

Project 1: Spectroscopy of I₂ and polyiodide ions.

The iodine test for starch is well known to biologists – in the presence of the two substances a deep blue-black color forms. This phenomenon is also the basis of the titration techniques of iodometry and iodimetry [1]. (Yes, they're different techniques – in the former case the iodine is part of the analyte, in the latter it is part of the titrant.) The color is due to a complex formed between the triiodide ion (I₃⁻) and the *amylose* fraction of natural starch, which forms a helical, “coiled-spring” structure.

Additionally, iodine itself (I₂) forms donor-acceptor complexes with a variety of solvents capable of donating lone pairs (notably pyridine, but also for example water). For this reason the visible light absorption spectrum of iodine dissolved in these substances exhibits maxima shifted from their positions in the gas phase spectrum or in spectra recorded in “inert” solvents such as cyclohexane.

One of the interesting attributes of the starch:triiodide complex is that its absorption of visible light seems much more intense than that of either the triiodide ion itself or the uncomplexed neutral molecule. Triiodide ion also forms complexes with cyclodextrin [2], and more complex polyiodide ion arrangements are known to form in complexes with the prototypical conducting polymer polyacetylene [3].

Our aim in this project is to explore these systems using computational chemistry tools such as time-dependent density functional theory to calculate structures and spectra, and spectroscopic methods such as UV-Vis absorption, FT-IR, fluorescence, and Raman scattering [4].

Initial references:

1. Harris, D. C., *Quantitative Chemical Analysis*, 6ed., Freeman 2003, p. 355-6, 361.
2. Minns, J. W., and Khan, A., *J. Phys. Chem. A* **106** (2002) 6421.
3. Murthy, N. S., *et al.*, *J. Phys. Chem.* **89** (1988), 2523.
4. Yu, X., Houtman, C., and Atalla, R. H., *Carbohydrate Res.* **292** (1996) 129.