

# Femtosecond Laser Spectroscopy

Priv.-Doz. Dr. Andreas-Neil Unterreiner | Institute of Physical Chemistry, Molecular Physical Chemistry

## Principal Research Interests

*Our group – as part of the Molecular Physical Chemistry Group (Prof. M. Olzmann) at KIT – is interested in the elucidation of relaxation pathways in molecules and nanostructures on a femto- (fs) and picosecond (ps) time scale after photoexcitation. As experimental tools serve fs pump-probe and stationary absorption spectroscopy as well as transient anisotropy<sup>[1]</sup> from the ultraviolet (UV) to the near-infrared (NIR) spectral region. By chemical substitution and changing the environment (e.g. by viscosity and polarity variation), the ultrafast response of such systems can be used to extract valuable information on elementary photophysical and -chemical processes. Often, nonradiative ultrafast internal conversions involving one-photon dipole-forbidden, so-called dark electronic states play an important role in these systems. The detailed characteristic of excited bright and dark states crucially depends on the system to be investigated. Studied systems in our group cover a wide range from the molecular level (e.g. nitrophenol with M. Olzmann), systems with small nano-meter-sized extension (e.g. porphyrins<sup>[2]</sup>, lanthanide complexes<sup>[3]</sup>, charge transfer in DNA<sup>[4]</sup> and photoinitiator molecules<sup>[5]</sup>) up to larger systems such as single-walled carbon nanotubes. In the following we present selected topics in more detail.*

## Excess Electrons in Polar and Ionic Liquids

Solvated electrons (i.e. solvation of excess electrons by solvent molecules) in polar and ionic liquids usually show broad absorption spectra with half widths of 0.5 to 1 eV; the investigation of such species requires a spectral tunability of the laser system from the UV- to the NIR-

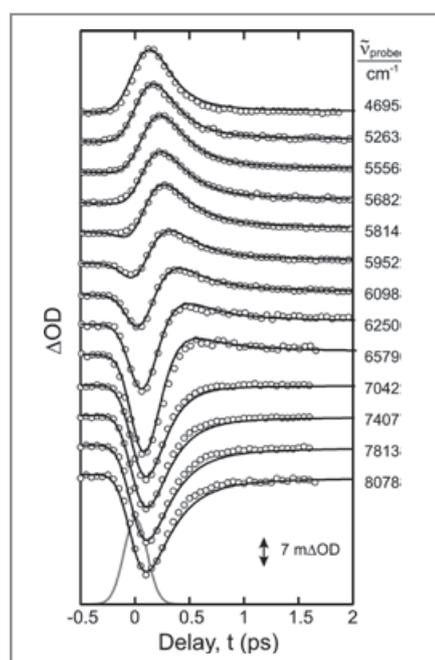


Figure 1: NIR pump-probe response for a Na/ND<sub>3</sub> system at -50°C. Lines show simulations as described in ref. 6b.

region with pulse durations below 100 fs. According to our analysis the lifetime of the excited state of solvated electrons in polar liquids (water and ammonia) is on the order of 100 fs and the subsequent ultrafast response can be interpreted as

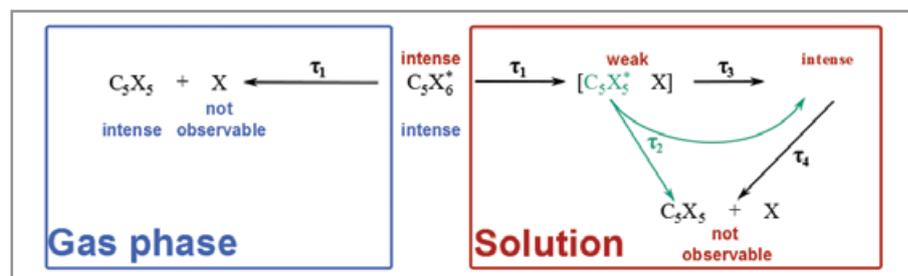


Figure 2: Simplified relaxation scheme for C<sub>5</sub>X<sub>6</sub> (X = Cl, Br) in the gas phase and in solution (adapted from ref. 9).

ground state dynamics where a combination of temperature and density jumps can satisfactorily explain the underlying dynamics (see Figure 1)<sup>[6]</sup>. In contrast to polar liquids, excess electrons in molten salts are primarily governed by hopping processes of F-centre-type electrons with a time constant of 200 fs. Excess electrons can also be localized in room-temperature ionic liquids, but the underlying photochemistry after UV-photolysis is much more complex leading, for example, to the build-up of various long-lived intermediate products. A more profound discussion on this issue can be found in reference<sup>[7]</sup>.

## Polyenes in Solution

Investigation of small molecules with 25 to 40 degrees of freedom is important to develop a high-level understanding of relaxation pathways, their corresponding time scales for internal conversions in dependence of chemical substitution (e.g., halogenation) and solvent variation (e.g., friction influence on potential energy surfaces of chromophores) between 10 fs and the nanosecond regime. Model systems comprise cycloheptatrienes<sup>[8]</sup> and cyclopentadienes<sup>[9]</sup>. As an example, Figure 2 illustrates the solvent influence on (homolytic) bond dissociation in perhalogenated cyclopentadienes. The analysis was performed by comparing data from time-resolved photoelectron spectra, transient absorption spectroscopy in solution and theoretical investigations. As a result, solvent-dependent formation of charge transfer complexes between geminate radicals with surprisingly long lifetimes exceeding hundreds of ps can be postulated to occur in the liquid phase.

## Single-Walled Carbon Nanotubes and Clusters

In collaboration with Prof. M. Kappes time-resolved photoelectron spectroscopy of multiply charged clusters<sup>[10]</sup> and femtosecond pump-probe absorption spectroscopy of quasi mono-dispersed single-walled carbon nanotubes (SWNT) in solution are performed. As an example for the latter case, ultrafast population transfer in SWNT with chirality vector (9,7) has been observed between bright and dark states within 1 ps (see Figure 3). The existence of dark states and their coupling to bright states may explain that

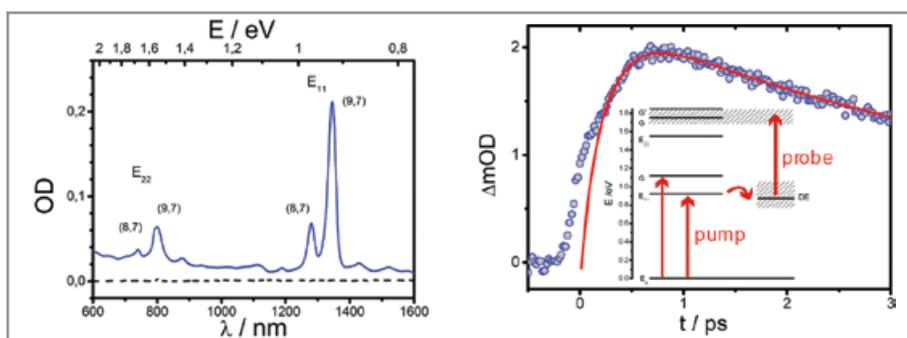


Figure 3: Left: Absorption spectrum of quasi-monodispersed SWNT. Right: Direct observation of dark state population in (9,7)-SWNT and schematic energy level diagramme (adapted from ref. 11).

even under the best conditions achieved so far, nonradiative relaxation channels are still dominant in SWNT after photoexcitation. Furthermore, investigations under nonresonant conditions demonstrated evidence of phonon-assisted coupling (G-phonon) within the first electronically excited state<sup>[11]</sup>.

### Selected Publications

- [1] Oliver Schalk, Andreas-Neil Unterreiner, "Transient anisotropy in degenerate systems: A semi-classical approach", *Z. Phys. Chem.*, 225, 927-938 (2011).
- [2] O. Schalk, H. Brands, T.S. Balaban A.-N. Unterreiner, "Near-Infrared Excitation of the Q-band in Free Base and Zinc

Tetratolyl-porphyrins", *J. Phys. Chem. A*, 112, 1719 (2008).

- [3] Dominique T. Thielemann, Melanie Klinger, Thomas J. A. Wolf, Yanhua Lan, Wolfgang Wernsdorfer, Madleen Busse, Peter W. Roesky, Andreas-Neil Unterreiner, Annie K. Powell, Peter C. Junk, Glen B. Deacon, "Novel Lanthanide-Based Polymeric Chains and Corresponding Ultrafast Dynamics in Solution", *Inorg. Chem.*, 50, 11990 (2011).
- [4] T. Ehrenschwender, Y. Liang, A.-N. Unterreiner, H.-A. Wagenknecht, and T. J. A. Wolf, "Fluorescence Quenching over Short Range in a Donor-DNA-Acceptor System", *ChemPhysChem*, accepted (2013).
- [5] Thomas J. A. Wolf, Dominik Voll, Christopher Barner-Kowollik, and Andreas-

Neil Unterreiner, "Elucidating the Early Steps in Photoinitiated Radical Polymerization via Femtosecond Pump-Probe Experiments and DFT Calculations", *Macromolecules*, 45, 2257 (2012); Thomas J. A. Wolf, Joachim Fischer, Martin Wegener, Andreas-Neil Unterreiner, "Pump-probe spectroscopy on photoinitiators for stimulated-emission-depletion optical lithography", *Opt. Lett.*, 36, 3188 (2011).

- [6] a) A. Hertwig, H. Hippler, and Andreas-N. Unterreiner, "Transient spectra, formation, and geminate recombination of solvated electrons in pure water UV-photolysis: an alternative view", *Phys. Chem. Chem. Phys.*, 1, 5633-5642 (1999); b) J. Lindner, A.-N. Unterreiner, and P. Vöhringer, "Femtosecond spectroscopy of solvated electrons from sodium-ammonia-d3 solutions: Temperature jump versus local density jump", *J. Chem. Phys.*, 129, 064514 (2008).
- [7] Perspective: C. Nese and A.-N. Unterreiner, "Photochemical processes in ionic liquids on ultrafast timescales", *Phys. Chem. Chem. Phys.*, 12, 1698-1708 (2010).
- [8] O. Schalk, J.-P. Yang, A. Hertwig, H. Hippler and A.-N. Unterreiner, "Vibrational cooling in the liquid phase studied by ultrafast investigations of cycloheptatriene", *Mol. Phys.*, 107 (20), 2159 (2009).
- [9] T. J. A. Wolf, O. Schalk, R. Radloff, G. Wu, P. Lang, A. Stolow and A. N. Unterreiner, "Ultrafast photoinduced dynamics of halogenated cyclopentadienes: observation of geminate charge-transfer complexes in solution", *Phys. Chem. Chem. Phys.*, DOI: 10.1039/C3CP44295K, (2013).
- [10] Phuong Diem Dau, Hong-Tao Liu, Ji-Ping Yang, Marc-Oliver Winghart, Thomas J. A. Wolf, Andreas-Neil Unterreiner, Patrick Weis, Yu-Run Miao, Chuan-Gang Ning, Manfred M. Kappes, and Lai-Sheng Wang, "Resonant tunneling through the repulsive Coulomb barrier of a quadruply charged molecular anion", *Phys. Rev. A*, 85, 064503 (2012).
- [11] Frank Hennrich, Manfred M. Kappes, Melanie Klinger, Andreas-Neil Unterreiner, "Ultrafast Dynamics of the First Excited State of Quasi Monodispersed Single-Walled (9,7) Carbon Nanotubes", *J. Phys. Chem. C*, 115, 23711 (2011).



### Andreas-Neil Unterreiner

Privatdozent at KIT, Institute of Physical Chemistry, born 1969, diploma in Chemistry



1995; doctoral degree 1998 (with Prof. H. Hippler), both University of Karlsruhe (TH); postdoctoral fellow 1998-99 (Prof. N. Scherer, The University of Chicago and DFG fellowship); research group leader since 2004; habilitation in Physical Chemistry in 2006.