# Where Are the Electrons? Charge Transfer and Dissociation from a Femtosecond Electronic-structure Perspective

**Philippe Wernet**
*Helmholtz-Zentrum Berlin, Institute of Methods and Instrumentation for Synchrotron Radiation Research, Albert-Einstein-Str. 15, 12489 Berlin, Germany*
*wernet@helmholtz-berlin.de*

**Abstract:** Time-resolved electronic-structure spectroscopy is used to reveal the coupling of transient electronic structure and nuclear dynamics in charge-transfer and dissociation reactions in the gas phase and in solution.

Molecular structure and chemical bonding determine the dynamic pathways of molecules in their multidimensional landscapes and hence define the outcome of chemical reactions. Characterizing chemical bonding in short-lived reaction intermediates and transient states of molecules is hence the key to understanding chemical selectivity.

Spectroscopy with femtosecond light pulses with energies ranging from the ultraviolet to the x-ray regime enables a unique approach to the atomic-scale chemical dynamics as it allow for a complete mapping of the electronic structure of atoms and molecules during chemical reactions (Fig. 1) [1]. Time-resolved femtosecond x-ray spectroscopy in particular reveals chemical bonding both in real time of the reaction and from the atom's perspective in an element-selective way [2].

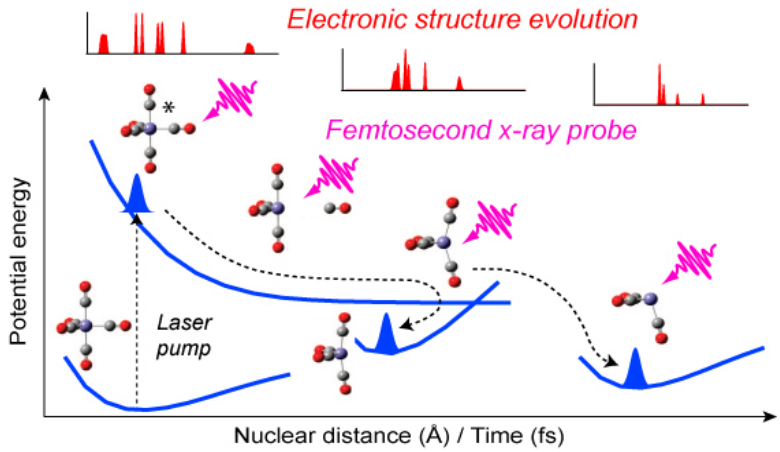


**Fig. 1.** Schematic representation of a photo-dissociation reaction triggered by an optical laser pulse with concomitant nuclear dynamics and transient electronic structures as probed by time-resolved x-ray spectroscopy.

Here we present our view on charge-transfer and dissociation reactions both in the gas phase and in solution from a femtosecond electronic-structure perspective. We apply femtosecond laser pulses from laboratory laser sources and from large scale x-ray free-electron lasers to map the electronic structure evolution in prototypical systems such as NaJ, $Fe(CO)_5$ and other molecules. Our results reveal how the transient electronic structure and the nuclear dynamics are coupled and they elucidate the role of the solvent from a chemical-bonding perspective.

Detailed insight into the various cases is discussed and an outlook for the investigation of chemical reaction dynamics with x-ray laser spectroscopy is given.

## References

[1] Ph. Wernet, M. Odelius, K. Godehusen, J. Gaudin, O. Schwarzkopf, W. Eberhardt, "Real-time evolution of the valence electronic structure in a dissociating molecule", Phys. Rev. Lett. **103**, 013001 (2009).

[2] Ph. Wernet, "Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions", Phys. Chem. Chem. Phys. **13**, 16941 (2011).