Molecular Modeling Exercises and Experiments

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Interaction of Simple Ions with Water: Theoretical Models for the Study of Ion Hydration

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Molecular modeling is becoming a common component of inorganic chemistry courses. This usage is a consequence of the growing inclusion of computational techniques in all research fields. Some articles have appeared in this *Journal* that present molecular modeling exercises designed to show the bonding and acid–base properties of compounds *(1–3)*. We devised a computational experiment to examine the hydration of simple cations and show the geometrical and thermochemical parameters of the hydrated ions. Most undergraduate students have only a limited exposure to the application of molecular modeling to inorganic chemistry problems. This exercise offers a good first approach to the theoretical study of interesting systems.

The exercise is divided in two parts. In the first part, a structural study is performed for the species $M^{n+}(H_2O)$ where M = Li, Na, K, Be, Mg, Ca and n = 1 or 2. The influence of the charge and size of the cation on the M–O equilibrium distance is discussed, as well as the distortions on the water molecule caused by the cation. In the second part, the $\Delta_{hyd}H_{298}^{\circ}$ for the hydration reaction of the six metals is calculated. Finally, the performance of the different computational models is discussed.

Description of the Exercise

It is necessary to show the students how to build the system, choose the level of calculation, carry out geometry optimizations, and obtain the relevant information once convergence has been attained. No attempt is made to provide a description of the mathematical formalism and principles of physical chemistry involved in the theoretical models.[1] However, we recommend that the students use Hehre's book on molecular mechanics *(4)* to get a general idea of the information that can be obtained from this exercise and the limitations it has.

Molecular mechanics (MM) employing the MM+ force field, the semiempirical AM1 method, and the ab initio Hartree–Fock (HF) model with a small 6-31G* basis set are used for the structural studies. The Hyperchem program *(5)* is employed for these calculations because of its wide availability and the existence of an inexpensive student version. HF/6-31G* and the hybrid density functional (DFT) method B3LYP with the 6-31G* basis set are used for the thermochemical studies. The addition of the DFT method includes the correlation energy in a reasonably low-cost manner. Students are also provided with results obtained at a much more expensive level, MP2/6-311++G(3df,2pd), to make them aware of the limit values expected for the properties. To expose the students to an extra level of sophistication—introducing them to a different computer program—the Windows version of the Gaussian 03 program *(6)* is also employed for the calculations.

The singly charged ions (Li^+, Na^+, and K^+) and doubly charged ions (Be^{2+}, Mg^{2+}, and Ca^{2+}) are used as examples of simple ions. Water is employed as the solvent. The interaction of each ion with the solvent is studied through models that involve one to four water molecules. The students can be grouped in several manners: (a) to investigate singly charged or doubly charged cations, (b) by the method to be used, or (c) by the property to be determined. Repetition of calculations should be avoided. Summing up of the information should be the final step where the contributions of all the students are assembled in an open discussion. This last step is aimed to reinforce the concept of cooperation in science.

Part 1: Structural Studies

Purpose

The exercise shows the changes introduced by a simple ion on the water molecule in the first solvation sphere. The influence of the charge and size of the ion are explored, as well as the accuracy of the different computational methods.

Procedure

1. Systems are drawn, starting from a given cation and a single water molecule. It is stressed that the initial disposition of the components is not relevant for the final result.

2. The geometry of each system is optimized using molecular mechanics, semiempirical, and HF methods. The meaning of the gradient—the derivative of the energy with respect to the nuclear coordinates—is explained and the need to establish criteria for convergence is emphasized. Calculations are carried out to a gradient value of 0.01 kcal mol^{-1} $Å^{-1}$.[2]

3. It is discussed how the second derivatives of the energy with respect to nuclear coordinates give a method to verify that the optimized structure is actually a minimum instead of a transition-state structure and a fair approximation to the IR spectrum. A vibrational analysis is carried out for each of the complexes using the electronic-structure methods (AM1 and HF/6-31G*).

Results and Discussion

All geometry optimizations converge toward structures in which the ion interacts with the oxygen atom of the water molecules. This is the expected result; however, noting this with the students is prudent as some students build the initial structures with the water H atoms pointing to the cation. The latter cases can be used as examples of how convergence to the same structure is still attained but at a larger cost (more optimization cycles resulting in more computer time).

Selected geometrical parameters of the optimized structures are presented in Table 1. Not all data are generated by the students; some MP2 calculations using the extended 6-311++G(3df,2pd) basis set as an example of the limit of the theoretical procedures are generated by the instructors. Students are also referred to an article by Trachtman and co-workers *(7)* that addresses the same problem from a research point of view. AM1 results for Mg^{2+} and Ca^{2+} require the use of some nonstandard parameters *(8),* which may not be present in all versions of the Hyperchem program. These results should be given to the students.

Table 1. Selected Geometrical Parameters of the Isolated Water Molecule and the Water Molecule Interacting with Simple Ions

Water Species	Model	Distance of O–H/Å	Angle of HOH/deg	Distance of M–O/Å
H_2O	MM	0.942	104.5	–
	AM1	0.961	103.5	–
	HF[a]	0.947	105.5	–
	B3LYP[a]	0.969	103.7	–
	MP2[b]	0.959	104.1	–
$Li^+(H_2O)$	MM	0.942	104.5	1.89
	AM1	0.964	105.1	2.33
	HF[a]	0.954	106.4	1.86
	B3LYP[a]	0.973	105.9	1.84
	MP2[b]	0.963	104.9	1.86
$Na^+(H_2O)$	MM	0.942	104.6	2.19
	AM1	0.964	104.4	2.59
	HF[a]	0.952	105.6	2.21
	B3LYP[a]	0.972	104.9	2.19
	MP2[a]	0.962	104.1	2.27
$K^+(H_2O)$	MM	0.942	104.6	2.69
	AM1	0.964	104.2	2.76
	HF[a]	0.951	105.0	2.65
	B3LYP[a]	0.971	104.0	2.60
	MP2[a]	0.961	103.1	2.58
$Be^{2+}(H_2O)$	MM	0.942	104.6	1.65
	AM1	0.962	108.5	1.79
	HF[a]	0.982	108.3	1.50
	B3LYP[a]	1.003	108.1	1.50
	MP2[b]	0.989	107.6	1.50
$Mg^{2+}(H_2O)$	MM	0.942	104.5	2.11
	AM1[c]	0.961	103.6	2.36
	HF[a]	0.968	105.6	1.93
	B3LYP[a]	0.987	106.0	1.93
	MP2[b]	0.974	104.8	1.93
$Ca^{2+}(H_2O)$	MM	0.942	104.5	2.49
	AM1[c]	0.961	103.6	2.36
	HF[a]	0.961	104.2	2.33
	B3LYP[a]	0.980	103.7	2.31
	MP2[b]	0.971	103.4	2.24

[a]Obtained using the 6-31G* basis set. [b]Obtained using the 6-311++G(3df,2pd) basis set. [c]Parameters from ref *8*.

A result of this experiment is that the molecular mechanics method can be used to make reliable predictions of the relative disposition of the cation and the water molecule, but is useless for the prediction of changes within the solvent molecules. Structural changes on the water molecules in the first solvation shell are expected as a consequence of the interaction with the cation, and this modification is responsible for the relatively ordered second solvation shell, after which come the disordered region and the bulk solvent. Only methods that account explicitly for the electrons (electronic-structure methods) are able to show changes in the electron-density distribution induced by polarization by the cation. The results of electronic-structure calculations can be analyzed from several points of view that are discussed separately so that the concepts can be grasped appropriately by the students.

Reliability of Methods

Because the $M^{n+}(H_2O)$ complexes as such only exist in gas phase or rare-gas matrices, it is convenient to compare the student results with the theoretical limit values represented by the MP2 calculations. There are many ways of presenting and discussing these results, but we find plotting graphs showing the variation of the HOH angle and the M−O distance with the charge and size of the cation (Figure S1 in the online material) is the most instructive. Qualitatively all electronic-structure methods predict the same behavior: (a) increase of the cation size tends to close the HOH angle and to increase the M−O distance and (b) increase of the charge has the opposite effect (the angle increases and the distance decreases). Quantitatively, however, the AM1 method is not very reliable: all M−O distances are larger than the distances obtained with the more accurate methods, and the HOH angles are reasonable for the singly charged ions but not for Mg^{2+} and Ca^{2+}. The ab initio and DFT methods are almost coincident in the case of the M−O distances and maintain an almost systematic difference for different cations in the case of the HOH angle.

Physical Meaning of the Results

Ignoring the AM1 results for this analysis, one observes that the changes in the geometry of the complexes are in accordance with the polarization capability of the cation. The opening of the HOH angle and the decrease of the M–O distance depend on the charge *and* the size of the cation. Thus, increasing first the charge (Li^+ to Be^{2+}) and then the size (Be^{2+} to Mg^{2+}) produces complexes with relatively similar HOH angles (104.9° vs 104.8° at the MP2 level) and M−O distances (1.86 Å vs 1.93 Å at the MP2 level).

Ionic radius is a property that varies with the charge and size of the ion. This exercise allows us to investigate whether any correlation exists between the calculated M−O distances and the ionic radius of the metals. The M−O data calculated at the three electronic-structure levels (HF, B3LYP, and MP2) are com-

pared with the ionic radii (Table 2). A correlation between the calculated M−O distances, $d_{(M-O)}$, and the ionic radii is found, R_M. A regression equation using the MP2/6-311++G(3df,2pd) results can be expressed as $d_{(M-O)}/Å = 1.18R_M/Å + 1.02$, with a regression coefficient $R^2 = 0.97$. Interestingly, one can calculate the effective ionic radius of oxygen in the complexes as the difference between the calculated M−O distance and the ionic radius of the metal. The MP2 values of the oxygen vary between a minimum of 1.05 Å and a maximum of 1.25 Å, with an average of 1.18 Å, compared with the value of 1.27 Å for O^{2-}. The students can be prompted to discuss whether the ionic radius is a constant property for a given ion or depends on the counterion.

The different polarization capabilities can be examined from an electronic point of view. The results arising from a standard population analysis such as Mulliken are useful to describe changes in the electronic density by condensing it into point charges at the nuclei. The change in electronic density after complex formation can be examined with the help of the results presented in Figure 1. The presence of a cation interacting with the solvent induces a shift in the electronic density in the direction of the oxygen atom. This shift affects the O−H bond distance because most of the bonding orbitals contribute to the O−H bond *(9)*. The effects on the HOH angle can be rationalized by taking into account that the shift of the electronic density to the O atom produces an increase in the repulsion of the bonding electron clouds, causing an opening of the HOH angle. Alternatively, the electronic displacement can be discussed through the change in the shape of the HOMO orbital (see the online material).

Table 2. Calculated M–O Distances and Ionic Radii of the Metals

Cation	Ionic Radius/Å	M–O Distance/Å		
		HF	B3LYP	MP2
Be^{2+}	0.45	1.50 (1.05)	1.50 (1.05)	1.50 (1.05)
Mg^{2+}	0.72	1.93 (1.21)	1.93 (1.21)	1.93 (1.21)
Li^{+}	0.76	1.86 (1.10)	1.84 (1.08)	1.86 (1.10)
Ca^{2+}	1.00	2.33 (1.33)	2.31 (1.31)	2.25 (1.25)
Na^{+}	1.02	2.21 (1.19)	2.19 (1.17)	2.27 (1.25)
K^{+}	1.38	2.65 (1.27)	2.60 (1.22)	2.58 (1.20)

NOTE: The values in parenthesis correspond to the ionic radius of oxygen in each complex.

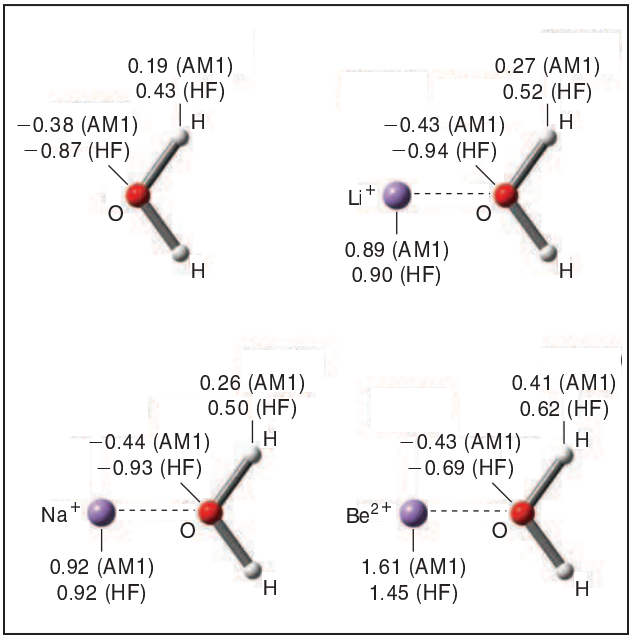

Figure 1. Mulliken population results for the water isolated and interacting with simple ions obtained with the AM1 and HF/6-31G* methodologies.

Part 2: Thermodynamical Studies

Purpose

The purpose of the second part of the exercise is to explore some thermochemical aspects of the interaction of the cations with water molecules. The exercise is carried out using two models: (a) one applied for each ion with one water molecule, and (b) one applied to Li^+ and Be^{2+} with more than one water molecule. The reactions studied are the complexing of the cation with one to four water molecules. We will call them "hydration reactions", bearing in mind that it is actually only a way of speaking, the process actually being gas phase. The ab initio Hartree–Fock procedure and the DFT B3LYP method were both used with the 6-31G* basis set. The MP2/6-311++G(3df,2pd) results are included for comparison purposes but are not calculated by the students. All of the results are compared to experimental data.

Procedure

1. The first step is already done in the first part of the exercise: optimizing the geometry of the complexes and verifying that the optimum structures are actually minima. Because a vibrational analysis was performed, the necessary information to calculate thermodynamic data is already available for the 1:1 complexes.

2. The second step is to extend the previous optimizations to the $Li^+(H_2O)_n$ complexes with $n = 2$, 3, and 4 and the $Be^{2+}(H_2O)_4$ complex. This step is intended to provide further insight into the structure of the first solvation shell, as it is well known that Li and Be cations have four water molecules in this shell *(10)*.

3. The third step implies the compilation of the absolute enthalpies at room temperature ($H_{298}°$) from the previous calculations and to calculate the enthalpy of reaction using the HF and B3LYP models. MP2 and experimental results *(10–12)* are given. To calculate the enthalpy change involved in the interaction of the solvent with the ion ($\Delta_{hyd}H_{298}°$), the following hydration reactions are used:

$$M^{n+}(g) + mH_2O(g) \rightarrow M^{n+}(H_2O)_m(g) \qquad (1)$$

where n is the charge of the cation and m is 1 to 4 depending on the model studied.

Results and Discussion

The thermodynamic information[3] is extracted from the vibrational analysis of the equilibrium geometries. Geometries of the $M^{n+}(H_2O)_m$ complexes are not discussed in great detail, other than showing the main characteristics of the spatial disposition of the water molecules around the cation (tetrahedral, trigonal, linear).

The use of semiempirical methods for this type of calculation is discussed. Because AM1 has been parametrized to reproduce enthalpies of formation, the calculated AM1 heats of formation can, in principle, be used directly to calculate the enthalpies of reaction. To illustrate the point, the enthalpy of one of the complexes is calculated and the results are shown to be poor, thus explaining why the method is not even considered for this task.

The results obtained with the three methods (HF, B3LYP, and MP2) as well as the experimental results for the 1:1 cation–water complexes are shown in Table 3. Similar data for the 1:*n* $Li^+(H_2O)_n$ n = 1, 2, 3, 4 and the $Be^{2+}(H_2O)_4$ complexes are shown in Table S1 in the online material. There are several observations from this experiment. Firstly, as the students should expect from their previous knowledge, the hydration reactions are strongly exothermic. There is no need to perform any theoretical calculation to arrive at this result because it is obvious from the experimental data, but it is instructive to have the data collected and to show that they are qualitatively coherent. Secondly, the computational results are reasonably similar to the experimental data. Relative errors are shown in Table 3 and it should be noted that at the best theoretical level employed, errors are below 10% except in the case of potassium. Thirdly, even the simplest method, HF/6-31G*, gives results that are semiquantitatively correct. The observation that the correlated method (B3LYP), which uses the same basis set, gives worse results, while the correlated method (MP2), with a much larger basis set, improves the data to the point that they are better than the HF ones, can be used to explain the importance of balance in the theoretical methods employed and that for these complexes correlation energy is not exceedingly important. The influence of basis set superposition error (BSSE) on the results obtained with the smaller basis sets can be discussed. Generally, the goal should be to show that the complexes can be described appropriately as charge–dipole complexes.

Table 3. Thermodynamic Results of the Interaction of a Water Molecule with First and Second Group Cations

Complex	Method	$-\Delta_{hyd}H_{298}°$/ (kcal/mol)	Error (%)
$Li^+(H_2O)$	HF/6-31G*	38.6	13.5
	B3LYP/6-31G*	41.4	21.8
	MP2/6-311++G(3df,2pd)	33.6	1.1
	Exp[a]	34.0	
$Na^+(H_2O)$	HF/6-31G*	27.9	16.3
	B3LYP/6-31G*	30.3	26.3
	MP2/6-311++G(3df,2pd)	22.3	7.1
	Exp[a]	24.0	
$K^+(H_2O)$	HF/6-31G*	19.6	9.5
	B3LYP/6-31G*	21.5	20.1
	MP2/6-311++G(3df,2pd)	15.0	16.2
	Exp[a]	17.9	
$Be^{2+}(H_2O)$	HF/6-31G*	145.6	0.4
	B3LYP/6-31G*	154.6	5.7
	MP2/6-311++G(3df,2pd)	142.5	2.5
	Exp[b]	146.2	
$Mg^{2+}(H_2O)$	HF/6-31G*	83.4	2.0
	B3LYP/6-31G*	90.1	10.1
	MP2/6-311++G(3df,2pd)	79.8	2.4
	Exp[b]	81.8	
$Ca^{2+}(H_2O)$	HF/6-31G*	55.2	2.3
	B3LYP/6-31G*	59.2	4.8
	MP2/6-311++G(3df,2pd)	55.0	2.7
	Exp[b]	56.5	

[a]The experimental value are taken from ref *11*.
[b]Experimental values from ref *12*.

Information can be gleaned from the way the results vary with the size and charge of the cation. Students may be encouraged to graph the enthalpy of formation of the complexes versus the size of the cation separately for the singly and doubly charged ions or to discuss the tendencies directly from the data in Table 2. Whichever procedure is followed, the following trends should be noted:

1. The enthalpy of hydration increases (i.e., it is less negative) with the size of the cation, independently of the charge.
2. The enthalpy of hydration decreases (i.e., is more negative) as charge increases.
3. The beryllium complex seems to have a more negative enthalpy of hydration than what could be expected extrapolating from the Mg and Ca complexes.

Finally, the students are encouraged to study the hypothesis that these complexes can be explained using a charge–dipole electrostatic interaction description. They are reminded that in these types of complexes the energy of interaction should correlate linearly with $1/d_{(M-O)}^2$. This is shown in Figure 2. Only

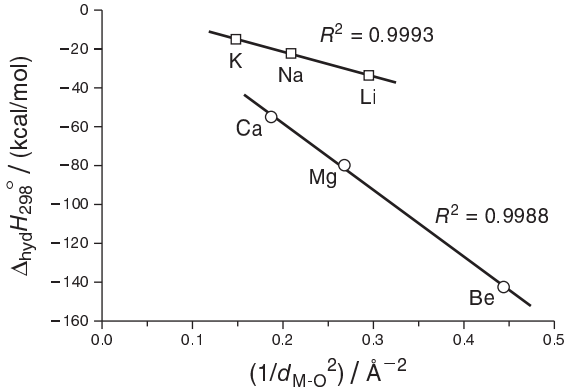

Figure 2. Correlation between the enthalpies of hydration of the 1:1 complexes and the square of the reciprocal optimum distance between the cation and the oxygen atom in the water molecule. Only the MP2/6-311++G(3df,2pd) results have been plotted.

the MP2 results are used, but the data from the other methods could also be used. Clearly the correlation between $\Delta_{hyd}H_{298}^{\circ}$ and $1/d_{(M-O)}^{2}$ is high, as shown by the correlation coefficients, and the data points are segmented according to the charge of the cations. This fact, taken together with the lack of importance of the correlation energy, serves to highlight that the interaction is mainly electrostatic (something that may or may not be the case with ions that do not have the noble gas-like structure of the present ions).

An additional step in the exercise is to analyze the difference between the 1:1 cation–water complexes and a complex where the full first solvation shell of the cation has been filled. This is described in the online material.

Conclusions

We present a computational experiment to systematically analyze models of simple cation hydrates. Both the physical implications of the results and the internal consistency of the theoretical models are discussed. It is shown that the electronic-structure theoretical models can describe the variation in the dependence of the geometry of water molecules in the first solvation sphere with the change in both the charge and size of the ions. Data show the behavior of the complexes as ion–dipole systems. It is also shown that the hydration reactions are exothermic, but that additional water molecule interacting with the ion is progressively less exothermic. This lays the basis for discussing first and additional solvation shells.

The need to carefully compare the results from molecular modeling with more accurate results, if available, is stressed. The ability of the computational models to predict accurate properties is demonstrated and it is shown that simple methods can provide qualitatively and even semiquantitatively correct results; however, this is not true in all models and in all cases. While electronic-structure methods are reasonably precise, MM and AM1 methods can be employed only for qualitative assessment of relative spatial disposition of the cation and the water molecules, not for accurate determination of the properties. In particular, the results show that simple HF calculations with a small basis set are able to predict the trends in the periodic table and can thus be used for exploratory purposes before any in-depth and much more costly calculations are undertaken. The exercise provides a simple example in which the interactions are governed by electrostatics, for which reason correlation energy is not a determinant factor in the calculations. However, the exercise also shows how the accumulation of small errors can lead to a large discrepancy between the calculated and experimental results for larger complexes unless the more sophisticated methods of calculation are used.

Notes

1. Such a description would be appropriate if the exercise were incorporated in a physical chemistry or molecular modeling course.

2. It is pedagogically important to show the students that an optimization with a simple method (MM) prior to the optimization with the more expensive one (HF/6-31G*) results in a time reduction for the total procedure. Although with modern computers and such small systems this is only of academic interest, the procedure is certainly relevant for actual research in much larger systems.

3. The students are briefly reminded of basic statistical thermodynamics information from the general chemistry course (how to calculate enthalpies from total energies using translational, rotational, and vibrational contributions for atoms and molecules).

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