useful even for the qualitative interpretation of results obtained at distances near the energy minimum. The situation is certainly different for systems (e.g., $(LiH)_2$)[5] where overlap effects dominate. In such a case it is not possible to discuss the interaction energy near the equilibrium geometry in terms of the asymptotic expansion.

Conclusion

Equilibrium distances and force constants for the intermolecular stretching vibration and shifts of the intramolecular stretching vibration calculated with the IEPA method agree well with the values obtained with the more sophisticated CEPA and PNO–CI methods. The effect of electron correlation is very small for the geometries treated in this paper. From the discussion in the preceeding section it is clear that we do not expect in every case a vanishing influence of the correlation energy. Especially the corrections to the Coulomb interaction may modify the anisotropy of the intermolecular potential considerably.

We find negligible differences between the force constants of the intramolecular stretching vibration in the hydrogen bond and that of the isolated hydrogen fluoride. This fact supports previous experimental[31b,34,35] and theoretical[1,22,36] results that the observed

shifts of infrared absorption frequencies of 10–15% are due to higher polymers in the gas phase as well as in the liquid and that the properties of polymers larger than dimers cannot be explained from calculations of the dimer alone.[37]

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The Hydration Number of Li+

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Abstract: We present calculations on Li+ hydrates that predict that the preferential first coordination sphere of Li+ is tetrahedral.

In view of the current interest in ion hydration, we have examined[1] cation monohydrate potential surfaces as well as single points on the potential surfaces for cation di- and trihydrates. An important conclusion of the previous study was that one should be able to represent the energetics of $Li^+(H_2O)_n$ surfaces ($n > 3$) in terms of appropriate $Li^+(H_2O)$ and $Li(H_2O)_2$ surfaces. In this paper we explore this approach for calculation of the relative energies of lithium hexahydrates. Tetra- and pentahydrates are also considered. The general method involves *ab initio* calculations on $Li^+\cdots OH_2$ as a function of $R(Li\cdots O)$ and $Li^+\cdots (OH_2)_2$ and $H_2O\cdots H_2O$ surfaces as a function of R ($Li\cdots O$) and $\theta(OLiO)$. We have used the double ζ + polarization basis set previously[1] described. For $Li^+\cdots (H_2O)_2$ and $(H_2O)_2$ surfaces, we have done explicit calculations for $\theta = 90, 109° 28'$, and $180°$ (Table I) and interpolated assuming an exponential repulsion which is a function of the O–O separation to find the energy at $120°$. We then added up the $Li^+\cdots OH_2$, $Li^+\cdots (OH_2)_2$, and $OH_2\cdots OH_2$ energies as a function of

$R(Li\cdots O)$ for a particular coordination geometry. For example, the ΔE for the reaction $6H_2O + Li^+ \rightarrow Li^+(H_2O)_6$ (octahedral) was determined by the following expression[1] at different $Li\cdots O$ distances: $\Delta E = 6E^{(2)} (Li^+\cdots OH_2) + 3E^{(2)}(H_2O\cdots H_2O, \theta = 180°) + 12E^{(2)} (H_2O\cdots H_2O, \theta = 90°) + 3E^{(3)}(Li^+\cdots (OH_2)_2, \theta = 180°) + 12E^{(3)}(Li^+\cdots (OH_2)_2, \theta = 90°)$.

The results of such *ab initio* calculations are summarized in Table II and are compared with the experimental gas phase hydration energies.[2] We calculate directly the energy of two-, four-, and six-coordinated Li^+ hydrates as well as the minimum energy $Li^+\cdots O$ distance. Using our interpolated potential surfaces for $\theta = 120°$, we predict ΔE for $n = 3$ (trigonal) and 5 (trigonal bipyramid), assuming the axial $R(Li-O)$ equals the equatorial $R(Li-O)$.

What is the optimum coordination geometry for a given number of water molecules around Li^+? To answer this question one must compare the energies for different arrangements of the same number of water molecules and include the possibility that there might be an energetic preference for a water to be in the second

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Table I. Potential Surface for Li+···OH2 and Li+(OH2)2[a]

Li+···OH2		Li+···(OH2)2, θ = 180°		
R	−ΔE	R	−ΔE	ΔE'[b]
3.32	36.4	3.32	67.7	5.1
3.535	37.2	3.535	70.1	4.3
3.82	36.0	3.82	68.2	3.8
4.12	33.1			
4.52	28.9			

Li+···(OH2)2, θ = 109° 28'			Li+···(OH2)2, θ = 90°		
R	−ΔE	ΔE'[b]	R	−ΔE	ΔE'[b]
3.32	63.2	9.6	3.32	58.9	13.9
3.535	66.6	7.8	3.535	63.6	10.8
3.82	65.7	6.3	3.82	63.7	8.3
4.12	61.5	4.7	4.12	60.1	6.1

	Li+···(OH2)2,[c] θ = 120°			
R	−ΔE'[b]	A, kcal/mol	α, au⁻¹	R0, au
3.535	6.8	10.8	0.42	5.00
3.82	5.4	8.3	0.33	5.40
4.12	4.2	6.1	0.29	5.83

[a] Energies in kcal/mol relative to isolated Li+ + H2O + H2O distances in atomic units; see Figure 1 for geometries. [b] $\Delta E' = \Delta E - 2\Delta E(\text{Li}^-\cdots\text{OH}_2)$; $\Delta E' = E^{(2)}(\text{OH}_2\cdots\text{OH}_2) + E^{(3)}(\text{Li}^+\cdots 2\text{OH}_2)$. [c] Extrapolated from $\theta = 90$ and $109° \, 28'$ assuming an exponential repulsion of the form $E = Ae^{-\alpha(R-R_0)}$ where R is the O–O distance for $\theta = 120°$, R_0 is the O–O distance for the $\theta = 90°$ configuration, and A and α are found by fitting the $\theta = 90°$ and 109° 28' points.

coordination sphere instead of the first. We and others[1,3] have examined the energetics for the process Li+···OH2 + H2O → Li+···OH2···OH2 where the second water is forming a hydrogen bond to the first. Because Li+ makes the hydrogens of the water bound to it more positive, the second water can form a very strong hydrogen bond to the first ($\Delta E = -8.6$ kcal/mol vs. $\Delta E = -5.0$ for an isolated water dimer H bond); in addition there is a direct ion-dipole interaction of the Li+ with the further water ($\Delta E = -6.6$ kcal/mol).[1]

Using the *ab initio* potential surfaces for Li+···OH2···OH2 interactions and electrostatic calculations to determine the energy of interaction between water in the second coordination sphere and first coordination sphere waters not directly H bonded to them, we have calculated the ΔE for different Li+(H2O)$_n$ coordinations. In reference 3, for

$$\text{Li}^+\overset{R_1}{\cdots}\text{OH}_2\overset{R_2}{\cdots}\text{OH}_2$$

with R_2 at the optimum water dimer H bond distance of 3.0 Å, the net ΔE for the second coordination sphere water was −14.9, −13.8, and −11.7 kcal/mol at R_1 = 3.5, 4.0, and 5.0 au. Thus, we have used a linear interpolation for the ΔE for a second coordination sphere water starting with our calculated $\Delta E = -15.2$ kcal/mol at $R_1 = 3.535$ au and assuming a decrease in ΔE of −2.2 kcal/mol/au in the range from 3.5 to 4.5 au. There is no compelling reason for making a better approximation unless one optimizes the angular variables in the Li+···(OH2)a···(OH2)b surface which we have kept at the geometry of the optimum water dimer and Li+–OH2 complex.[1,3] The "electrostatic" calculations evaluated the two-body water–water interactions for waters in the second coordination sphere with waters not directly H bonded to them. We use a

(3) G. H. F. Diercksen and W. P. Kraemers, *Theor. Chim. Acta*, **23**, 387, 393 (1972).

monopole approximation, placing partial charges at the nuclei whose magnitude reproduced the calculated water dipole moment ($\mu = 2.23$ D). For example, at $r(\text{Li–O}) = 3.82$ au for a tetrahedral coordination of water around Li+, the electrostatic repulsion of a fifth water in the second coordination sphere with the three distant first coordination sphere waters is 0.5 kcal/mol per water or a total of 1.5 kcal/mol.

For Li+(H2O)6, one can imagine four possibilities: (1) six waters octahedrally coordinated to Li+, (2) five waters forming a trigonal bipyramid with the sixth in the second coordination shell H bonding to one in the first, (3) tetrahedral coordination to Li+ with two waters in the second coordination sphere, (4) trigonal coordination to Li+ with three waters in the second coordination sphere. Using our approach the tetrahedral coordination is the most favorable energetically. This is in contrast to the optimum coordination predicted by semiempirical MO methods,[4] which underestimate O···O repulsion and predict the optimal first coordination number of Li+ to be 6. The table also contains similar comparisons for different three, four, and five H2O coordination possibilities. CNDO/2 calculations[4] predict Li–O distances for tetrahedral and octahedral coordination of 4.55 and 4.71 au and ΔE (Li+ + nH2O → Li+(H2O)$_n$) = 163 kcal/mol for $n = 4$ and 217 kcal/mol for $n = 6$.

It is of interest to inquire whether a similar qualitative result would have been found if one had not included $E^{(3)}(\text{Li}^+\cdots(\text{OH}_2)_2)$ terms; *i.e.*, can one predict coordination numbers and energies considering the total interaction energy to be a sum of two-body energies? Using the approximation that the interaction energy is a sum of two-body energies the minimum energy *geometries* for octahedral and tetrahedral (+2H2O in the second coordination sphere) are similar to those in the table, but the hydration *energies* are −170 kcal/mol for octahedral and −150 for tetrahedral +2 waters in the second coordination sphere. Not only are these energies in the reverse order to those calculated including $E^{(3)}(\text{Li}\cdots(\text{OH}_2)_2)$, but they do not agree well with the experimental energy[2] for Li+ + 6H2O → Li+(H2O)6 ($\Delta E = -123$ kcal/mol). However, empirical two-body potential functions could probably be devised to incorporate this three-body repulsion in an exaggerated water–water repulsion term. Let us consider the magnitude and angular dependence of these three-body interactions. For example, at $R(\text{Li–O}) = 3.82$ au $E^{(2)}(\text{H}_2\text{O}\cdots\text{H}_2\text{O}, \theta = 90°) = 4.10$ kcal/mol, $E^{(2)}(\text{H}_2\text{O}\cdots\text{H}_2\text{O}, \theta = 180°) = 1.84$ kcal/mol, $E^{(3)}(\text{Li}^+\cdots(\text{OH}_2)_2, \theta = 90°) = 8.20$ kcal/mol, and $E^{(3)}(\text{Li}^+\cdots(\text{OH}_2)_2, \theta = 180°) = 3.66$ kcal/mol. Not only are the three-body terms of comparable magnitude to the two-body water repulsions, but they are very dependent on $\theta(\text{OLiO})$. If charge transfer effects (the second water sees a less positive Li+ than the first) were responsible for the large $E^{(3)}$, one would predict that $E^{(3)}$ would be not especially sensitive to $\theta(\text{OLiO})$. Polarization effects also cannot explain the θ dependence of $E^{(3)}$ since the changes in atomic polarities observed are much smaller than the original magnitudes of the polarities (for example, the Mulliken populations for the water H's are +0.32 in water and +0.40 in

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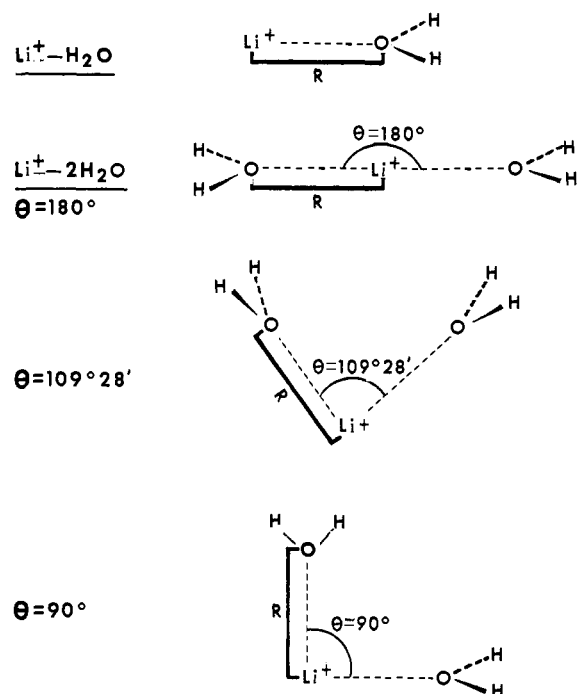
Li$^+$–H$_2$O

Li$^+$–2H$_2$O
$\Theta=180°$

$\Theta=180°$

$\Theta=109°28'$

$\Theta=90°$

$\Theta=109°28'$

$\Theta=90°$

Figure 1.

Li$^+$···OH$_2$). The only way the angle dependence of $E^{(3)}$ can be satisfactorily rationalized is through an important contribution to the nonadditivity of exchange repulsion terms, which one would expect to be sensitive to θ(OLiO).

These are a number of approximations in our calculations; we must consider how these might affect the calculated properties. First, is our *ab initio* basis set adequate? The calculated dipole moment of our H$_2$O molecule is somewhat too high (μ = 2.23 D vs. 1.82 D exptl)[1] and this provides some rationalization why our Li$^+$···OH$_2$ ΔE is 3 kcal/mol more attractive than experiment; with higher coordination numbers, the fact that the dipolar water–water repulsion is overestimated appears to compensate somewhat for excess Li$^+$···OH$_2$ attractions since our ΔE's compare well with the experimental energies,[2] with the exception of the energy for the reaction Li$^+$(H$_2$O) + H$_2$O → Li$^+$(H$_2$O)$_2$, where the experimental ΔH is 25.8 kcal/mol and the calculated ΔE = 33 kcal/mol. Based on the results for the lithium monohydrate, we expect the calculated ΔE to be ~29 kcal/mol, and the reason for the discrepancy is not obvious. The use of the correct dipole moment (1.82) for electrostatic calculations on both Li$^+$–H$_2$O and H$_2$O–H$_2$O interactions indicates that the larger dipole moment (2.23 D) does not appear to significantly alter the energy difference between octahedral and tetrahedral coordination. The most accurate calculation on Li$^+$···OH$_2$ yielded a ΔE of -35.2 kcal/mol at R-(Li–O) = 3.48 au.[5] Much empirical evidence indicates that the correlation contribution to closed shell intermolecular interactions involving polar systems is quite small.[6] The most drastic limitation in these studies is the restricted search over geometrical variables; for example, in the Li$^+$···(OH$_2$)$_2$ θ = 90° geometries the

external hydrogens were staggered to minimize the H···H repulsions for the octahedron; for the θ = 180° surfaces the hydrogens were all placed in the same plane. For the tetrahedral case, we used the energies from the geometry shown in Figure 1. If we consider the tetrahedral Li$^+$(H$_2$O)$_4$ and label the water molecules 1–4, water molecules 1 and 2 and water molecules 3 + 4 can have the relative H positions shown in the figure. In the other four combinations of H$_2$O···Li$^+$···OH$_2$ (*e.g.*, 1–3, 1–4, 2–3, 2–4) the hydrogens are skewed with respect to one another with no element of symmetry other than the identity element. To see if the skewed orientation of the hydrogens was energetically significantly different from the ones shown in the figure, we carried out one calculation at R = 3.82 au, θ = 109° 28', with skewed hydrogens and found an interaction energy (ΔE = -66.2 kcal/mol) slightly greater than that found with the hydrogens depicted in Figure 1. Thus, we expect that optimizing the hydrogen positions will not have a great influence on the interaction energies determined with "idealized" geometries. Our interpolation to find the θ(OLiO) = 120° surface is less accurate because of differences in the H positions for the θ surfaces. Computing long distance second coordination sphere–first coordination H$_2$O···H$_2$O repulsions electrostatically is also a severe approximation, but as indicated above these repulsions are quite small. Finally, the inclusion of higher body interactions may tend to favor the more open over the more tightly packed structures, although our results for Be^{2+}(OH$_2$)$_3$ indicate that the four-body Be^{2+}–3H$_2$O energy is attractive.

All of our considerations to this point have dealt with the gas phase hydrates. We find a tetrahedral first coordination sphere favored with five coordination and three coordination structures competitive. *In the liquid* a three-coordinated (trigonal) structure would leave a large cavity above and below the plane, so this structure would not be as important as first coordination spheres containing four and five water molecules.

Table II. Structure and Energetics of Li$^+$(H$_2$O)$_n$

n	Structure	R(O–Li), au	$-\Delta E$ (total)[a]	$-[(\Delta E)_n - (\Delta E)_{n-1}]$[a]	$-[(\Delta H)_n - (\Delta H)_{n-1}]$[b]
1	Linear	3.52	37	37	34.0
2	Linear	3.58	70	33	25.8
3	Trigonal	3.70	92	22	20.7
4	Tetrahedral	3.82	107	15	16.4
4	Trigonal + ext	3.70	105		
5	Tetrahedral + ext	3.82	120	13	13.9
5	Trigonal + 2 ext	3.70	118		
5	Trigonal bipyramid	4.10	114		
6	Tetrahedral + 2 ext	3.82	132	12	12.1
6	Trigonal + 3 ext	3.70	130		
6	Trigonal bipyramid + 1 ext	4.10	125		
6	Octahedral	4.30	119		

[a] This study, energies in kcal/mol. [b] Reference 2, energies in kcal/mol.

(5) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972).
(6) See, for example, P. A. Kollman, C. F. Bender, and S. Rothenberg, *J. Amer. Chem. Soc.*, **94**, 8016 (1972).

If the relative energies in Table II are correct, octahedral coordination should contribute negligibly to the liquid structure of Li^+ hydrates. The solvation enthalpy for Li^+ at $298°$ is -227.6 kcal/mol; one could imagine this is due to tetrahedral first coordination sphere water (-107 kcal/mol), second coordination sphere water (8×-10 kcal/mol), and a substantial contribution from more distant waters. Thus, we conclude that Li^+ has an important ordering effect on the water at least through the third coordination sphere.

If one makes the (very drastic) assumption that the $E^{(3)}(Na^+\cdots(H_2O)_2) = E^{(3)}(Li^+\cdots(H_2O)_2)$, one finds for Na^+ that octahedral coordination is approximately equal energetically to tetrahedral coordination plus two

external waters.[7] Further studies are in progress along these lines.

(7) We calculate a $\Delta E = -80$ kcal/mol for $Na^+(H_2O)_4$ ($R = 4.5$ au) and $\Delta E = -100$ kcal/mol ($R = 4.9$ au) for $Na^+(H_2O)_6$ octahedral with this very crude approximation. Reference 2 finds $\Delta E(Na^+ + 6H_2O \rightarrow Na(6H_2O))$ to be -92 kcal/mol. At the $Na^+\cdots OH_2$ separation of 4.5 au, we expect the attractive energy for a second coordination sphere to be $ca. -10$ kcal/mol, so one predicts the two coordination possibilities (tetrahedral + $2H_2O$ and octahedral) to be approximately equoenergetic.

A Simple Two-Group Model for Rayleigh and Raman Optical Activity

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Abstract: Rayleigh and Raman circular intensity differentials are calculated for a dissymmetric molecule comprised of two neutral optically inactive groups. The dominant mechanism has no counterpart in optical rotation, being of longer range than Kirkwood's dynamic-coupling interaction that leads to optical rotation. Differential scattering increases with increasing separation of the two groups, whereas optical rotation decreases. Predicted magnitudes are of the order of those observed. The signs of the effects give the absolute configuration of the molecule.

Recent theoretical and experimental work[1-6] has shown that optical activity can be studied through differential Rayleigh and Raman scattering of right and left circularly polarized light. The Raman experiment measures vibrational optical activity and provides information complementary to that obtained from the extension of optical rotatory dispersion and circular dichroism into the infrared, which has recently been observed for the first time in simple molecules.[7,8] Since optical activity increases with the frequency of the exciting light and vibrational frequencies are several orders of magnitude smaller than visible frequencies, vibrational optical activity is barely detectable through infrared rotatory dispersion and circular dichroism; it is accessible through the Raman CID (circular intensity differential) because the Raman effect provides vibrational spectra with visible exciting light. Also the large and interesting effects associated with skeletal vibrations occur at lower frequencies; it has not proved possible to extend infrared rotatory dispersion and circular dichroism into the far infrared, whereas Raman CID can give the entire vibrational optical activity spectrum with a single instrument.

In this article, Rayleigh and Raman CID's generated by a dissymmetric molecule comprised of two neutral optically inactive groups 1 and 2 are calculated. The dominant CID mechanism has no counterpart in optical rotation and circular dichroism, even in an anisotropic sample.[9] In the Kirkwood model the optical rotation generated by a dissymmetrically arranged pair of groups involves dynamic coupling between the groups;[10] only forward-scattered waves that have been deflected from one group to the other have sampled the dissymmetry and can generate optical rotation and circular dichroism on combining with the transmitted wave at the detector[11] (Figure 1). But the transmitted wave is unimportant in Rayleigh and Raman CID, so interference between waves independently scattered from the two groups provides chiral information (Figure 2). Dynamic coupling is not required, although it can make other less important contributions.

The relevant experimental quantity in Rayleigh and Raman optical activity is a dimensionless circular in-

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