95+(d,p) | 236.3 | 275.8 | X | 251.7 | 272.7 |
| MP2/D95V(d,p) | 234.4 | 287.4 | X | 260.1 | 238.9 |
| MP2/D95(d,p) | 242.1 | 293.9 | X | 263.3 | 247.0 |
| MP2/D95+(d,p) | 239.5 | 289.0 | X | 262.9 | 240.2 |
| HF/CEP-4G | 254.7 | 290.0 | X | NS 2i | 289.3 |
| HF/CEP-31G(d) | 173.2 | 249.7 | NS Ei | 186.2 | 245.6 |
| HF/CEP-121G(d) | 239.5 | 281.6 | X | 256.5 | 278.4 |
| MP2/CEP-31G(d) | 169.8 | 272.6 | X | 197.2 | 248.9 |
| MP2/CEP-121G(d) | 239.0 | 294.2 | X | 265.6 | 288.6 |
| HF/SVP | 253.4 | 297.0 | X | 267.6 | 290.2 |
| HF/TZV | 253.0 | 305.4 | X | NS 2i | 299.0 |
| HF/SDDAll | 254.1 | 315.2 | X | NS 2i | 295.4 |
| MP2/SVP | 253.2 | NS | X | 268.7 | 267.9 |
| MP2/TZV | 241.7 | 309.8 | X | NS 2i | 269.2 |
| MP2/SDDAll | 242.7 | 312.9 | X | NS 2i | 273.0 |
| HF/cc-pVDZ | 250.1 | 292.9 | X | 264.6 | av276 |
| HF/aug-cc-pVDZ | 239.8 | 274.0 | X | 253.2 | 271.4 |
| HF/cc-pVTZ | 239.6 | 274.6 | X | 252.0 | 270.4 |
| HF/aug-cc-pVTZ | 239.2 | 272.1 | X | 252.1 | 266.5 |
| MP2/cc-pVDZ | 253.3 | | X | 268.1 | 268.5 |
| MP2/aug-cc-pVDZ | 235.7 | | X | | |
| MP2/cc-pVTZ | 239.3 | | X | | |
| MP2/aug-cc-pVTZ | 234.3 | | X | | |
| A/B | | | | ONIOM(MP2/A:HF/B) | |
| 6-31G*/6-31G* | | | | 262.3 | |
| 6-31G*/6-31+G* | | | | 261.8 | |
| 6-31+G*/6-31G* | | | | 252.6 | |
| 6-31+G*/6-31+G* | | | | 251.6 | |

NS - not stable, Ei - imaginary E mode, 2i - two imaginary modes, av - average

Table 3. Unscaled Frequencies (cm^{-1}) of $\text{Li}(\text{H}_2\text{O})_3\text{X}(\text{H}_2\text{O})_3, (\text{C}_3) \Gamma_{\text{vib}} = 16A + 16E$

| MP2 Frequency | | | | | | |
|---------------|--------|---------|--------|---------|-----|---|
| Cl | Br | | I | | sym | mode |
| 6-31+G* | 6-31G* | 6-31+G* | 6-31G* | 6-31+G* | | |
| 25.9 | 22.1 | 19.0 | 21.9 | 19.2 | E | HOH (2) trans. perp. to LiX |
| 50.1 | 49.4 | 49.4 | 49.6 | 40.4 | A | HOH (2) trans. about LiX |
| 59.3 | 62.4 | 59.0 | 61.3 | 58.8 | E | LiO ₃ def. |
| 89.9 | 79.0 | 77.4 | 70.0 | 69.7 | A | LiO ₃ def. |
| 117.2 | 113.6 | 110.2 | 107.2 | 101.4 | E | LiX def. |
| 153.0 | 137.9 | 140.6 | 122.0 | 123.2 | A | HOH (2)...X H-bond |
| 190.8 | 154.0 | 156.2 | 130.2 | 132.7 | E | HOH (2)...X H-bond |
| 210.5 | 186.2 | 181.5 | 168.6 | 164.2 | A | LiO ₃ def + LiX |
| 241.1 | 252.3 | 235.2 | 226.2 | 222.5 | E | HOH lib. |
| 247.5 | 257.5 | 243.2 | 225.9 | 229.1 | A | HOH lib. |
| 261.4 | 266.2 | 260.5 | 263.7 | 257.5 | E | HOH (1)...HOH (2) H-bond |
| 269.9 | 273.6 | 268.7 | 271.1 | 264.9 | A | HOH (1)...HOH (2) H-bond+ LiO ₃ def. |
| 345.5 | 321.0 | 340.2 | 304.9 | 321.4 | E | HOH lib. |
| 363.3 | 325.2 | 349.7 | 315.9 | 325.2 | A | HOH lib. |
| 374.3 | 398.2 | 359.6 | 398.5 | 352.0 | E | HOH lib. |
| 381.7 | 391.4 | 374.1 | 391.8 | 368.5 | A | LiX str + HOH lib. |
| 400.2 | 438.7 | 390.6 | 436.8 | 390.4 | A | LiX str + HOH lib. |
| 449.8 | 488.6 | 452.3 | 482.8 | 452.0 | E | LiO str. + HOH lib. |
| 545.2 | 565.5 | 544.1 | 544.0 | 530.3 | E | LiO str. + HOH lib. |
| 556.2 | 573.7 | 547.5 | 550.0 | 533.0 | A | HOH lib. |
| 655.0 | 625.0 | 624.2 | 611.5 | 594.7 | A | HOH lib. |
| 671.5 | 638.0 | 642.2 | 618.1 | 609.3 | E | HOH lib. |
| 919.5 | 964.5 | 916.1 | 950.5 | 910.8 | E | HOH lib. |
| 943.8 | 989.5 | 937.3 | 972.2 | 929.0 | A | HOH lib. |
| 1712.3 | 1741.0 | 1709.9 | 1738.5 | 1704.6 | A | HOH bend |
| 1719.5 | 1749.0 | 1715.5 | 1744.0 | 1709.4 | E | HOH bend |
| 1743.5 | 1753.8 | 1743.6 | 1753.7 | 1743.6 | A | HOH bend |
| 1745.5 | 1757.5 | 1746.5 | 1757.8 | 1747.0 | E | HOH bend |
| 3463.3 | 3418.1 | 3463.0 | 3426.4 | 3467.7 | E | OH str. |
| 3479.9 | 3438.4 | 3479.7 | 3445.8 | 3483.4 | A | OH str. |
| 3565.1 | 3642.9 | 3579.5 | 3668.3 | 3602.2 | E | OH str. |
| 3585.6 | 3655.1 | 3596.0 | 3675.4 | 3613.4 | A | OH str. |
| 3826.1 | 3828.0 | 3824.3 | 3826.9 | 3822.8 | E | OH str. |
| 3826.3 | 3828.0 | 3824.2 | 3826.9 | 3822.6 | A | OH str. |
| 3833.3 | 3845.5 | 3831.5 | 3845.7 | 3830.0 | E | OH str. |
| 3836.0 | 3848.3 | 3834.1 | 3848.0 | 3832.2 | A | OH str. |

Table 4. Orbital energies (eV) of cationic species at 6-31G*, 6-31+G* levels.

| | H ₂ O | Li ⁺ (H ₂ O) |
|-----------------|------------------|------------------------------------|
| a ₁ | -1.345, -1.361 | -1.602, -1.606 |
| b ₂ | -0.712, -0.732 | -0.968, -0.973 |
| a ₁ | -0.571, -0.483 | -0.861, -0.867 |
| b ₁ | -0.498, -0.509 | -0.759, -0.762 |
| Li ⁺ | | |
| 1s | -2.792, -2.792 | -2.704, -2.705 |
| 2s, LUMO | -0.196, -0.196 | -0.151, -0.152 |
| 2p | -0.125, -0.126 | -0.09, -0.09 |

Table 5. Orbital energies (eV) of anionic species at 6-31G*, 6-31+G* levels,

| | F | Cl | Br | I |
|------------------|------------------|------------------|----------------|----------------|
| n | 2 | 3 | 4 | 5 |
| Core (frozen) | | | | |
| (n-1)s | -25.695, -25.844 | -10.195, -10.230 | -9.564, -9.574 | -6.955, -6.961 |
| (n-1)p | | -7.664, -7.697 | -7.172, -7.182 | -5.187, -5.192 |
| Valence (active) | | | | |
| (n-1)d | | | -2.901, -2.911 | -2.110, -2.116 |
| ns | -0.966, -1.073 | -0.704, -0.733 | -0.677, -0.687 | -0.550, -0.557 |
| np | -0.077, -0.178 | -0.124, -0.150 | -0.130, -0.139 | -0.123, -0.129 |

this overall effect is electrostatic in nature. The higher-energy occupied a_1 orbital is lowered by an additional 0.05 eV, and the lithium 2s orbital raised by about the same amount, suggesting a small interaction. The “core” lithium 1s orbital rises in energy by 0.09 eV. The halogen valence and outer-core orbital energies are given in Table 5. We note that the bromine 3d orbital energy, treated as part of the valence space in the frozen core approximation within MP2, is lower than the lithium 1s orbital energy. Because the Gaussian program uses an energy criterion to decide which orbitals are core and which are valence, the default selection is incorrect, and as a result, the lithium 1s orbital is active, but one of the bromine 3d orbitals is frozen. In the case of 3 water molecules, atypical bond lengths and an unexpected imaginary E mode was obtained. In the case of 6 water molecules, nonsensical analytical frequencies arose. This problem has been noted before for similar systems (44).

Gaussian 98 does not allow the specification of a non-contiguous valence space for MP2. Some possible frozen core definitions are to (1) exclude the Li 1s and Br 3d orbitals, (2) include the Li 1s but exclude the Br 3d orbitals, or (3) include both the Li 1s and Br 3d orbitals in the valence space. We examined these possibilities first for Li(H₂O)₃Br (Table 6, MP2=Window(X,0), X=19,18,13

respectively). It is clear that there is a very large effect of including the Li 1s orbital in the correlation space, as the Li-O and Li-Br distances shorten significantly and the frequencies of Li-O and Li-Br stretching increase. Excluding the lithium 1s orbital from the correlation space brings the geometry in line with the other systems. The 6-31G* basis set for lithium describes the core function with six contracted Gaussians. This is probably not sufficient to model properly the effects of core correlation. In addition, the bromine basis set uses four contracted Gaussians to describe the 3d orbital, and the same argument would apply. We therefore elect to exclude the lithium 1s and bromine 3d from the valence space. We note that the selection of valence orbitals, a subspace at a time, removes the imaginary frequency anomaly noticed before.

Armed with these new findings, we recalculated the geometry and vibrational frequencies of Li(H₂O)₃Br(H₂O)₃ at the MP2/6-31G* and MP2/6-31+G* levels with the larger frozen core. The Li-O distance (1.9688, 1.9730), Li-Br distance (2.5465, 2.5423), H . . . Br distance (2.4479, 2.4145), H . . . O distance (1.7625, 1.7908), and BrLiO angle (112.1, 111.4) are now consistent with the findings for the other halides.

Table 6. Geometry (Å or deg.) and unscaled MP2/6-31+G* frequencies (cm⁻¹) of Li(H₂O)₃Br, (C₃) Γ_{vib} = 16A + 16E.

| Core Definition | | | |
|-----------------|--------|----------|----------------------|
| 1 | 2 | 3 sym | mode |
| 1.9825 | 1.9271 | 1.9271 | Li-O |
| 2.5428 | 2.5090 | 2.4982 | Li-Br |
| 2.5757 | 2.5958 | 2.5959 | H...Br |
| 91.5 | 93.8 | 94.0 | OLiBr |
| 40.4 | 45.1 | 44.6 E | LiO def |
| 123.9 | 121.3 | 120.4 A | LiO def |
| 127.3 | 126.7 | 126.2 E | LiBr def |
| 204.5 | 226.4 | 228.8 A | LiBr str + LiO str |
| 235.8 | 229.6 | 229.1 E | H ₂ O lib |
| 254.6 | 242.6 | 244.4 A | LiBr str + LiO str |
| 270.2 | 267.8 | 267.2 A | H ₂ O lib |
| 402.0 | 394.1 | 393.5 E | H ₂ O lib |
| 420.0 | 410.3 | 410.6 A | H ₂ O lib |
| 516.2 | 536.2 | 535.6 E | Li-O str |
| 600.5 | 630.0 | 628.9 E | H ₂ O lib |
| 680.8 | 720.0 | 719.0 A | H ₂ O lib |
| 1703.9 | 1709.7 | 1709.5 A | H ₂ O def |
| 1705.5 | 1715.9 | 1715.7 E | H ₂ O def |
| 3597.6 | 3602.8 | 3604.4 E | H ₂ O str |
| 3609.8 | 3613.8 | 3615.2 A | H ₂ O str |
| 3830.0 | 3821.7 | 3821.7 E | H ₂ O str |
| 3830.0 | 3821.7 | 3821.7 E | H ₂ O str |
| 3831.4 | 3823.0 | 3823.0 A | H ₂ O str |

Conclusion

A series of basis sets for studying lithium ion-water clusters has been ranked relative to aug-cc-pVTZ. Several possible structures and their totally symmetric Li-O vibrational frequency for lithium ion with eight water molecules (as a simple model of a second hydration sphere) have been compared both with each other and with the structure containing only four water molecules. ONIOM calculations using MP2 theory for the inner sphere and HF theory for the outer sphere did not give satisfactory results compared with MP2 theory throughout. Some anomalous results for hydrated lithium bromide examined previously have been traced to an inappropriate default selection of frozen core orbitals for the MP2 calculations.

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