

# Computational Chemistry at Marian College

Roderick M. Macrae

# What is computational chemistry?

- Schrödinger equation describes “all of chemistry and most of physics” (Dirac)
- Solving the Schrödinger equation for molecules leads to energies (eigenvalues), orbitals (eigenfunctions), and ultimately all molecular properties.
- Drawbacks: SE can only be solved exactly for H atom.
- Approximate numerical solution is possible using computers.
- Self-consistent methods: Hartree-Fock theory; Density Functional Theory (“ab initio” methods)

# Computational Quantum Chemistry

- The ultimate “green chemistry” - no need for actual molecules!
- Self-consistent field methods - description of molecular orbitals is based on LCAO (Linear Combination of Atomic Orbitals)
- An initial guess is made, then orbitals are refined until energy ceases to change between cycles (convergence).
- It is possible to calculate molecular geometries (geometry optimization), vibrational and electronic spectra, and (in principle) any property depending on electronic wavefunction.

# Computational Chemistry at Marian College

- Computational engines: Gaussian 03, GAMESS, Orca
- Calculations implemented on Unix backend machine (actually Apple G4)
- Access through user-friendly WebMO interface
- Computation is “numerically intensive” - typical jobs require storage  $O(N^3)$  to  $O(N^7)$ , where  $N$  is the number of basis functions, and CPU time on the order of days.

# Spectroscopic and Computational Studies of Polyiodide Ions and Their Guest/ Host Interactions.

Andrew Johnson and Roderick Macrae



## Introduction:

The blue starch/iodine complex is well-known and is used both as an indicator of the presence of starch and to aid in end-point determination in iodimetric titrations.

Experimental evidence suggests that the complex consists of chains of I atoms encapsulated in the interior of amylose helices.

However, much remains to be better understood: for example, (1) what is the charge on the complexed polyiodide species? (2) what is the source of their stabilization? and (3) what is the origin of the UV absorption lineshape of the complex?

Finally, why does starch work so well as an indicator in the iodine/iodide system? Is it simply that complexation leads to a bathochromic shift of the absorption band from the UV into the visible, or does complexation contribute to the overall intensity of the band?

# Overview

- Experimental and Computational Methods
- Iodine- Iodide Chemistry
- Polyiodide Chemistry
- Starch- Iodide Complex
- Summary
- Future Research

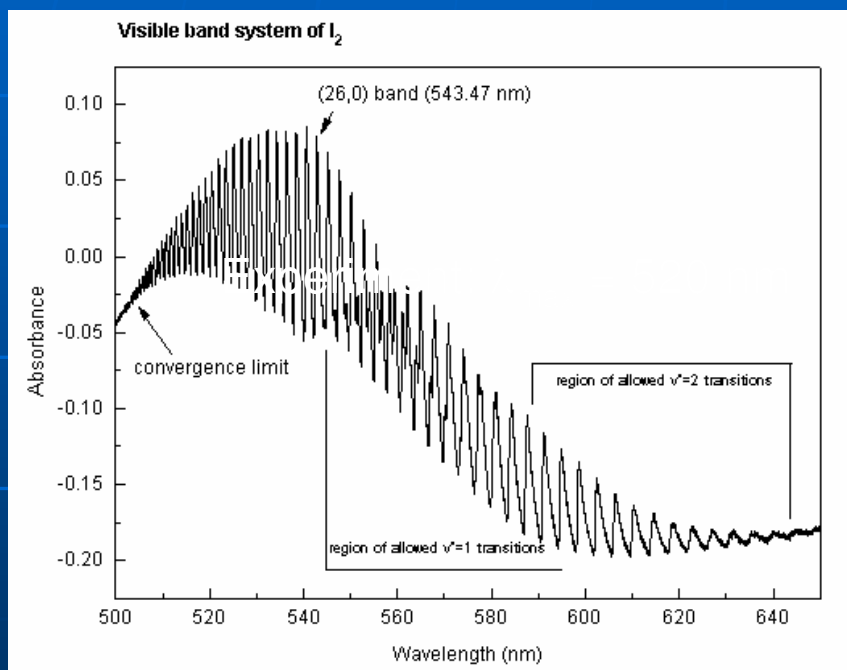
# Experimental and Computational Methods

- UV- Vis spectra obtained using a Varian Cary 50 Bio UV- Vis spectrometer.
- Calculations were run on Gaussian 03 software.
- B3LYP level theory and SDB-aug-cc-TZVP basis set used on all Iodine/Polyiodide species.
- TD-DFT and CIS methods were used to obtain calculated UV- Vis absorption energies.

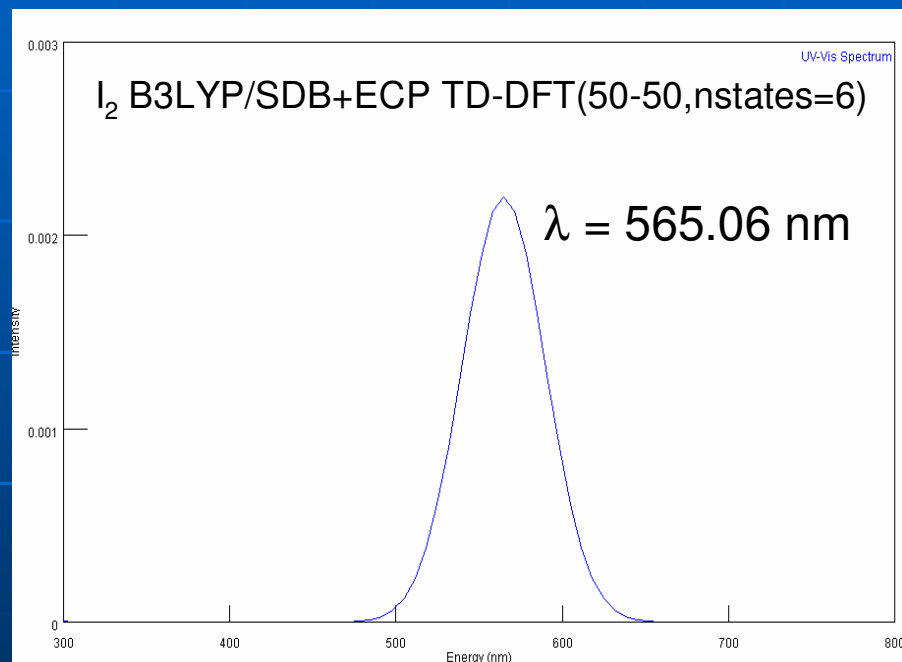
# Iodine- Iodide Chemistry

- I<sub>2</sub> in gas phase - complex vibronic spectrum with  $\lambda_{\text{max}} \sim 540 \text{ nm}$
- Spectrum is simplified in solution with nonpolar solvents such as cyclohexane
- Polar solvents lead to a shift in  $\lambda_{\text{max}}$  due to the formation of donor-acceptor complexes

# Iodine- Iodide Chemistry

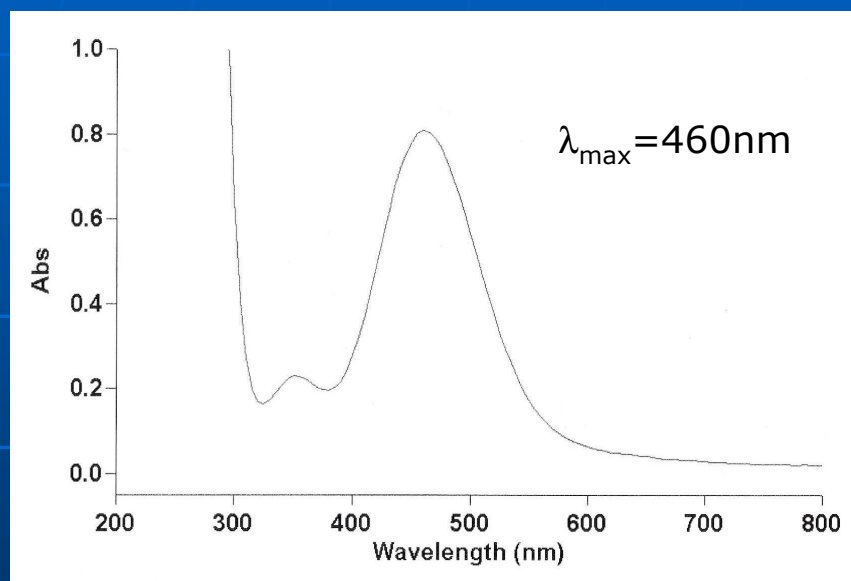


Gas phase UV- Vis Spectrum of  $I_2$ .

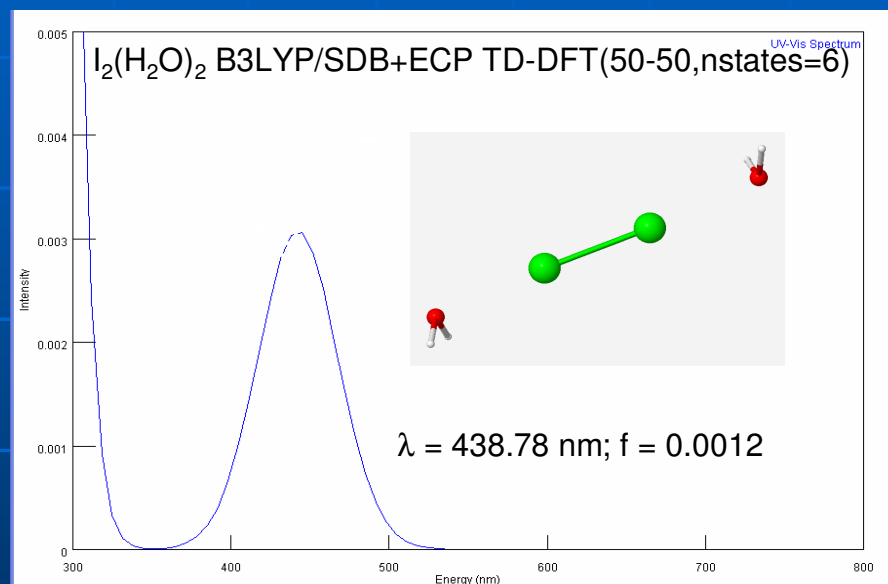


Calculated UV-Vis Spectrum of  $I_2$ .

# Iodine- Iodide Chemistry

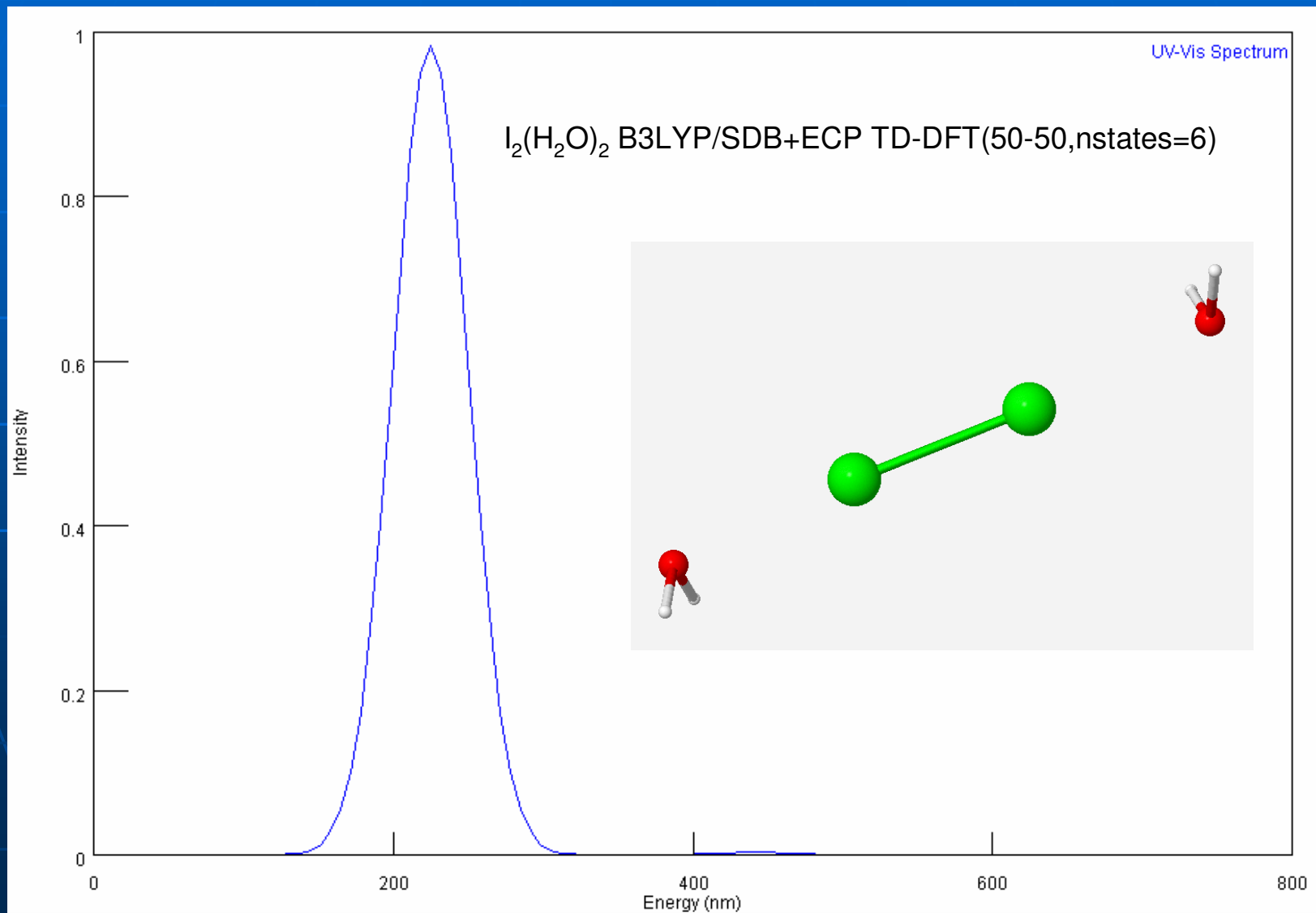


Experimental UV- Vis Spectrum  
of  $I_2$  in water.



Calculated Spectrum of  $I_2$  in  
water using TD-DFT.

# Iodine- Iodide Chemistry

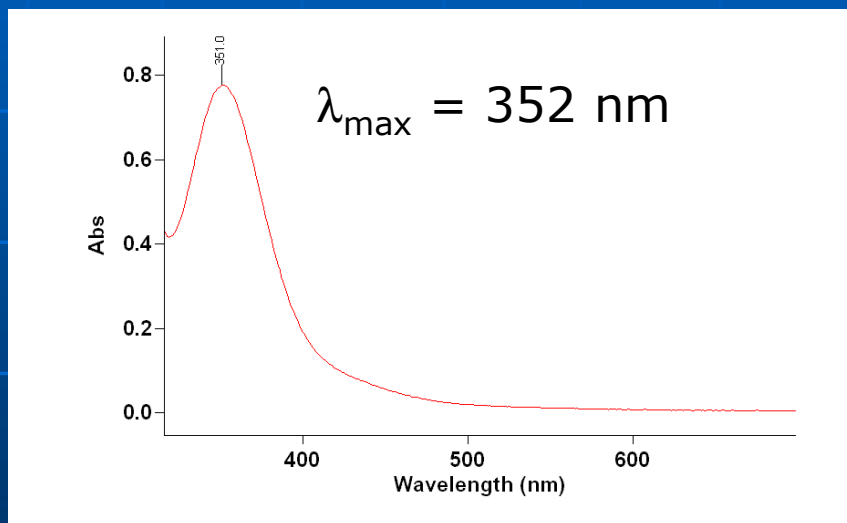


# Iodine- Iodide Chemistry

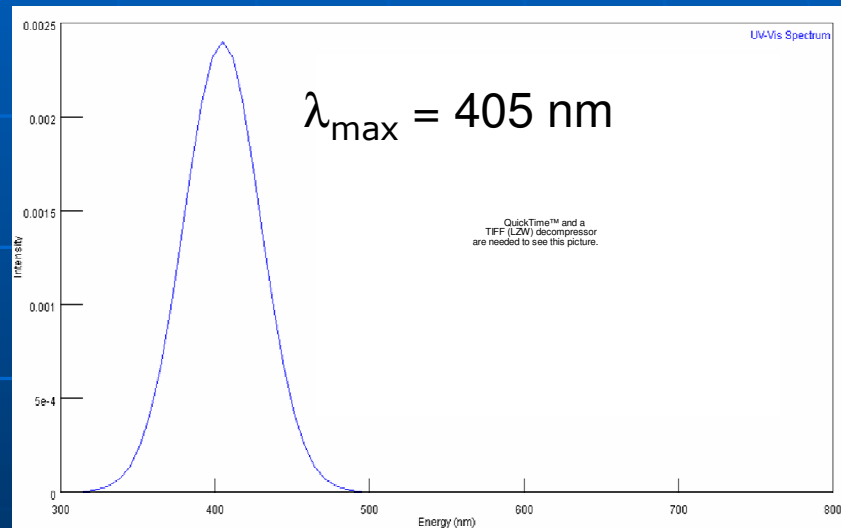
- On addition of  $I^-$  to a solution of  $I_2$  in water, an equilibrium occurs between  $I_2$ ,  $I^-$ ,  $I_3^-$ , and possibly other species.
- $I_2 + I^- \rightleftharpoons I_3^- \quad K_{eq} = 7 \times 10^2$

# Iodine- Iodide Chemistry

(In this case, inclusion of explicit solvent has little effect.)



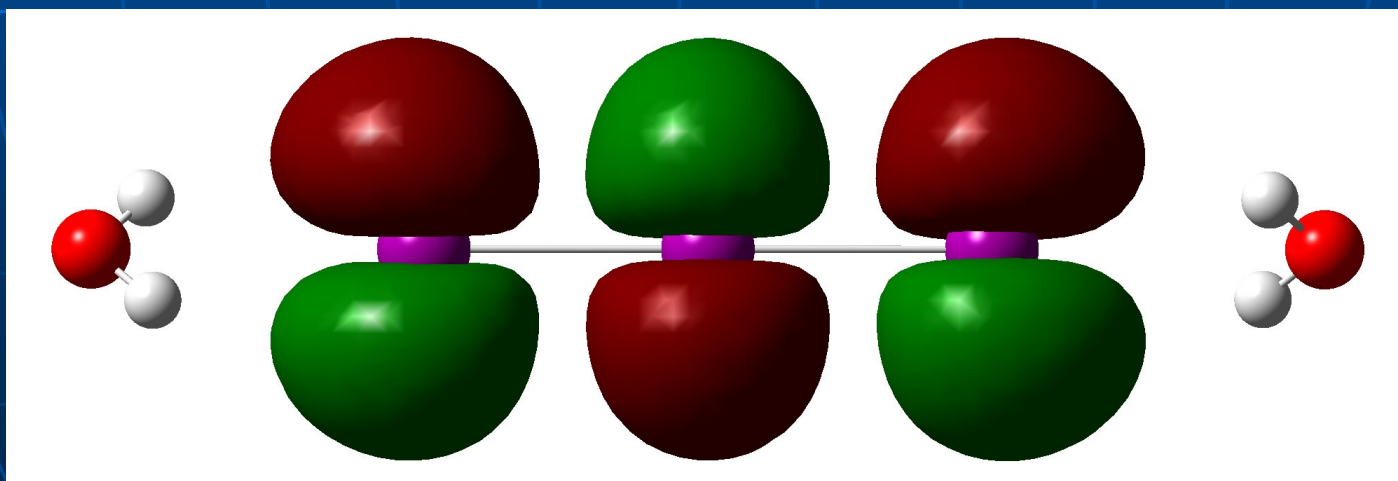
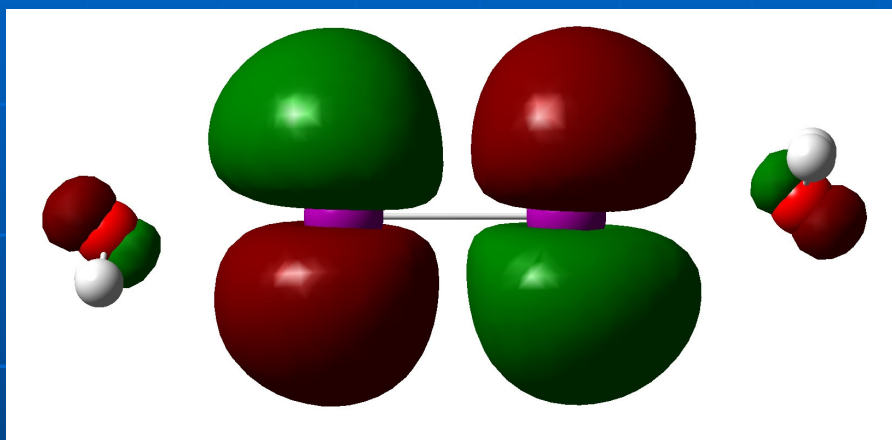
Experimental UV- Vis spectrum  
of  $I_3^-$  in water.



Calculated UV- Vis spectra of  
 $I_3^-(H_2O)_2$ .

# Iodine- Iodide Chemistry

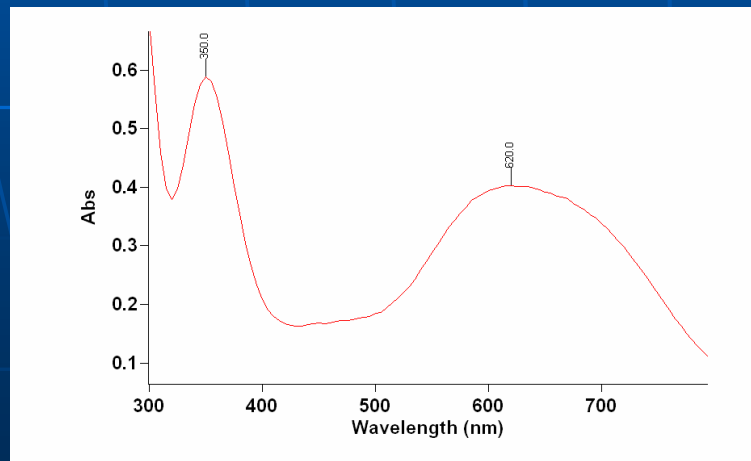
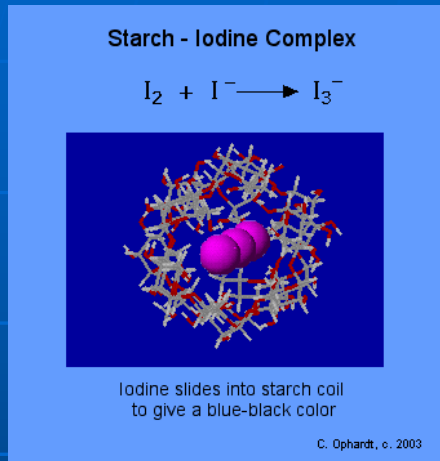
HOMO structures in solution:



# Polyiodide Chemistry

- Calculations were performed on several polyiodide chains to determine the factors influencing stability. (The species were constrained to be linear and the optimizations were started in an arrangement with all Iodine atoms 3 Angstroms apart.)
  - $I_5^-$  was found to be a stable species with a bent geometry in agreement with the literature.
  - Linear  $I_5^-$ ,  $I_7^-$ , and  $I_8^{2-}$  are found to be saddle points.
  - $I_9^{3-}$ , and larger species seem to be dissociative.
  - Criterion for “stable” species: alternating  $I_2$  and  $I_3^-$  segments separated by a somewhat longer internuclear distance, suggesting a donor- acceptor arrangement.

# Starch- Iodide Complex



UV- Vis spectrum of Starch- Iodide complex.

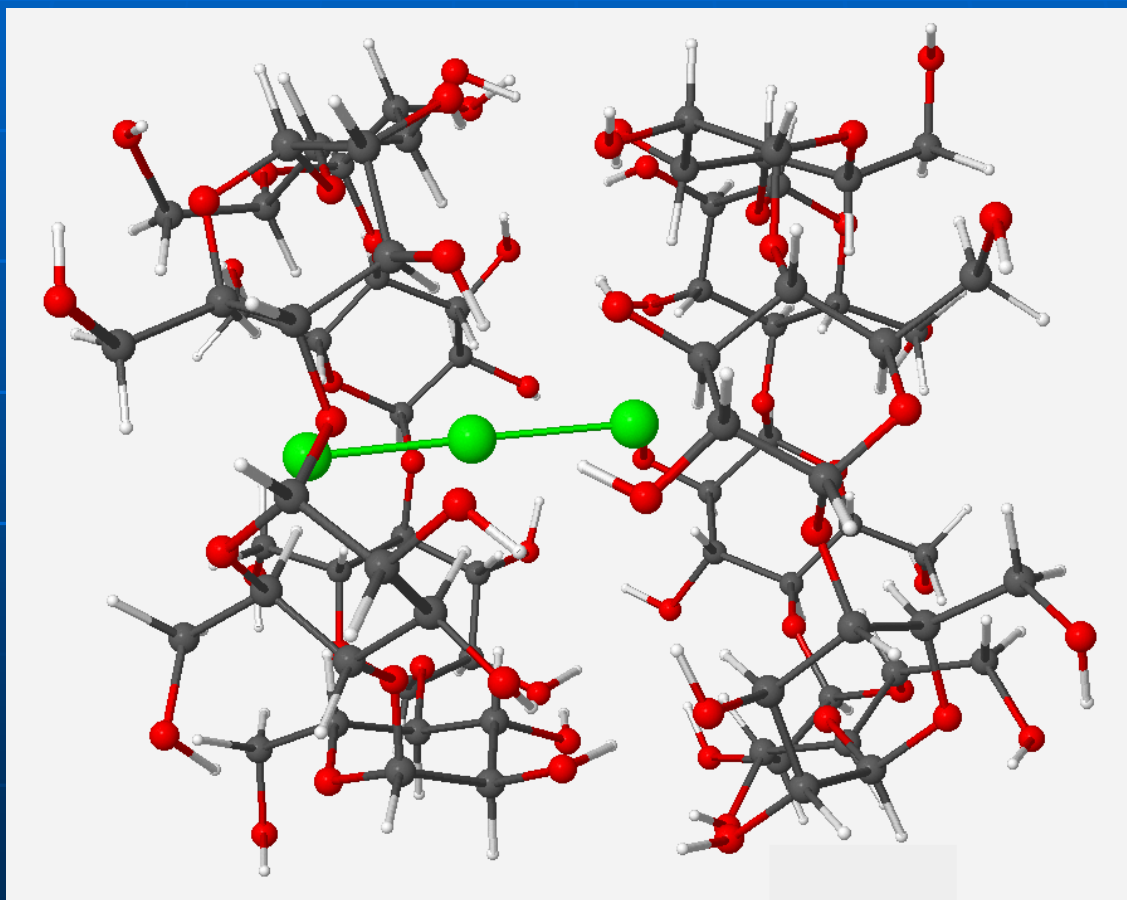
- The Starch- Iodide complex is formed when the polyiodide molecule/s are encapsulated inside the amylose helix giving the solution a deep blue- black color.
- Complex exhibits a broad absorption peak at wavelengths longer than  $I_2$  or  $I_3^-$ .

# Starch- Iodide Complex

- Literature: Kuhn free-electron model (S. Ono, S. Tsuchihashi, T. Kuge, *J. Amer. Chem. Soc.* **75** (1953) 3601).
- Extended Hückel crystal orbital method (M. Kértész and F. Vonderviszt, *J. Amer. Chem. Soc.* **104** (1982) 5889).
- AM1 (X. Yu, C. Houtman, R. H. Atalla, *Carbohydrate Res.* **292** (1996) 129).
- Still relatively poorly understood.

# Starch- Iodide Complex

Presently modeled via encapsulation in cyclodextrin dimer.



Large-scale calculations - require complex approach.

# Summary

- We were able to calculate UV- Vis spectra of  $I_2$  in reasonable agreement with experiment for gas phase and aqueous solution using B3LYP level theory and the SDB-aug-cc-TZVP basis set.
- Calculations on  $I_3^-$  showed weaker solvent effects and somewhat poorer agreement with experiment.
- Several conditionally stable polyiodide species (candidate guest species in starch/iodine complex) were found.
- The strong visible range absorption of the starch/iodine complex originates from the encapsulated polyiodide chain, where (it can be speculated that) increased electron delocalization with increasing chain length leads to a bathochromic shift into the visible range of the strong absorption found in the UV for  $I_3^-$  .

# Future Research

- In the near future we plan to perform ONIOM calculations involving partial optimization of polyiodide chains introduced into experimentally-determined amylose structures.
- Subsequently, using TD-DFT and CIS methods, we will calculate the UV- Vis spectra of the starch/iodine complex more accurately than has hitherto been attempted.

# References

- (1) Svensson P. H, Kloo L. *Chem. Rev.* **2003**. *103*. 1649
- (2) Thompson J. C., Hamori E. *Journal of Physical Chemistry.* **1971**. *75*. 272
- (3) Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003. (4) <http://www.webmo.net/>
- (5) J.M.L. Martin and A. Sundermann, *J. Chem. Phys.* **114**, 3408 (2001).
- A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **80**,1431 (1993)
- (6) M. J. S. Dewar, E. G. Zoebisch, and E. F. Healy, *J. Am. Chem. Soc.* **107**, 3902 (1985).
- (7) R. E. Stratmann, G. E. Scuseria, and M. J. Frisch, *J. Chem. Phys.* **109**, 8218 (1998).
- (8) J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, *J. Phys. Chem.* **96**, 135 (1992).
- (9) Calabrese, V.T., Khan A., *J. Phys Chem A.* **96**, 1287 (2000)
- (10) J. Broehema, E. E. Haringa, G. H. Wieberga, *Acta Crystalloga*, **10**, 596, (1957)