Solvent effects on optical activity

Jason Lambert
University of Tennessee
Department of physics
Outline

- Optical activity
  - Chirality
  - Circular Dichroism
  - Optical Rotation
- General Solvent effects
- Solvent effects Specific to Optical Activity
- Modeling of Solvent effects on optical activity
- conclusion
Chirality
Chirality in Chemistry
Optical Rotation & Circular Dichroism

- Inherently related by the Kronig-Kramer's relation.

\[ \epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \]

\[ \Delta \theta = \frac{2\pi \Delta n}{\lambda} \]

\[ \Delta \epsilon = \epsilon_l - \epsilon_r \]
Circular Dichroism & Optical Rotation

\[ \alpha_{ij} = \frac{2}{h} \sum_k \frac{\omega \langle n | \mu_i | 0 \rangle \langle 0 | \mu_j | n \rangle}{\omega_n^2 - \omega^2} \]

\[ \beta_{ij} = -\frac{2}{h} 3 \sum_k \frac{\omega \langle n | \mu_i | 0 \rangle \langle 0 | m_j | n \rangle}{\omega_n^2 - \omega^2} \]
General Solvent effects

- Hydrogen Bonding
- Dipole Dipole Interactions
- Dipole induced Dipole interactions
- Van Der Waals Forces
- Conformational Stabilization
- Protonation, deprotonation, ions, etc.
Solvent Effects

- Solvochromatic shifting
- Resolution Alterations
- Sign changes


Solvent Effects

Watheq Ahmad Al-Basheer, Linear and Nonlinear Chiroptical Effects, 2006

\[ \alpha = k \alpha_{MBA} + (1 - k) \alpha_{MBA^+} \]

Fischer, A. T.; Compton, R. N. & Pagni, R. M.
Solvent Effects on the Optical Rotation of (S)-(−)-α-Methylbenzylamine
The Journal of Physical Chemistry A, American Chemical Society, 2006, 110, 7067-7071
Solvent effects.

<table>
<thead>
<tr>
<th>Relative energy between conformers in solvents</th>
<th>Joules/mole</th>
<th>cyclohexane</th>
<th>DMSO</th>
<th>methanol</th>
<th>acetone</th>
<th>acetonitrile</th>
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</thead>
<tbody>
<tr>
<td>equatorial 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>equatorial 2</td>
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<td>2507.35</td>
<td>2444.34</td>
<td>2461.93</td>
<td>2486.09</td>
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<td>equatorial 3</td>
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<td>1769.59</td>
<td>1727.32</td>
<td>1781.67</td>
<td>1742.02</td>
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</table>
Induced Chirality

Figure 2. Illustration of the computational test carried out in Ref. [9] to decompose the optical rotation of the solute and solvent shell. The optical rotation sampled over snapshots of the solute and solvent is comparable when calculated for the full system (solute + solvent; left) or for the empty solvent shell only (solute removed from the snapshots; right). Graphics were created with the program VMD.\textsuperscript{[15]}

Modeling Solvent Effects

- Polarization continuum Models
- Empirical Solvent Parameters
- Coupled Molecular Mechanics and Quantum chemistry calculations.
Empirical Parameters

- Predict the solvent effects on optical activity by using known solvent quantities.
  - Dipole moments
  - Polarizabilities, etc
  - Solvoochromatic absorption shift.
Polarization Continuum Model

- First constructs a cavity of interlocking spheres to make “solvent exclusion zone”
- Moves spherical cavity along surface to probe solute solvent interactions.
PCM Model Continued

- Cavitation Energy
- Dispersion Repulsion (Van der Waals forces)
- electrostatic (dipole dipole etc)

http://www.science.uva.nl/research/molphot/MM08files/MM08_intro/Gaussian_solvent.pdf
Molecular Mechanics

- Good for optimizing large systems
- Couple with QM calculations required for the calculation of ORD.
- May be needed to predict less intuitive solvent effects
Results

United Atom Topological Model (UA0 parameters set).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Methanol</th>
<th>Eps</th>
<th>32.630000</th>
</tr>
</thead>
</table>

1st derivatives : Analytical V*U(x)*V algorithm (CHGder, D1EAlg=0).

Cavity : GePol (RMin=0.200 OFac=0.890).

Solution method : Matrix inversion.

Charge compensation : None.

Polarization charges : Total charges.

Atomic radii : UA0 (Simple United Atom Topological Model).

Model : PCM.

Polarizable Continuum Model (PCM)

- Added spheres: 41.35  0.038  -1.85  0.00  0.00
- Sphere on Atom  Surface  Charge  GEl   GCav  GDR

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Repulsion energy : (kcal/mol) = 0.64
Dispersion energy : (kcal/mol) = -13.57
Cavitation energy : (kcal/mol) = 18.60
Total non electrostatic : (kcal/mol) = 5.68

(Polarized solute)-Solvent : (kcal/mol) = -9.74

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
<th>Surface</th>
<th>GEl</th>
<th>GCav</th>
<th>GDR</th>
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<tr>
<td>C1</td>
<td>0.04</td>
<td>0.000</td>
<td>0.00</td>
<td>0.09</td>
<td>0.00</td>
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<tr>
<td>C2</td>
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<td>-0.005</td>
<td>0.00</td>
<td>0.29</td>
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<td>C3</td>
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<td>-0.19</td>
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<td>-0.29</td>
<td>1.94</td>
<td>-1.49</td>
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<tr>
<td>C6</td>
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<td>-0.64</td>
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<td>-1.51</td>
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<tr>
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<td>-1.19</td>
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<td>-0.029</td>
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<td>0.41</td>
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<tr>
<td>C9</td>
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<td>0.000</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
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<tr>
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<td>40.83</td>
<td>-0.041</td>
<td>-0.33</td>
<td>3.61</td>
<td>-2.28</td>
</tr>
</tbody>
</table>

Added spheres: 41.35  0.038  -1.85  0.00  0.00
Conclusion

- The Basis of chirality was discussed
- Circular dichroism and optical rotation were examined.
- General solvents are the only way a solvent effects the optical activity of a solute
- More exotic effects could be examined where the an achiral solvent has a large contribution to the optical activity