

Open PhD project:

Femtosecond time-resolved imaging of bimolecular reactions using cold helium nanodroplets

Where: Femtolab, Aarhus University

When: Application GSST, Aug 1, 2018. Expected start: Nov 1, 2018 – possibly later

Program: Chemistry, Physics, or Nanoscience

Requirement: Bachelor in Physics, Chemistry, Nanoscience

Supervisor: Henrik Stapelfeldt

Before applying: Contact Henrik Stapelfeldt, henriks@chem.au.dk for more information

Project description:

The scientific goal of this PhD project is to image molecules with femtosecond (fs) time resolution during fundamental bimolecular reactions. The goal will be achieved by applying fs time-resolved imaging methods to molecular complexes, sharply oriented in space, formed inside helium nanodroplets.

As a unique approach molecules will be studied inside helium nanodroplets. The helium droplets are created by expanding a cryogenically cooled, high pressure gas of helium into vacuum. They consist of about 10,000 He atoms, have a diameter of ~ 10 nm and a temperature of 0.4 K. The droplets move with a few hundred meters per second and when they pass a doping cell, containing a gas of molecules, they can pick up one or several molecules. The pressure of the gas determines how many molecules each droplet pick up. Thereby, it becomes possible to study either single molecules, using a low doping cell pressure, or dimers (or larger oligomers) of molecules, using a higher doping cell pressure, since two (or more) molecules inside a droplet will bond due to intermolecular interactions. It is also possible to form hetero-dimers by using two consecutive doping cells containing different molecular gases.

To study bimolecular reactions a precursor consisting of two reagent molecules, weakly bonded in a well-defined, yet non-reactive geometry will be made. Experimentally, this will be realized in the form of a molecular dimer created inside the He droplets. The reaction will be initiated by selectively photoexciting one of the reagents by a femtosecond (fs) pump pulse and imaged as a function of time by a delayed fs probe pulse through Coulomb explosion or single-ionization.

The project will aim at studying a range of fundamental photoinduced reactions. One concerns photoinduced cycloadditions, which are central to a range of reactions in organic synthesis and biology. The archetypical reaction is the dimerization of (derivatives) of ethylene (C_2H_4) to (substituted) cyclobutane by π - π^* photoexcitation. One objective may be the photodimerization of 2-butene to 1,2,3,4-tetramethylcyclobutane – a reaction long known to occur when liquid 2-butene is irradiated by UV light around 229 nm. The initial goal is to observe the cyclobutane adduct and how it kinematically competes against photo-fragmentation. We will try to image directly how the geometry changes during the reaction using laser-induced Coulomb explosion. It may be necessary to halogenate the reagents to provide marker ions for the structure determination via Coulomb explosion.

Another goal is to study the photodimerization of nucleobases. When UV light from the sun hits human tissue it can induce covalent bonding between two adjacent thymine or cytosine nucleobases in one part of the

strand of a DNA molecule. This dimerization disrupts the hydrogen-bonding to the nucleobases on the opposing strand and thus destroys part of the base-pairing which leads to a loss of the function of the DNA molecule. The effect is believed to be the primary cause of skin cancer in humans. We plan on exploring the atomistic foundation for the nucleobase dimerization using UV excitation with a pump pulse and an (intense) probe pulse to follow the evolution – possibly by Coulomb explosion. Other processes to be studied include charge transfer reactions.