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Hydration of Lithium Ion in Aqueous Solution†

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Raman spectra of aqueous lithium salt solutions (LiCl, LiBr, and $LiClO_4$) were measured from saturation concentrations to more dilute solutions at room temperature. In the saturated LiCl and LiBr solutions a polarized band at 380 and 335 cm^{-1}, respectively, was detected. This band was assigned to a symmetric vibrational mode from an inner sphere complex $LiCl/Br(OH_2)_n^+$ where n is probably three. In more dilute aqueous LiCl and LiBr solutions the high frequency component disappeared, and a new polarized band at 255 cm^{-1} (FWHH 60 cm^{-1}) was observed and assigned to the Li–O symmetric stretching motion of $Li(OH_2)_4^+$. This is the first definitive report of the symmetric stretching motion of an univalent cation. Ab initio geometry optimizations and frequency calculations at the 3-21G and 6-31G* level were performed on the tetraaquolithium species and support our assignment.

1. Introduction

Although the hydration of Li^+ in aqueous solution was studied extensively by a broad variety of structural[1–6] and physicochemical techniques,[7–11] the hydration number of the first sphere is still not established. Hydration numbers between 3.3 and 9.1 have been reported and depend on the method of study.

Nevertheless the knowledge of the hydration structure of electrolytes is important for the understanding of transport properties in solutions and in membranes. Improved information is required on the average coordination number, the structural geometry, and the residence lifetime of the water molecules in the first coordination sphere.

Previous attempts[12–14] to identify the Li–O modes of the $Li(OH_2)_n^+$ hydrate by Raman spectroscopy are inconsistent. The measurements were complicated by overlap from the low frequency bands of water and the intense quasi-elastic wing of the central Rayleigh line. It has been shown recently[15,16] that for most accurate relative intensity measurements it is essential to normalize the low-frequency Raman data for the Bose–Einstein temperature factor, B, and a frequency factor in order to present the data in a spectral form that is directly related to the relative molar scattering factor, $S_Q(\bar{\nu}) \propto (\partial\alpha/\partial Q_i)^2$, where Q_i is the mass-weighted normal coordinate. The relation between Q_i and q_i, the dimensionless normal coordinate is the following: $Q_i = (2\pi c\bar{\nu}_i/h)^{-1/2} \cdot q_i$. It should be pointed out that also another normalization procedure is used in the literature, namely $R_q(\bar{\nu})$. This form of the spectrum has not been normalized to include the frequency factor and will be proportional to the molar scattering activity, $S_q(\bar{\nu})$ (see ref 16 and references therein).

The reduced or $R_Q(\bar{\nu})$ spectrum was constructed after eq 1:

$$R_Q(\bar{\nu}) = I(\bar{\nu}) \cdot (\bar{\nu}_0 - \bar{\nu}_i)^{-4} \cdot \bar{\nu}_i \cdot B \qquad (1)$$

Equation 1 is valid under the condition that the normal coordinates are taken to be harmonic and the polarizability expansion is terminated after the first-order term (i.e., the double harmonic approximation). The $R_Q(\bar{\nu})$ spectrum has been related to the vibrational density of states spectrum and may also be considered as the energy absorbed in a scattering process (see ref 16 and references therein).

Raman difference methods employed in earlier studies[12–14] cannot be considered reliable because it has been shown[17] that dissolved ions alter the low-frequency Raman spectrum of water. Difference spectra obtained by subtracting the spectrum of pure water from the spectrum of an aqueous solution must be viewed with caution.

Raman spectra (in R_Q format) were measured for lithium salts (LiX: X = Cl^-, Br^-, ClO_4^-) at room temperature with different mol ratios $LiX:H_2O$ in order to characterize the cation influence on the low frequency Raman area of water. Studies of the perchlorate solutions have the advantage that the intensity due to water in the low frequency region is reduced.

It was felt necessary to corroborate the experimental results with theoretical calculations. For this purpose, Hartree–Fock calculations with three different basis sets were employed. The geometry of the tetraaquolithium ion was optimized as explained in detail in the Experimental Section.

2. Experimental Section

LiCl and LiBr (Fisher certified) were used without further purification to prepare saturated stock solutions at 22 °C. Distilled water was treated with activated charcoal to remove fluorescent impurities and filtered through a fine sintered-glass frit. All diluted solutions were prepared by weight. The density of the solutions were checked with a 5 mL pycnometer. $LiClO_4$ was prepared by reacting Li_2CO_3 with $HClO_4$. The $LiClO_4$ was recrystallized twice, and from these crystals a stock solution was prepared.

Raman spectra were obtained with a Coderg PHO spectrophotometer after sample excitation with a Control Laser Model 552 argon ion laser. The 90° scattering geometry was employed with the incident light analyzed with polaroid film to give the $I_{\parallel}[X(ZZ)Y]$ and $I_{\perp}[X(ZX)Y]$ scattering geometries. A quarter-wave plate before the entrance slit served to compensate for the grating polarization preference. Raman wavenumber accuracy was ±2 cm^{-1} and was checked with plasma lines of the laser. The laser power at the sample was about 800 mW. The slit width of the double monochromator were set at 4 cm^{-1}. The PMT was cooled to −30 °C, and the signals were collected via photon counting. The scan rate was 50 cm^{-1}/min, and the

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total counts were collected for the time intervals that corresponded to a 0.5 cm^{-1} spectral interval. Six to eight spectra at each orientation were collected, and the digital output was stored on the Memorial University VAX 4500 computer. Spectra were signal averaged and smoothed twice with a Savitsky–Golay three-point smoothing function. A baseline program was applied which corrected the measured intensity, $I(\bar{\nu})$, for the fourth power scattering factor and normalized the spectra. These normalized $I(\bar{\nu})$ spectra (which should be independent of excitation intensity) must be further normalized to account for the temperature factor $B = [1 - \exp(-h\bar{\nu}c/kT)]$ and the frequency factor to give the R_Q spectra as shown in eq 1.

The reduced spectra are most important in the low-frequency region where the effect of temperature is most pronounced. The normalized isotropic spectra in R_Q format was constructed by the subtraction

$$R_Q(\bar{\nu})_{iso} = R_Q(\bar{\nu})_{\parallel} - {}^4/_3 R_Q(\bar{\nu})_{\perp} \quad (2)$$

Digitalized isotropic spectra in R_Q format (in the following text shortly R format) were fitted to a sum of Lorentzian–Gaussian product functions:[20]

$$f(\bar{\nu}) = \sum_{i=1}^{n} \frac{I_i \exp[-4 \ln(2)(\bar{\nu} - \bar{\nu}_i)^2/b_{Gi}^2]}{1 + 4(\bar{\nu} - \bar{\nu}_i)^2/b_{Li}^2} \quad (3)$$

where I_i are the band heights at the peak positions $\bar{\nu}_i$, b_{Gi}, and b_{Li} are the full widths at half height (FWHH) of the Gaussian and Lorentzian fractions of the bands and n the number of component bands.

The FWHH b_i of the two Lorentzian–Gaussian product functions were determined by an iterative procedure solving the nonlinear equation

$$0 = \frac{\exp(-\ln(2) b_i^2/b_{Gi}^2)}{1 + b_i^2/b_{Li}^2} - 1/2 \quad (4)$$

The Lorentzian–Gaussian shape ratio can be defined as $R = b_{Gi}/(b_{Gi} + b_{Li})$. Pure Lorentzian band shape character is obtained for $R = 1$ (in the case $b_{Gi} \gg b_{Li}$) and a pure Gaussian band shape for $R = 0$ (in the case $b_{Gi} \ll b_{Li}$).

Ab initio calculations (Hartree–Fock approximation) with the STO-3G,[21] 3-21G[22] and 6-31G* [23,24] basis sets were employed. The geometry was optimized with MUNGAUSS[25] by Davidon's Optimally Conditioned (OC) method,[26] and for incompletely converged structures the structure was further optimized with a version of Pulay's DIIS method.[27] The calculations were performed on a Silicon Graphics Indigo 2 workstation. Frequencies were calculated at the 3-21G and 6-31G* levels with Gaussian 86[28] on a VAX 4500.

3. Results and Discussion

The isotropic Raman spectra in the R format of LiCl solutions at 22 °C at three different mol ratios are given in Figure 1. Whereas in a saturated solution (mol ratio (R) LiCl:H_2O = 1:2.83) the spectrum showed two relative intensive bands centered at 204 and 376 cm^{-1}, in the more dilute solutions the high frequency band disappeared, and a shoulder was observeable at around 255 cm^{-1} on the high frequency side of the 204 cm^{-1} band.

Quite similar behavior was found in the R_α spectrum of a saturated LiBr solution (mol ratio LiBr:H_2O = 1:2.72) at 22 °C, where besides the 191 cm^{-1} band a high frequency band appeared at 342 cm^{-1}. The 342 cm^{-1} band also disappeared with dilution, as can be seen in Figure 2.

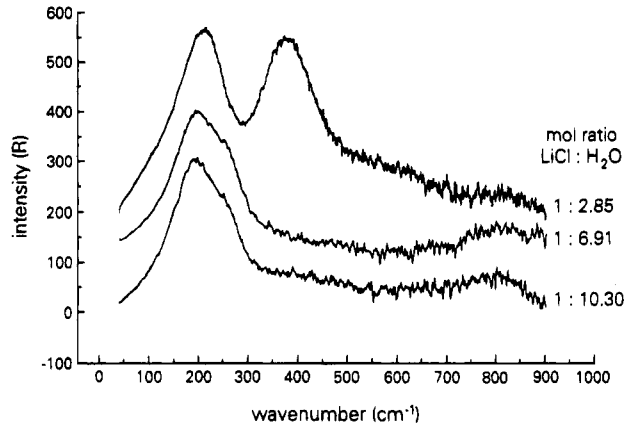

Figure 1. Isotropic Raman spectra in R-format for LiCl solutions at three different mol ratios LiCl:H_2O at room temperature between 40 cm^{-1} and 900 cm^{-1}.

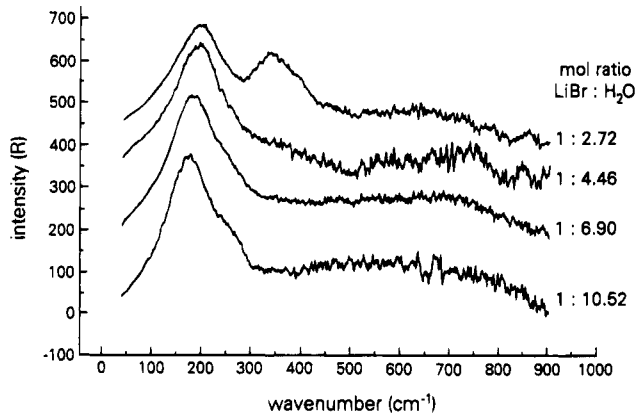

Figure 2. Isotropic Raman spectra in R-format for LiBr solutions at four different mol ratios LiBr:H_2O at room temperature between 40 cm^{-1} and 900 cm^{-1}.

TABLE 1. Results of the Band Separation procedure of LiCl Solutions in the Region 40–400 cm^{-1}

component	band position (cm^{-1})	H (au)[a]	FWHH (cm^{-1})[b]	area (au)
	LiCl (19.62 molal; R = 2.83)			
O–H···X	204	353	112	27 087
Li–Cl	376	301	117	24 110
libration	527	92	277	17 366
	LiCl (8.10 molal; R = 6.91)			
O–H···X	192	237	103	16 757
Li–O	260	88	64	3 930
libration	350	28	262	4 136
	LiCl (5.38 molal; R = 10.30)			
O–H···X	190	256	107	18 820
Li–O	260	70	54	2 635
libration	386	51	273	9 473

[a] H = peak height. [b] FWHH = full width at half height.

Besides these striking spectroscopic features, very broad bands of low intensity were also observed between 300 and 600 cm^{-1}. Quantitative results of the curve resolution procedure of the bands of LiCl solutions (mol ratio salt:H_2O = 1:2.83, 1:6.9 and 1:10.30) are presented in Table 1 and the results for LiBr solutions in Table 2.

The discussion of these spectroscopic results in LiCl and LiBr solutions are straightforward. The band around 200 cm^{-1}, is also seen in pure water. The frequency for pure water at room temperature is about 190 cm^{-1}. This band is moderately intense

TABLE 2. Results of the Band Separation Procedure of LiBr Solutions in the Region 40–600 cm^{-1}

component	band position (cm^{-1})	H (au)[a]	FWHH (cm^{-1})[b]	area (au)
	LiBr (20.40 molal; R = 2.72)			
O–H··X	191	265	113	20 539
Li–Br	342	159	112	12 272
libration	476	68	337	15 673
	LiBr (12.45 molal; R = 4.46)			
O–H··X	182	225	109	16 770
Li–O	260	27	50	912
libration	340.5	44	340	10 145
	LiBr (8.11 molal; R = 6.90)			
O–H··X	178	279	107	20 433
Li–O	259	42.7	64	1 870
libration	370	52.7	260	9 384
	LiBr (5.28 molal; R = 10.52)			
O–H··X	176	304	98	20 296
Li–O	256	83	70	4 2690
libration	570	107	533	39 070

[a] H = peak height. [b] FWHH = full width at half height.

TABLE 3. Results of the Band Separation Procedure of $LiClO_4$ Solution in the Region 40–400 cm^{-1}

component	band position (cm^{-1})	H (au)[a]	FWHH (cm^{-1})[b]	area (au)
O–H··X	187	8	111	614
Li–O	250	18.6	57	724

[a] H = peak height. [b] FWHH = full width at half height.

but slightly polarized and contributes only weakly in the isotropic spectrum. This band has been assigned as a restricted translatory mode of the hydrogen bonded water molecules connected mostly with the oxygen–oxygen O–H···O stretch about a relatively stationary hydrogen (see especially ref 18 and references therein). In highly concentrated lithium salt solutions ($(Li(OH_2)_nX$; X = Cl^-, Br^-, and ClO_4^-) other hydrogen bonds are important, namely OH···X^- (X^- = Cl^-, Br^- and ClO_4^-). In the most concentrated solutions the hydrogen bond configuration with X^- is most pronounced, but with dilution the OH···O configuration becomes more and more important and in fairly dilute solutions this band is more or less like that of water. The peak maxima are anion and concentration dependent with values for comparable 5 molal solutions of 190, 176, and 187 cm^{-1}; for O–H···X^- (X = Cl^-, Br^-, and ClO_4^-). The intensities and the depolarization properties are even more strongly anion dependent. Although the intensity of the band due to O–H···$OClO_3^-$ is very weak in the isotropic spectrum (similar to pure water), the intensity of the bands due to O–H···Cl^- and Br^- are very pronounced in the isotropic spectra. It would appear that the large polarizabilities of Cl^- and Br^- enhance the isotropic intensity of the mode associated with the hydrogen bond. From this qualitative consideration it follows directly that the region of the restricted translational band of water is strongly anion and concentration dependent (Tables 1–3) and unsuitable for creation of difference spectra for which the solvent is subtracted.

The very weak, broad bands in the region between 300 and 600 cm^{-1} were assigned to librational modes of the hydrogen bonded water molecules. The librational region of water and of alkali halide solutions was first studied by Walrafen,[17] and it was shown that only anions have a pronounced effect on the librational modes of water. No particular evidence of cation hydrates for alkali metal cations was detected. It should be pointed out that the librational bands are also very concentration dependent. The more dilute the solution, the more water-like are the librational bands (compare the frequency dependence

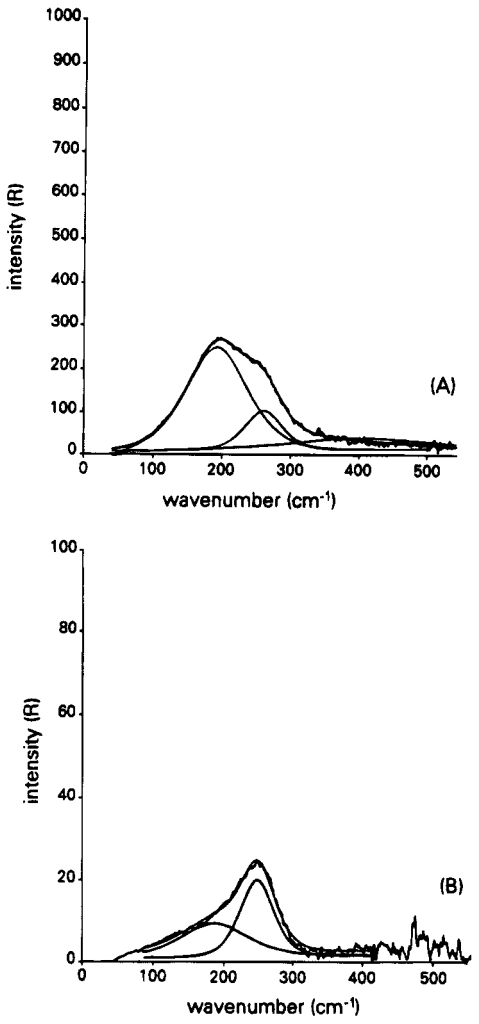

Figure 3. Raman spectra of R_{iso} for aqueous LiCl (mol ratio salt:water = 1:6.9) (A) and aqueous $LiClO_4$ (mol ratio salt:water = 1:10.50) (B). The best fit curve resolved components are indicated.

of the librational modes of water as a function of concentration in Table 1and 2).

The band at 376 cm^{-1} in a saturated LiCl solution (R = 1:2.83) is assigned to a Li–Cl vibration, because in this solution the water content is not high enough to form a complete first hydration sphere around Li^+, if we assume that n, the hydration number, is 4. This assignment is supported by the fact that in more dilute LiCl solution (LiCl:H_2O ≤1:6) this band disappears. The same behavior is true for LiBr solutions (see Figure 2) where the band at 342 cm^{-1} assigned as a Li–Br vibration also disappears with dilution (LiBr:H_2O ≤1:4). The band was found to remain at 376 cm^{-1} for a saturated solution of LiCl in D_2O, and this provides further evidence to indicate that the band at 376 cm^{-1} is due to the Li–Cl mode and is not affected by coordinated water (or heavy water).

The polarized band at 255 ± 5 cm^{-1} (FWHH = 60 ± 5 cm^{-1}) in LiCl and LiBr solutions with mol ratios LiX:H_2O (X = Cl^-, Br^-) ≤1:4 is assigned to the Li–O symmetric stretching mode of $Li(OH_2)_4^+$. In Figure 3A the R_α spectrum for a LiCl solution (R = 1:6.91) is given together with the component bands from the band fit.

In the R_α Raman spectrum for an aqueous $LiClO_4$ solution (R = 1:10.50) there is a well-defined polarized band at about 255 cm^{-1} with halfwidth of about 60 cm^{-1} (Figure 3B). The band is accentuated in the perchlorate solution, because the ClO_4^- disrupts the hydrogen-bond structure of water and causes a decrease in the relative intensity of the band due to the OH···X^-

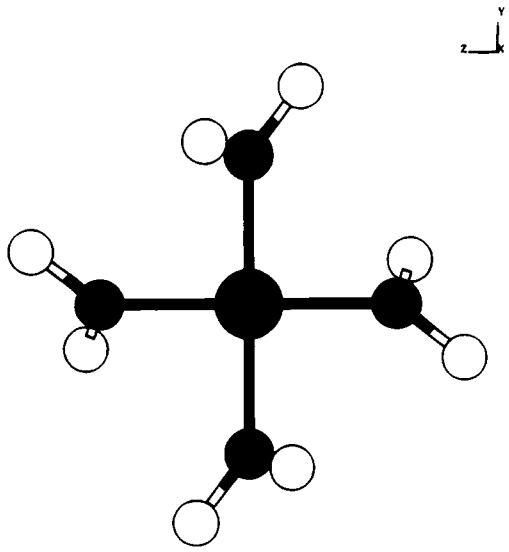

Figure 4. Structure of the $Li(OH_2)^{4+}$ ion.

stretching mode at about 187 cm^{-1}. The R_α spectrum is given in Figure 3B for a $LiClO_4$ solution (R = 1:10.50) together with the component bands from the curve resolution procedure.

In LiBr solutions the Br^- ion, on the other hand, enhances the intensity of the stretching mode O−H···X^- and the librational bands. Thus, in the LiBr solution with R = 1:4.46 the intensity ratio I_{182}:I_{260} is greater than in the solution with R = 1:6.90 and much greater in solution with R = 1:10.53. Bands due to the M−O stretching modes of aqueous divalent and trivalent cations have been identified (see ref 18 p 154ff), but the present work represents the first definitive result for an univalent cation.

Kanno[19] showed by a simple theoretical consideration (Born equation and linear harmonic oscillator model) a correlation between the symmetric stretching mode of $M-O_n$ (n = 4 , 6; with n being the number of water molecules in the first hydration sphere) and $\sqrt{z}/(r_{M-O})^2$, where z stands for the charge of the ion and r_{M-O} the bond distance r_{M-O}, equal to the equilibrium separation. From a recent neutron diffraction study of a 20% LiBr solution follows r_{Li-O} = 1.96 ± 0.02 Å.[6] The ν_1 mode of Li^+ and the r_{Li-O} value fit very well into this correlation.

Relative intensity measurements confirm that the Li−O mode is very weak. The S_h value for the ν_1 Li−O mode is 0.0035 using $\nu_1(a_1)$ ClO_4^- at 933 cm^{-1} as a reference band. The S_h value is defined as the corrected relative scattering efficiency of the M−O band and is given for a variety of stretching modes of $[M(OH_2)_n]^{m+}$ aqueous hydrates in ref 18 (it should be noted that the S_h values in ref 18 are compared to ν_1 NO_3^- and are taken as a percentage). As expected the S_h value for the Li−O mode is comparably smaller than the value for the Mg−O mode in $Mg(H_2O)_6^{2+}$ (S_h (Mg−O)= 0.0074[31]). The difference in the S_h value for Li^+ and Mg^{2+} reflects the difference in their polarizing power, P[18].

Computational Results.[32] The geometry of tetraaquolithium ion was optimized as described in the experimental section. C_2 symmetry was imposed initially, but the energy minimum was found to be of a more symmetrical point group, S_4. In Figure 4 the geometry of the tetraaquolithium ion is shown. Once an optimized geometry had been obtained, vibrational frequencies were obtained with Gaussian 86[28] both to confirm that the structure was indeed a minimum and to compare with experimental results. The geometrical parameters and the total energy are given in Table 4 for both basis sets employed.

The Li−O bond lengths calculated for these structures are 1.886 Å (3-21G) and 1.971 Å (6-31G*). The latter is remarkably close to the neutron diffraction results quoted above. It must be realized that the neutron diffaction measurements give r_a, (r_a means the averaged position of atoms at temperature of experiment) not r_e, and thus r_e would be somewhat shorter than r_a. In addition, the inclusion of correlation effects would probably change the calculated bond length. The unscaled frequencies for the symmetric stretching of the Li−O mode are 302 (3-21G) and 248 cm^{-1} (6-31G*). Applying a scaling factor of 0.9 to the 3-21G frequency gives 272 cm^{-1}, in reasonable agreement with our experimental result of 255 cm^{-1} but nowhere near a previously claimed result of 190 cm^{-1} [12,13] (this frequency is the frequency of the restricted translatory mode of the hydrogen bonded water molecules of O−H···O) or the result claimed by Nash et al.,[14] who observed the $\nu_1(a_1)$ mode at 440 cm^{-1} (this frequency of the symmetric stretch is higher than the frequency for most of the divalent metal ions; compare for instance the symmetric stretching frequency for $Cd(OH_2)_6^{2+}$ at 358 cm^{-1} in ref 29). The unscaled 6-31G* result is in close agreement with our experimental frequency. The ab initio data (6-31G*) provide firm and independent support for the assignment for the band at 255 cm^{-1}, and that the close agreement between the calculated Li−O bond length and the neutron diffraction results support the assignment of the species as $Li(OH_2)_4^+$. A paper summarizing our more extensive calculations on lithium water complexes, including the mono-, di-, tri-, tetra-, penta-, hexa-, octa-, and dodeca aquolithium species, is in preparation.

TABLE 4. Results of ab Initio Calculations of $Li(OH_2)_4^+$ Ion for Two Different Basis Sets

bond length r (Å)	3-21G	6-31G*
Li−O	1.8859	1.9713
O-H_1	0.9651	0.9501
O-H_2	0.9653	0.9503
angle Θ (deg)	**3-21G**	**6-31G***
$OLiO_1$	109.9	109.1
$OLiO_2$	109.3	109.6
$LiOH_1$	127.4	128.3
$LiOH_2$	122.2	124.5
H_1OLiO	39.2	39.4
H_2OLiO	134.0	132.4
energy (Hartree)	**3-21G**	**6-31G***
	−309.812 840	−311.472 424

4. Conclusions

The Raman spectra of aqueous lithium salt solutions were measured from saturation concentrations to more dilute concentrations. Saturated solutions of LiCl and LiBr display a polarized band at 380 and 335 cm^{-1}, respectively, which were assigned to a symmetric vibrational mode from an inner sphere complex $LiCl/Br(OH_2)_n^+$, where n is probably three. This band disappears on dilution, and a new polarized band at 255 cm^{-1} is assigned to the Li−O symmetric stretch of $Li(H_2O)_4^+$. Ab initio calculations at the 6-31G* level support the above assignment for the tetraaquolithium species, giving a frequency of 248 cm^{-1} and a Li−O distance of 1.971 Å.

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(32) Until recently, to the best of our knowledge, there have been no reports in the literature of ab initio calculations on $Li(OH_2)_n^+$ clusters larger than $n = 2$. In 1994 Feller et al.[30] published an extended basis set ab initio study of these clusters with $n = 1-6$. Our results are in very good agreement with the results given in ref 30, although for the tetraaquolithium cluster no frequencies were reported.

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