Dynamic Pathways in
Multidimensional Landscapes

Contribution ID : 11

Femtosecond RIXS of Fe(CO)5 in ethanol – resolving ultrafast excited state and ligand substitution dynamics in solution

Content :

Using ultrashort X-ray pulses from the Linac Coherent Light Source we carried out a pump-probe resonant inelastic x-ray scattering (RIXS) experiment on Fe(CO)5 photodissociation in ethanol. This allowed us to follow the evolution of the valence electronic structure of the iron carbonyl species in an element- and chemical-selective way with a 300 fs (FWHM) time resolution. Supported by novel ab initio electronic structure calculations, we were able to identify the relevant reaction steps all the way from excited-state relaxation involving changes in the spin state to subsequent complexation with solvent molecules of the first coordination sphere. Upon charge transfer excitation with 266 nm laser light the Fe(CO)5 molecule relaxes to a low-lying excited ligand field state which, due to the Jahn-Teller effect, leads to dissociation of one CO ligand. We identified that such relaxation is very fast (<100 fs) and results in the creation of electronically excited Fe(CO)4 as a primary photoproduct. The electronically excited molecule could be detected via a characteristic anti-Stokes RIXS peak at a negative energy transfer of -2 eV. This primary photoproduct then relaxes in only 150 fs to the triplet ground state of Fe(CO)4. Although in the electronic ground state, triplet Fe(CO)4 is highly reactive. Due to the missing CO ligand it is sterically unsaturated and lacking electrons in the valence shell. Reactive collisions with the hydroxyl groups of the ethanol molecules in the first solvation shell therefore lead to rapid complexation. As a result of the large amount of vibrational excess energy, a dynamical quasi-equilibrium between Fe(CO)4 and Fe(CO)4EtOH is established in less than 1 ps. Subsequent cooling of the system, which is expected to take 10-20 ps, leads to formation of final “cooled” Fe(CO)4EtOH product.

In addition to the well-known high chemical sensitivity of RIXS, we have experimentally demonstrated here the potential of femtosecond RIXS as a tool to probe excited state dynamics. This follows from the fact that RIXS probes directly the spectrum of valence states referenced to the energy of the RIXS initial state. Therefore RIXS from electronically excited states leads to appearance of characteristic anti-Stokes peaks well separated from the parent molecule signal. We

believe that femtosecond RIXS can become a very valuable technique in resolving complex excited-state dynamics.

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Session classification : X-Ray interactive with matter 1

Track classification : --not yet classified--

Type : contributed talk