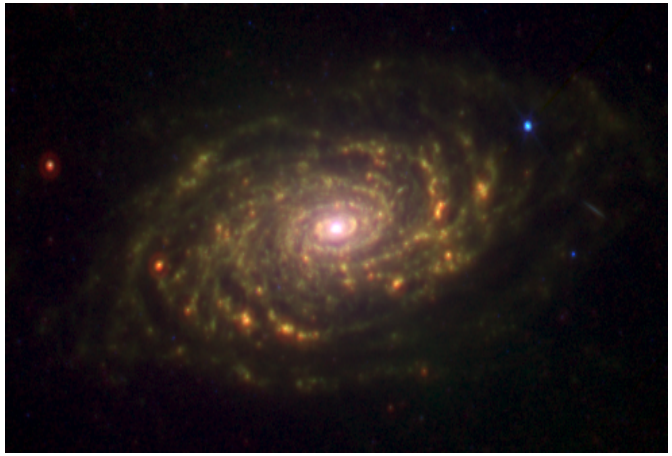
Solvent effects on optical activity

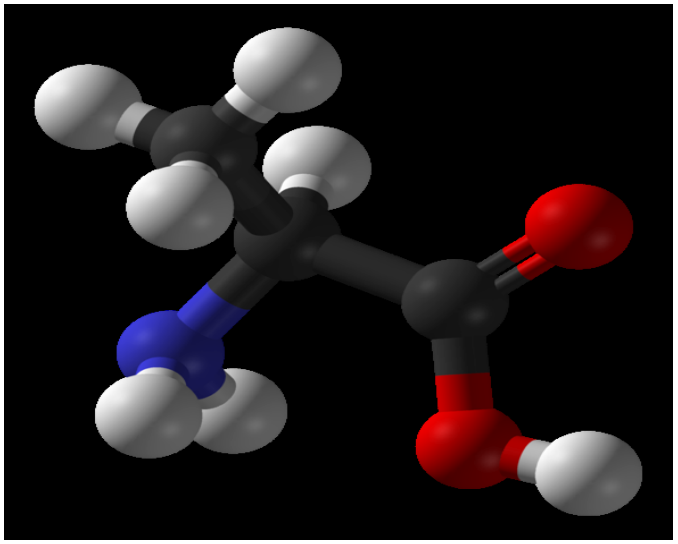
Jason Lambert
University of Tennessee
Department of physics

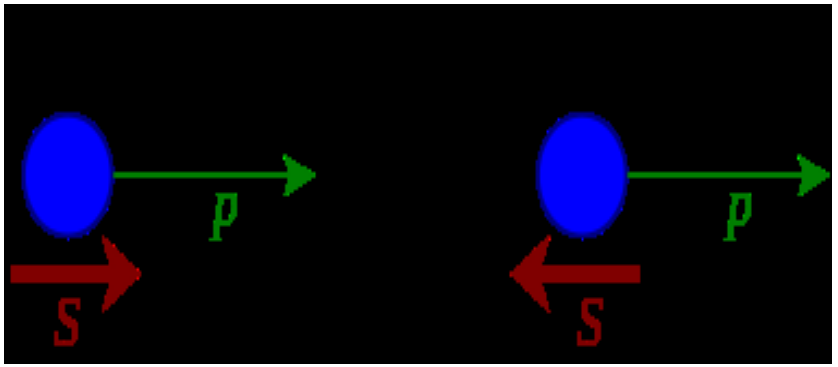
Outline

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

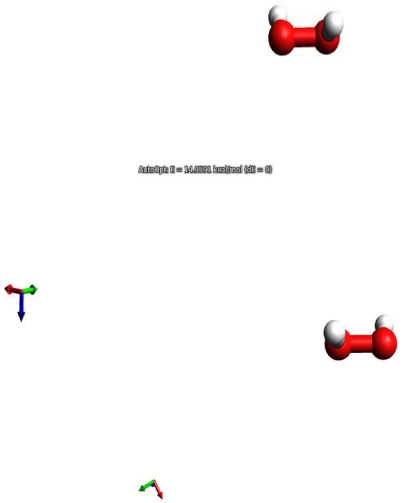
Chirality

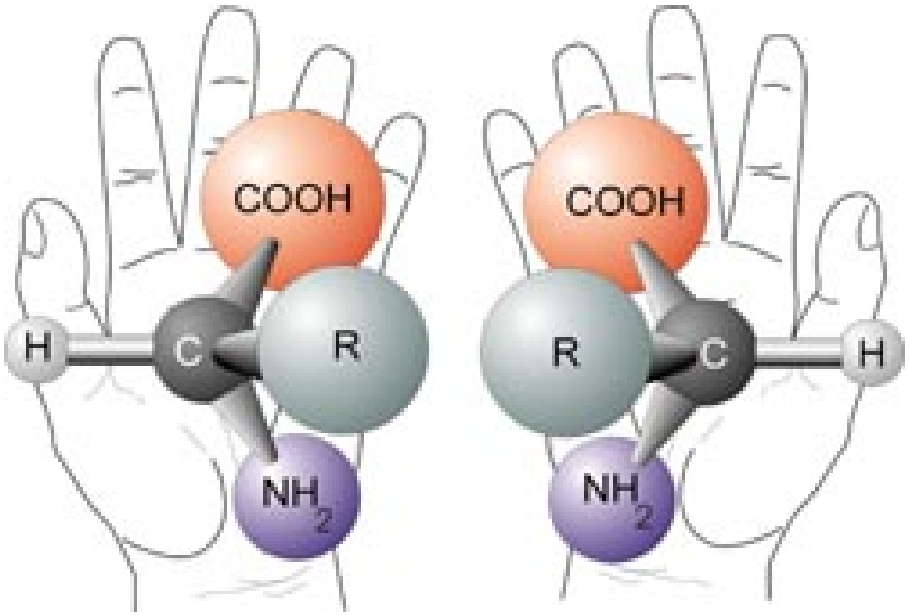






Chirality in Chemistry

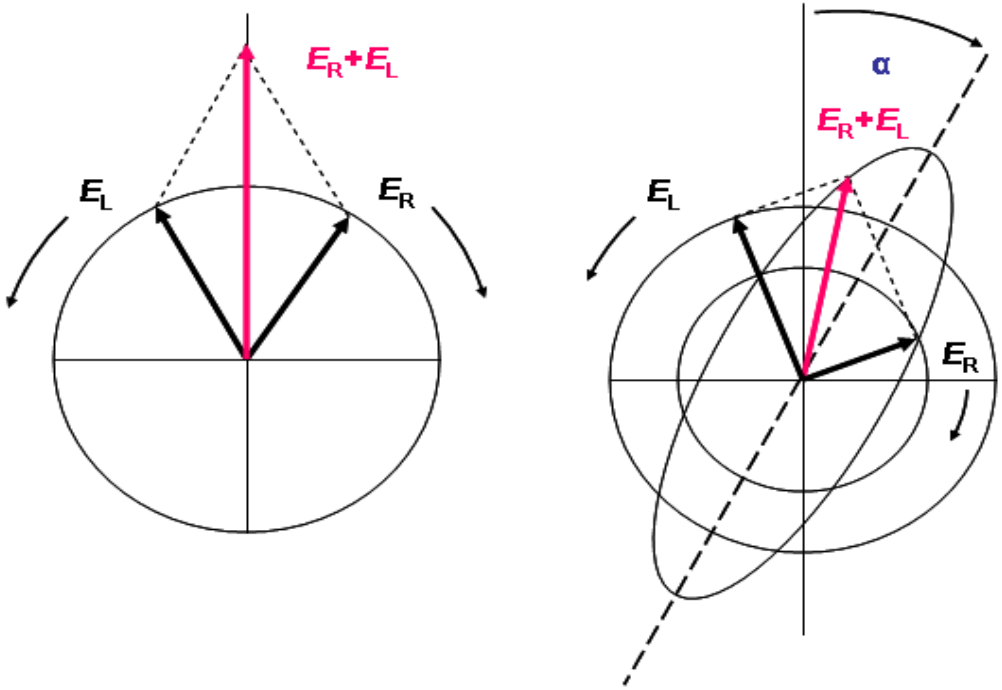




Optical Rotation & Circular Dichroism

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

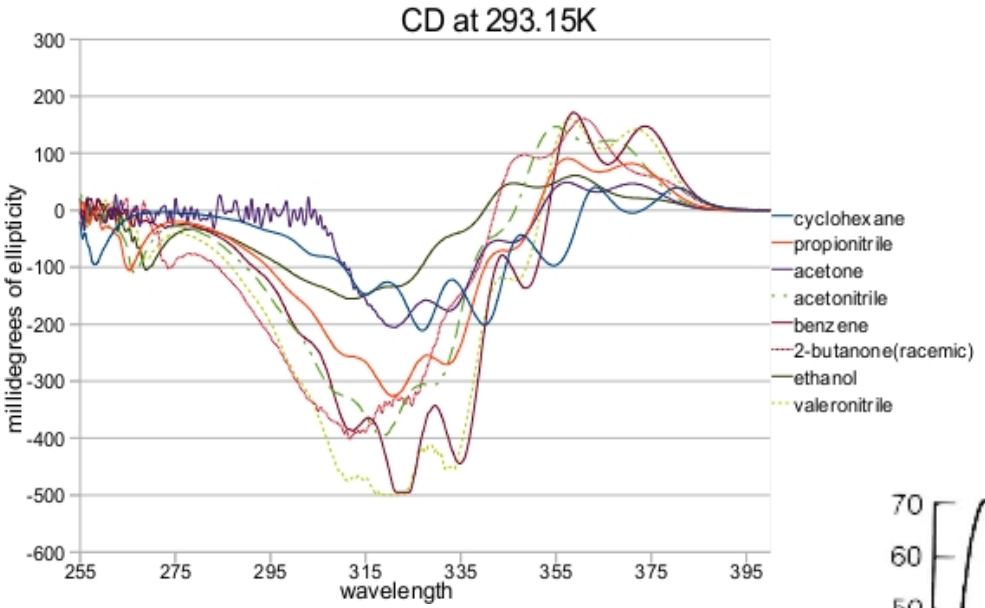
$$\epsilon(\omega)=\epsilon'(\omega)+i\epsilon''(\omega)$$

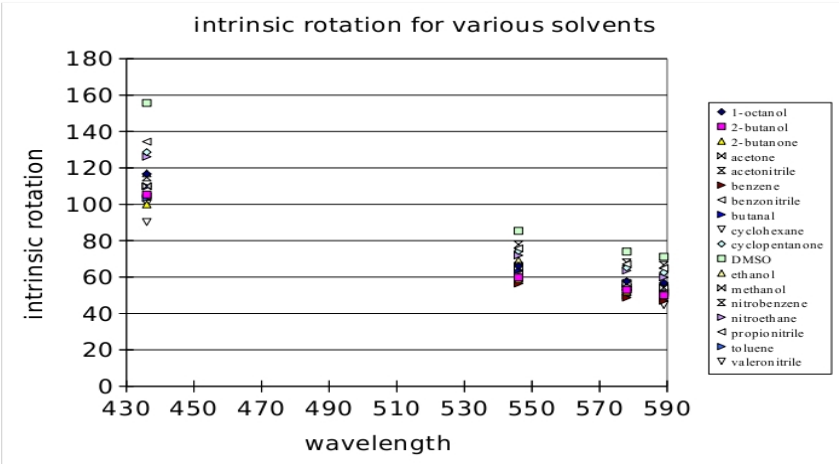


$$\Delta\theta=\frac{2\pi\Delta n}{\lambda}$$

$$\Delta\epsilon=\epsilon_l-\epsilon_r$$

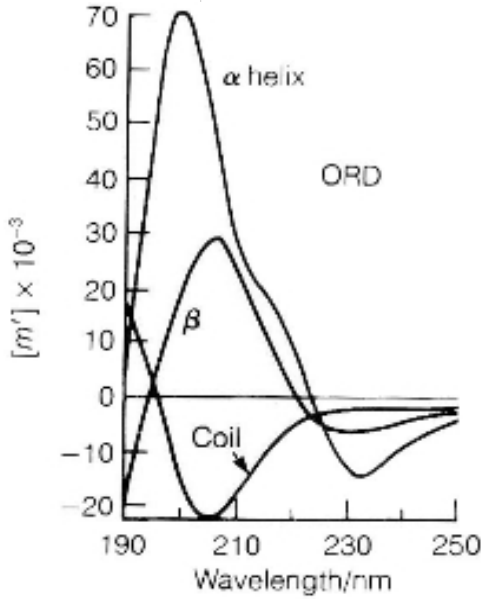
Circular Dichroism & Optical Rotation

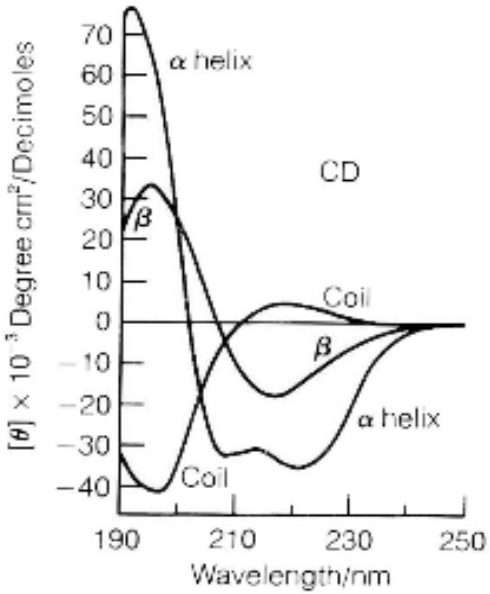




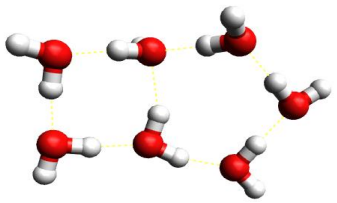
$$\alpha_{ij} = \frac{2}{\hbar} \sum_{k} \frac{\omega_{n0} \langle n|\mu_i|0\rangle \langle 0|\mu_j|n\rangle}{\omega_{n0}^2 - \omega^2}$$

$$\beta_{ij} = -\frac{2}{\hbar} \Im \sum_{k} \frac{\omega_{n0} \langle n|\mu_i|0\rangle \langle 0|m_j|n\rangle}{\omega_{n0}^2 - \omega^2}$$

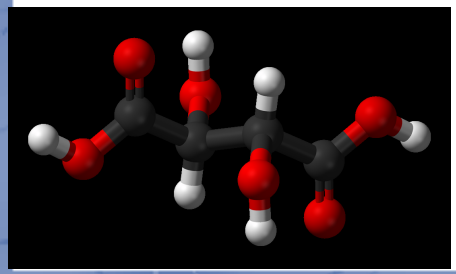




General Solvent effects



- 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

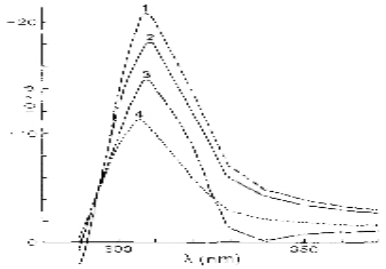


Figure 1. ORD spectra for (from top to bottom) dimethyl sulfoxide, acetonitrile, benzene, and methanol.

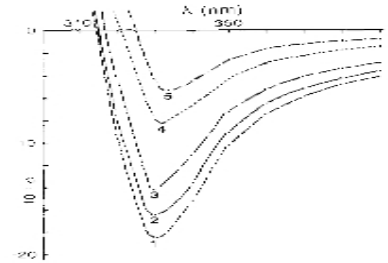
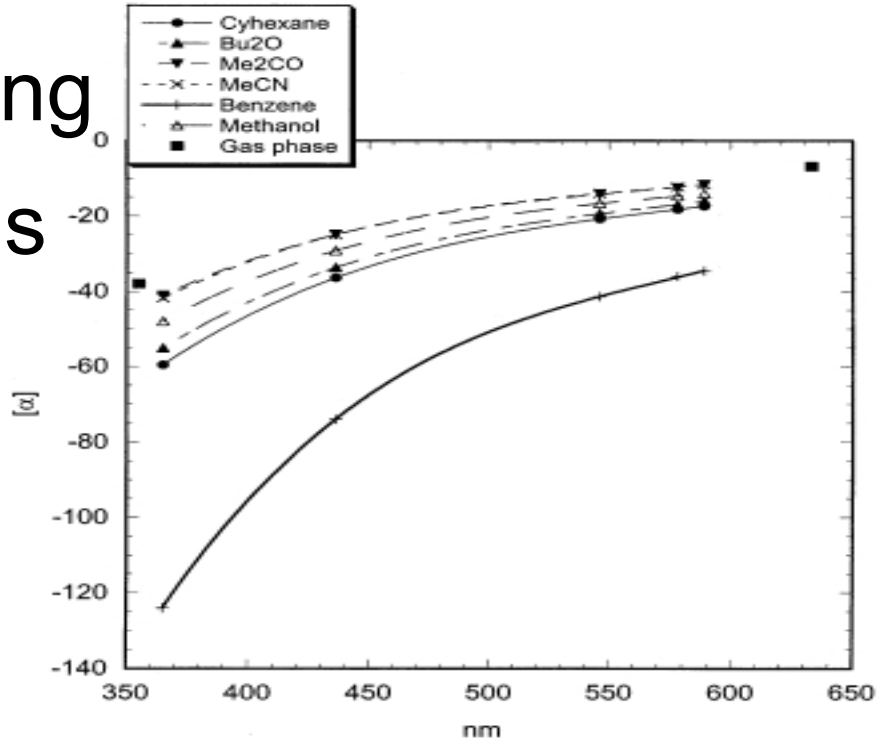


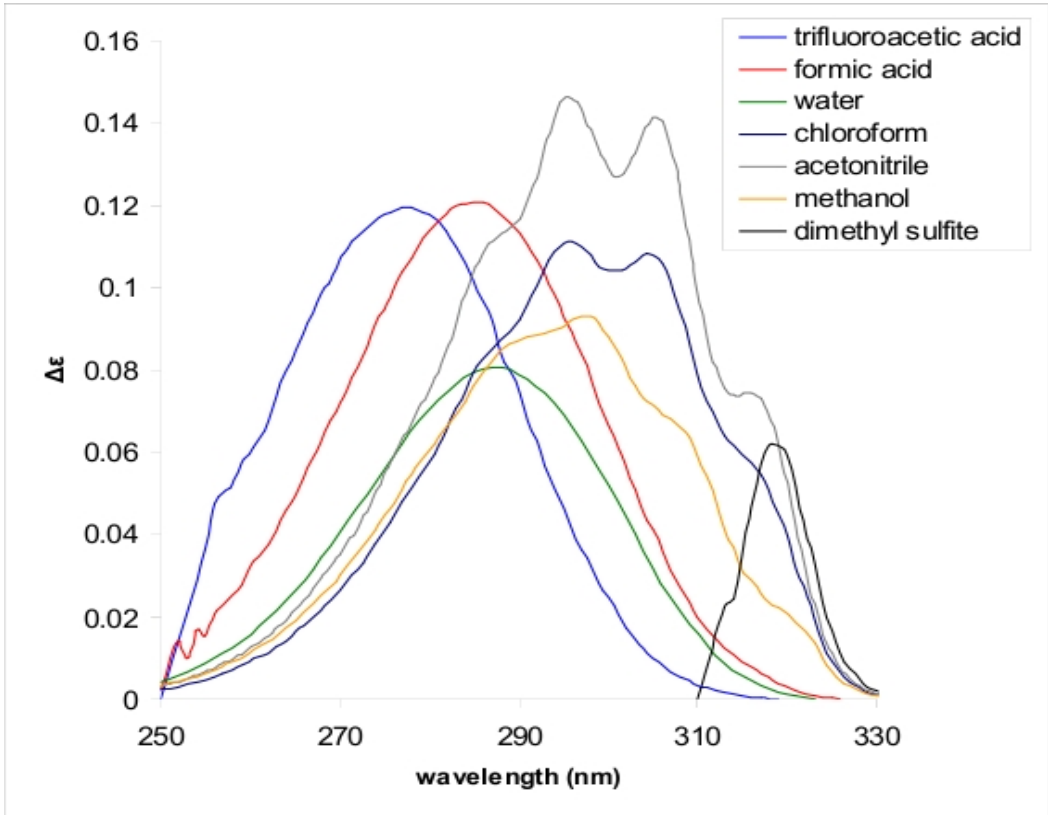
Figure 2. ORD spectra for (from bottom to top) cyclohexane, *n*-octane, carbon tetrachloride, *n*-butyl ether, and ethyl ether.



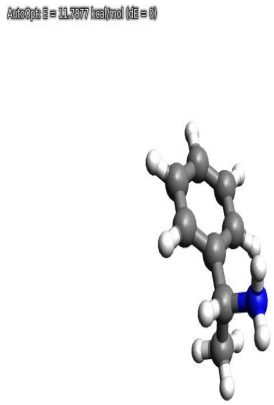
Kenneth Wiberg, Yi-gui Wang, Shaun M. Wilson, Patrick H. Vaccaro, James R. Chees "Chiroptical Properties of 2-Chloropropionitrile," J. Phys. Chem. A 109, 3448-3453(2

F. M. Menger, B. Boyer, "Solvent effects on conformation-dependent optical rotatory dispersion spectra," J. Org. Chem. 49, 1826-1828(1984)

Solvent Effects



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



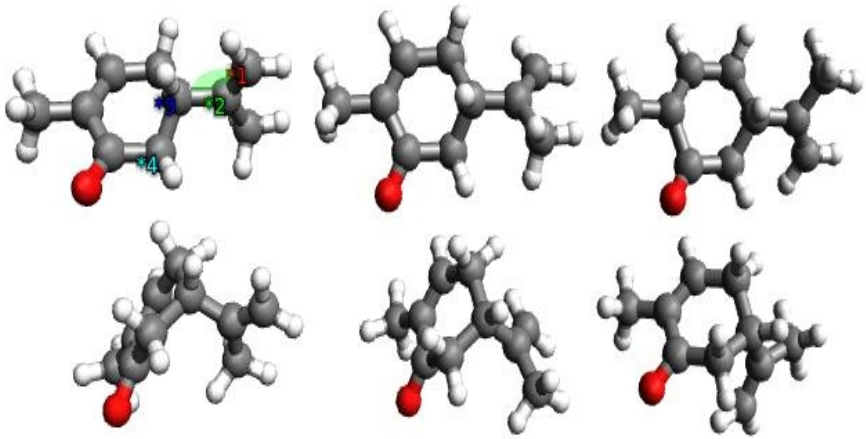
$$[\alpha] = k[\alpha]_{MBA} + (1-k)[\alpha]_{MBA^+}$$

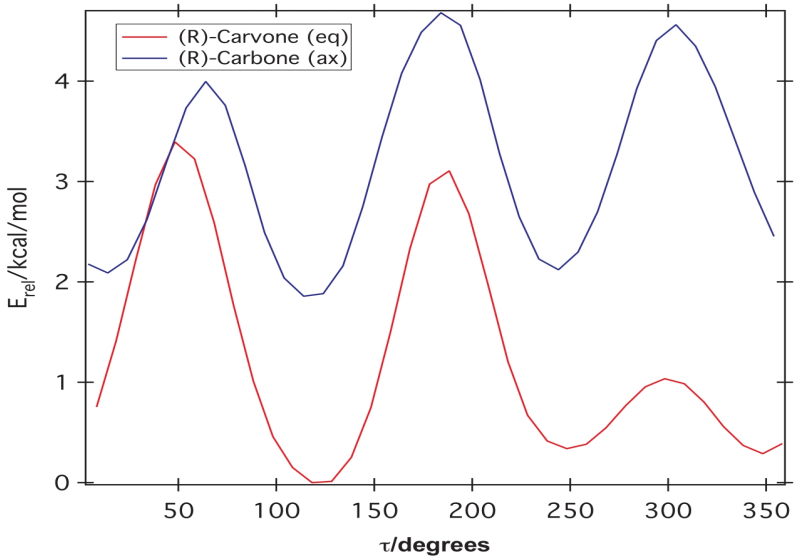
Fischer, A. T.; Compton, R. N. & Pagni, R. M.

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.





relative energy between conformers in solvents					
Joules/mole	cyclohexane	DMSO	methanol	acetone	acetonitrile
equatorial 1	0	0	0	0	0
equatorial 2	1980.94	2507.35	2444.34	2461.93	2486.09
equatorial 3	1604.97	1769.59	1727.32	1781.67	1742.02

Induced Chirality

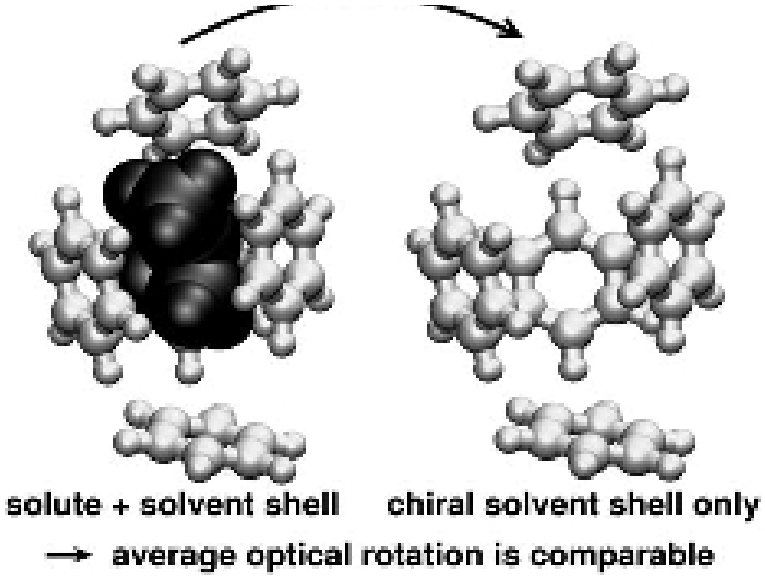


Figure 2. Illustration of the computational test carried out in Ref. [9] to decompose the optical rotation of the solute and solvent shell. The optical rotation sampled over snapshots of the solute and solvent is comparable when calculated for the full system (solute + solvent; left) or for the empty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

Johannes Neugebauer, "Induced Chirality in Achiral Media—How Theory Unravels Mysterious Solvent Effects," Angew. Chem. Int. Ed. 46, 7738-7740(2007).

Modeling Solvent Effects

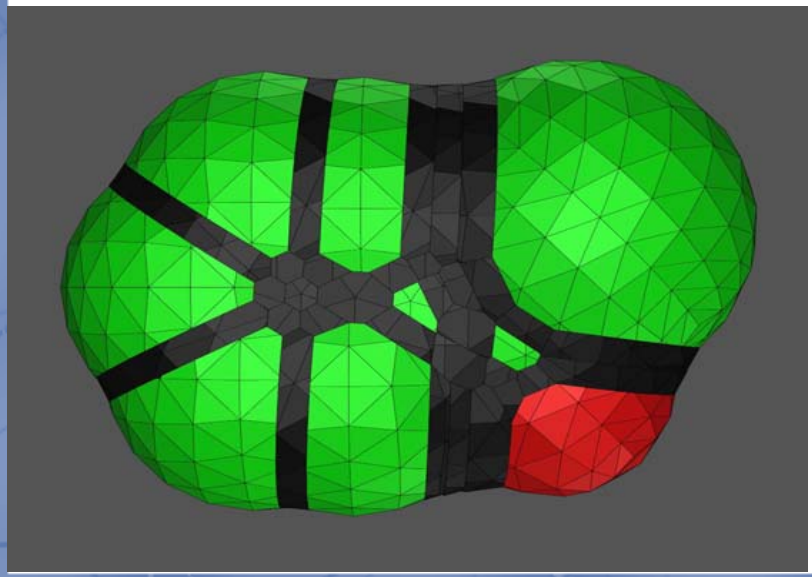
- Polarization continuum Models
- Empirical Solvent Parameters
- Coupled Molecular Mechanics and Quantum chemistry calculations.

Empirical Parameters

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

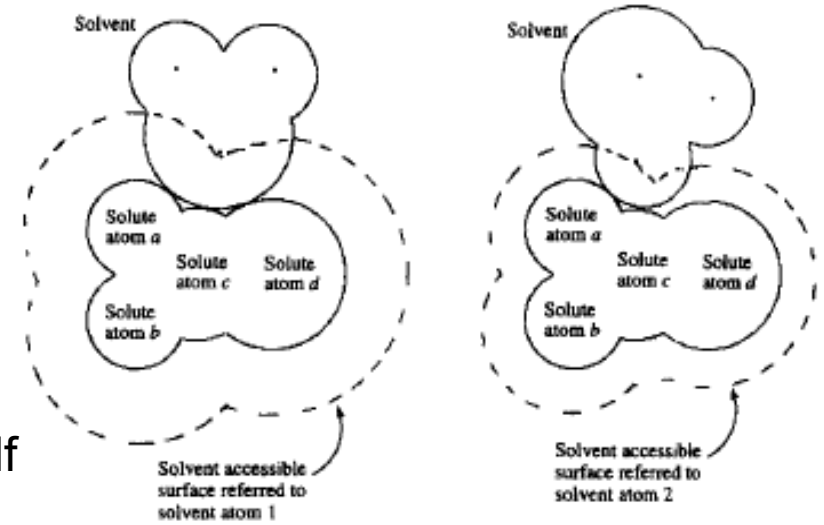
Polarization Continuum Model

- 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).

Nord	Group	Hybr	Charge	Alpha	Radius	Bonded to
1	C	*	0.00	1.00	1.925	C2 [s] C3 [d] C4 [s]
2	C	*	0.00	1.00	1.925	C1 [s] C5 [s] O7 [d]
3	CH	*	0.00	1.00	2.125	C1 [d] C6 [s]
4	CH3	*	0.00	1.00	2.525	C1 [s]
5	CH2	*	0.00	1.00	2.325	C2 [s] C12 [s]
6	CH2	*	0.00	1.00	2.325	C3 [s] C12 [s]
7	O	*	0.00	1.00	1.750	C2 [d]
12	CH	*	0.00	1.00	2.125	C5 [s] C6 [s] C17 [s]
17	C	*	0.00	1.00	1.925	C12 [s] C19 [d] C20 [s]
19	CH2	*	0.00	1.00	2.325	C17 [d]
20	CH3	*	0.00	1.00	2.525	C17 [s]

Polarizable Continuum Model (PCM)

==========

Model : PCM.
Atomic radii : UA0 (Simple United Atom Topological Model).
Polarization charges : Total charges.
Charge compensation : None.
Solution method : Matrix inversion.
Cavity : GePol (RMin=0.200 OFac=0.890).
Default sphere list used, NSphG= 11.
Tesserae with average area of 0.200 Ang**2.
1st derivatives : Analytical V*U(x)*V algorithm (CHGder, D1EAlg=0).
Cavity 1st derivative terms included.
Solvent : Methanol, Eps = 32.630000
Eps(inf)= 1.758000
RSolv = 1.855000 Ang.

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

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

Partition over spheres:

Sphere	on Atom	Surface	Charge	GEI	GCav	GDR
1	C1	0.04	0.000	0.00	0.09	0.00
2	C2	1.03	-0.005	0.00	0.29	-0.08
3	C3	9.50	-0.041	-0.77	1.25	-0.96
4	C4	49.00	-0.026	-0.19	4.25	-2.87
5	C5	18.67	-0.058	-0.29	1.94	-1.49
6	C6	18.70	-0.058	-0.64	1.91	-1.51
7	O7	13.32	0.191	-4.92	1.59	-1.19
8	C12	2.62	-0.029	-0.34	0.41	-0.27
9	C17	0.00	0.000	0.00	0.00	0.00
10	C19	34.51	0.011	-0.41	3.27	-2.27
11	C20	40.83	-0.041	-0.33	3.61	-2.28
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 a achiral solvent has a large contribution to the optical activity