Energies and Geometries for Ion-Water Complexes Using Quantum Chemistry Calculations

RM-MSMSP 2012 RET – Computational Chemistry

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Background Information

• Intermolecular interactions of water result in its physical properties
• Water has a pivotal role in solution and biochemistry as it relates to industrial and life systems
• The structures of ions in solution is not well understood and experimental data is difficult to obtain making computational simulations essential
• Power of computational models increasing with technology (Predictive process)

Krekeler, C., Hess, B., & Site, L. (2006). Density functional study of ion hydration for the alkali metal ions (Li+,Na+,K+) and the halide ions (F-,Br-,Cl-). Journal Of Chemical Physics, 125(5), 054305. doi:10.1063/1.2218338

Research Goals

• Identify the most stable geometry for Ion-Water Complexes with 1,2,3, & 4 water molecules
  – Cations
    • Lithium (Li⁺)
    • Sodium (Na⁺)
    • Potassium (K⁺)
  – Anions
    • Flouride (F⁻)
    • Chloride (Cl⁻)
    • Bromide (Br⁻)
Technical Details

- Spartan program for numerically solving the Schrödinger equation to calculate
  - Optimized complex geometry
  - Atomic partial charge at the ion
  - Complex binding energies

- Moderate theory level and basis set
  - Møller-Plesset perturbation theory (MP2)
  - Basis Set of 6-31G(D)
  - Provides adequate degree of accuracy
    - Error bar calculated to be +/- 6 Kcal/mol
  - Requires less time than higher theory levels and basis sets
Technical Details

- Equation used to calculate binding energy:
  \[ E_{\text{binding}} = E_{\text{complex}} - \left[ E_{\text{ion}} + n_{\text{water}} E_{\text{water}} \right] \]

- Online energy converter used to determine Boltzmann population based on relative energies when there was more than one stable geometry identified

  http://www.colby.edu/chemistry/PChem/Hartree.html
Accomplishments/Results
General Stable Geometry for Anion-Water Complexes for n=1

Distances are measured in angstroms (Å). $\alpha$ is defined by the H1, O1, H2 angle formed by the water. A single water molecule is 105°.

<table>
<thead>
<tr>
<th>Anion</th>
<th>d</th>
<th>$\Delta \alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>1.3</td>
<td>-6</td>
</tr>
<tr>
<td>Chloride</td>
<td>2.2</td>
<td>-5.6</td>
</tr>
<tr>
<td>Bromide</td>
<td>2.5</td>
<td>-5.5</td>
</tr>
</tbody>
</table>
General Geometries for Anion-Water Complexes for $n=2$

Distances are measured in angstroms (Å). Angles $\alpha$ and $\beta$ are defined by the H1-O1-H2 bonds and H3-O2-H4 bonds respectively.

<table>
<thead>
<tr>
<th>Anion</th>
<th>d1</th>
<th>d2</th>
<th>$\Delta \alpha$</th>
<th>$\Delta \beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>1.53</td>
<td>1.48</td>
<td>-7.30</td>
<td>-6.7</td>
</tr>
<tr>
<td>Chloride</td>
<td>2.71</td>
<td>2.19</td>
<td>-8.02</td>
<td>-4.94</td>
</tr>
<tr>
<td>Bromide</td>
<td>2.72</td>
<td>2.41</td>
<td>-4.75</td>
<td>-4.91</td>
</tr>
</tbody>
</table>
Stable Geometries for Anion-Water Complexes for n=3

<table>
<thead>
<tr>
<th>Anion</th>
<th>d1</th>
<th>d2</th>
<th>d3</th>
<th>Δα</th>
<th>Δβ</th>
<th>Δθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>2.59</td>
<td>2.59</td>
<td>2.59</td>
<td>-7.3</td>
<td>-6.7</td>
<td>-7.7</td>
</tr>
<tr>
<td>Chloride</td>
<td>3.27</td>
<td>3.27</td>
<td>3.27</td>
<td>-5.2</td>
<td>-5.2</td>
<td>-5.2</td>
</tr>
<tr>
<td>Bromide</td>
<td>3.35</td>
<td>4.62</td>
<td>3.36</td>
<td>-4.3</td>
<td>-2.4</td>
<td>-3.8</td>
</tr>
</tbody>
</table>

Distances are measured in angstroms (Å) and are defined by d1:O1-X, d2:O2-X, and d3:O3-X. X=(F, Cl, Br). Angles α, β, and θ are defined by the H1-O1-H2 bonds, H3-O2-H4 bonds H5-O3-H6 bonds respectively.
Stable Geometries for Anion-Water Complexes for n=4

Distances are measured in angstroms (Å) and are defined by d1:O1-F, d2: O2-F, d3: O3-F, and d4: O4-F. Angles α, β, and θ are defined by the H1-O1-H2 bonds, H3-O2-H4 bonds H5-O3-H6 bonds respectively.
General Stable Geometry for Cation-Water Complexes for n=1

Distances are measured in angstroms (Å). \( \alpha \) is defined by the H1, O1, H2 angle formed by the water. A single water molecule is 105°.
Stable Geometries for Cation-Water Complexes for n=2

Distances are measured in angstroms (Å) and are defined by O1-Y and O2-Y distances. \( Y = (\text{Li}^+, \text{Na}^+, \text{K}^+) \). Angles \( \alpha \) and \( \beta \) are defined by the H1-O1-H2 bonds and H3-O2-H4 bonds respectively.

<table>
<thead>
<tr>
<th>Cation</th>
<th>d1</th>
<th>d2</th>
<th>Δα</th>
<th>Δβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>1.94</td>
<td>1.94</td>
<td>-3.6</td>
<td>-3.6</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.25</td>
<td>2.25</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.62</td>
<td>2.62</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
Stable Geometries for Cation-Water Complexes for n=3

<table>
<thead>
<tr>
<th>Cation</th>
<th>d1</th>
<th>d2</th>
<th>d3</th>
<th>Δα</th>
<th>Δβ</th>
<th>Δθ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>3.27</td>
<td>3.27</td>
<td>3.27</td>
<td>-4.3</td>
<td>-4.2</td>
<td>-4.3</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.29</td>
<td>2.29</td>
<td>2.29</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.62</td>
<td>2.64</td>
<td>2.64</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Distances are measured in angstroms (Å) and are defined by O1-Y, O2-Y and O3-Y distances. Y = (Li⁺, Na⁺, K⁺). Angles α and β are defined by the H1-O1-H2 bonds and H3-O2-H4 bonds respectively.
Stable Geometries for Cation-Water Complexes for $n=4$

<table>
<thead>
<tr>
<th>Cation</th>
<th>d1</th>
<th>d2</th>
<th>d3</th>
<th>d4</th>
<th>Δα</th>
<th>Δβ</th>
<th>Δθ</th>
<th>Δφ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>3.95</td>
<td>1.82</td>
<td>3.93</td>
<td>1.91</td>
<td>+0.3</td>
<td>+4.0</td>
<td>+0.3</td>
<td>+0.9</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.65</td>
<td>4.51</td>
<td>2.64</td>
<td>2.63</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Distances are measured in angstroms (Å) and are defined by O1-Y, O2-Y, O3-Y and O4-Y distances. Y = (Li⁺, Na⁺, K⁺). Angles α and β are defined by the H1-O1-H2 bonds and H3-O2-H4 bonds respectively.
Binding Energies of Anion-Water Complexes

\[-E_{\text{binding}}\  \ \text{kcal/mol}\]

\[n_{\text{water}}\]

- Fluoride
- Chloride
- Bromide
Binding Energies of Cation-Water Complexes

$-E_{\text{binding}} \text{ kcal/mol}$

$n_{\text{water}}$

- Lithium
- Sodium
- Potassium
Unexpected Findings

• Geometry of water molecules varies between different ion-water complexes
• Larger ions are less likely to be bonded with water
• Ion is more stable in complexes that include more water molecules
• In ion-water complexes the net charge of the ion shifts
Challenges

• Developing research plan
• Managing use of time due to duration of computer calculations
• Consistency in data collection
• Organizing data in systematic manner
• Making meaning of data
• Limited prior content knowledge
Current and Future Applications of Computational Chemistry

- Development of new polymers
- Evaluate the ‘wear’ of polymer coatings
- Structure based drug design
  - Treatment for cancer
  - New antibiotics
- Identify functions of specific proteins
- Analyze atmospheric interactions
- Etc.
In the Classroom

• Use of Spartan software to present chemistry concepts and molecular structure to students

• Give students time
  – Explore new concepts
  – Develop hypothesis
  – Develop system for analysis
  – Work through frustrations
  – Enjoy success
Conclusion

• Transferring role from teacher to learner
• Difficult concepts become more manageable over time with effort and repetition
• Project results found to be very similar to previously published results