

Grammaticakis-Neumann Prize 2012, Lecture

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**Probing the evolution of molecular electronic structure in photochemical reactions**Hans Jakob Wörner

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The electronic structure of molecules determines most of their properties and the outcome of chemical reactions. Observing electronic dynamics in molecules is challenging because it occurs on the time scales of attoseconds (1 as =  $10^{-18}$ s) to femtoseconds (1 fs = 1000 as). In this lecture, we will discuss the application of attosecond pulse generation to study the electronic structure and dynamics of molecules. When a molecule is exposed to an intense ( $I \approx 10^{14}$  W/cm<sup>2</sup>) laser pulse, it emits attosecond pulses that contain detailed information about the valence electrons of the molecule, encoded in the spectral amplitude and phase of the pulses. We have applied this technique to resolve in time the evolution of the valence electronic structure of molecules during photochemical reactions. These measurements exploit the coherence of attosecond pulse generation to measure both the amplitude and phase of the emitted radiation. This technique has been applied to study the photodissociation of Br<sub>2</sub> following excitation to its C <sup>1</sup>Π<sub>1u</sub> state [1] and to the photodissociation of NO<sub>2</sub> following excitation to its  $\tilde{A}$  <sup>2</sup>B<sub>2</sub> state [2]. In NO<sub>2</sub> the measurements revealed several transfers of population between the excited  $\tilde{A}$  and the ground electronic  $\tilde{X}$  state mediated by a conical intersection, followed by a statistical photodissociation into NO(<sup>2</sup>Π)+O(<sup>3</sup>P). In our recent work in Zurich, we have extended attosecond pulse generation experiments to molecules that were fixed in space, which will provide insight into much finer details of the electronic structure and dynamics.

- [1] H. J. Wörner, J. B. Bertrand, D. V. Kartashov, P. B. Corkum and D. M. Villeneuve, *Nature* **2010**, 466, 604.  
 [2] H. J. Wörner, J. B. Bertrand, B. Fabre, J. Higuette, H. Ruf, A. Dubrouil, S. Patchkovskii, M. Spanner, Y. Mairesse, V. Blanchet, E. Mvel, E. Constant, P. B. Corkum and D. M. Villeneuve, *Science* **2011**, 334, 208.

Paracelsus Prize 2012, Lecture

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**How Peptides Transport Electrons over Long Distances**Bernd Giese

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A characteristic of cellular systems is that chemical reactions often occur in compartments. In the case of redox reactions the information transfer between the compartments is established by electron transfer (ET) where peptides can act as “nanowires”. Therefore, long range ET through proteins is a fundamental reaction in living organisms. It plays a role in energy conversion processes like photosynthesis, aerobic and anaerobic respiration as well as in enzymatically driven transformations. Two mechanisms are discussed to explain long range ET between an electron donor and an electron acceptor. The reaction might occur via bridge-assisted superexchange (single-step reaction) or by a stepwise (hopping) reaction. During superexchange, the amino acids mediate ET and do not undergo a change of their redox states, while during hopping certain amino acids are reversibly oxidized or reduced and serve as relay stations (stepping stones) for the ET process. Because of the strong distance influence on ET rates the hopping process is much faster than one-step reactions. We have therefore studied the question which amino acid is able to act as relay amino acid. It turned out that not only aromatic but also S-containing aliphatic amino acids are stepping stones for an electron hole hopping process.<sup>1</sup> Another surprising result is that the redox potentials of amide groups in  $\alpha$ -helical peptides are decreased by the dipole moment of the peptides to such an extent that they can also act as hopping stations.<sup>2</sup> This is of special importance for those microorganisms that live under “mineral respiration” using metal salts outside of the cell membrane.

- [1] M. Wang, J. Gao, P. Müller, B. Giese, *Angew. Chem. Int. Ed. Engl.* **2009**, 48, 4232; J. Gao, P. Müller, M. Wang, S. Eckhardt, M. Lauz, K. M. Fromm, B. Giese, *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 1926.  
 [2] M. Lauz, S. Eckhardt, K. M. Fromm, B. Giese, *PhysChemChemPhys.* **2012**, ASAP