Universität Bern
Institut für Angewandte Physik
Sidlerstrasse 5
3012 Bern, Schweiz

Telefon:+41 (0)31 631 89 11
E-Mail: iapemail@iap.unibe.ch
www.iap.unibe.ch

UNIVERSITÄT BERN

Seminar über Ultrafast Science and Technology

Referent/in: Professor Dr. A. Vlcek, FRSC
J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic and Queen Mary University of London, School of Biological and Chemical Sciences, London, UK

Titel: Photoinduced charge separation in chromophore-protein systems

Acceleration and control of electron transfer (ET) through and among proteins are necessary prerequisites for designing protein-based light-harvesting systems and photocatalysts. Herein, we will demonstrate that long-range electron transfer in azurins labeled with a $Re(CO)_3$(4,7-Me_2-1,10-phenanthroline)$^+$ chromophore (Re) is strongly accelerated by introducing a tryptophan (Trp) residue in the label vicinity. Initial steps of Re photoreduction are ultrafast (ps), accompanied by structural relaxation of the binding site. A charge-separated state Re^{-}---$Trp^{\bullet+}$ is produced, which undergoes ~30 ns $Cu^{I} \rightarrow Trp^{\bullet+}$ ET over 11 Å. Moving the Re chromophore two amino acid residues away from the active tryptophan shuts the direct intramolecular Re---W interaction, but the $Cu^{I} \rightarrow$*Re ET occurs on the same ns timescale, again involving ultrafast initial ET steps at the Re site, this time enabled by interfacial electron hopping across a hydrophobic protein-protein boundary. Fast ET kinetics and ultrafast initial steps were also found in a "tryptophan wire" azurin mutant, where ET takes place with the same rate but over a remarkably long distance of 23 Å through two tryptophans. Theoretical studies provided a deep insight into the mechanism, showing that 1) the ET probability depends on electron distribution in the excited chromophore that fluctuates with time and 2) the ET is enabled by water fluctuations around the tryptophan residues, taking place upon transient strengthening of indole solvation. Ultrafast charge separation in Trp-containing proteins seems to be characteristic of systems where the protein environment keeps the chromophore and the Trp indole group(s) at a close distance and the indole groups are well solvated. This is the case of the Re-azurins studied herein, as well as enzymes such as photolyases or cryptochromes.

Zeit: Donnerstag, 03.10.2019, 11.15h

Ort: **Hörsaal B116**, Gebäude Exakte Wissenschaften, Sidlerstrasse 5, Bern, Schweiz