

## Molecular iodine emission rates from *Laminaria digitata* as a function of algal part, irradiance and temperature

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Sea-to-air biogenic iodine fluxes play a key role in the global and local environmental iodine cycles, particularly in coastal areas where kelp beds are exposed to air during spring tides. The general knowledge of the marine sources and mechanisms of (elemental) iodine emission, either as molecular I<sub>2</sub> or volatile iodo-carbons, is still very limited.

Here time-resolved flux measurements of I<sub>2</sub> emitted by the brown macroalga *Laminaria digitata*, probably the strongest iodine accumulator amongst living organisms, were achieved by applying incoherent-broadband cavity-enhanced absorption spectroscopy (IBBCEAS) [1,2]. I<sub>2</sub> emission rates of three different (air-exposed) thallus parts of *L. digitata*, i.e. the distal blade, the meristematic area, and the stipe, were investigated under low-light and dark conditions [3]. Furthermore, impacts of light intensity and temperature on the I<sub>2</sub> emission rates were investigated for blades. Overall I<sub>2</sub> emissions were highly variable, but the release from stipes was ten times higher than that from meristematic areas and distal blades. Increased irradiances and temperatures resulted in higher I<sub>2</sub> emissions, indicating the importance of I<sub>2</sub> in algal stress responses. The results suggest that I<sub>2</sub> emission may be considered an indicator of the physiological status of the alga, and that iodine might have a multifunctional role in *L. digitata*.

[1] Fiedler *et al.* (2003) *Chem. Phys. Lett.* **371**, 284–294. [2] Dixneuf *et al.* (2009) *Atmos. Chem. Phys.* **9**, 823–829. [3] Nitschke *et al.* (2011) *Planta* **233**, 737–748.

## Computational studies of actinide clusters and hydrolysis reactions

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Advances in theory, algorithms, software, and computer architectures, have made it possible to begin to calculate reliably the thermodynamics for geochemical processes in solution. There is a need to develop a fundamental understanding of actinide-aggregate formation under conditions that promote hydrolysis. We are developing the scientific basis for a molecular-level understanding of nanoaggregate species in terms of their structures, stabilities, formation reactions, and surface reactivities, particularly the formation of colloidal particles containing heavy elements. In addition, this research will help us to meet the need to develop new separations strategies for next generation nuclear fuels that are better able to remove stable metal aggregates without the need for extreme solution conditions. Our focus is on the initial aqueous reactions including oxolation and oxoalation as well as the acidity of metal ions in solution. For the +2 metal aquo ions, it is possible to predict the size of the first solvation shell by predicting the correct pK<sub>a</sub> in terms of experiment. Positive ions with a charge > +2 require more solvent shells in order to predict the pK<sub>a</sub> reliably. We have studied a wide range of oxolation and oxoalation reactions of +2 cations and the type of reaction that dominates in terms of the thermodynamics is dependent on the cation size, the size of the first solvation shell, and the electronic structure of the ion. The structures of (ThO<sub>2</sub>)<sub>n</sub> nanoclusters have been studied and compared to the analogous transition metal nanoclusters. Calculations of the hydrolysis reactions of the nanoclusters provide for the first time an estimate of the physisorption and dissociative chemisorption energies of H<sub>2</sub>O on the ThO<sub>2</sub> surface. The electronic structure of nanoparticles containing a Th<sub>6</sub>O<sub>8</sub> core will be discussed including predictions of particle acidity and proton location. These particles are of interest as they contain a Th<sub>6</sub>O<sub>8</sub> core embedded in an anion shell. There is good agreement between theory and experiment for the structures of the clusters.

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