

## MO 42 Excitation and Coherence Decay

Zeit: Mittwoch 14:00–16:00

Raum: H12

MO 42.1 Mi 14:00 H12

**Photoinduced multielectron dynamics in large finite systems: A two-color pump-probe mass-spectroscopic study on C<sub>60</sub> — ●I. SHCHATSININ, T. LAARMANN, A. STALMASHONAK, N. ZHAVORONKOV, C. P. SCHULZ, and I. V. HERTEL** — Max-Born-Institute, Max-Born Str. 2a, D-12489 Berlin, Germany

C<sub>60</sub> fullerenes may be seen as a prototype of a large, finite system for investigations of the electronic and nuclear responses in strong laser field [1]. We have studied the ionization and fragmentation dynamics of C<sub>60</sub> with time-resolved, two-color, pump-probe spectroscopy using sub-30-fs pulses of 400 nm (pump) and 800 nm (probe) wavelength. The recorded signals of mother ions and fragments as a function of the delay time between pump and probe pulses and as a function of their laser intensities ( $5 \times 10^{12}$ – $1 \times 10^{14}$  Wcm<sup>-2</sup>) contain information on the energy redistribution within the molecule. The resonant pre-excitation of the "t<sub>1u</sub>-doorway" state by a weak, blue pulse results in a significant enhancement of highly charged mother ions and fragments by the strong, delayed probe pulse. The observed ultrafast dynamics will be discussed in the picture of nonadiabatic multi-electron dynamics (NMED) which is currently of great interest.

[1] I. V. Hertel, T. Laarmann, and C. P. Schulz, *Ad. At. Mol. and Opt. Phys.* 50, 219 (2005)

MO 42.2 Mi 14:15 H12

**Femtosecond time resolved Experiments on the *t*-Butyl Radical — ●BASTIAN NOLLER<sup>1</sup>, LIONEL POISSON<sup>2</sup>, RAMAN MAKSIMENKA<sup>1</sup> und INGO FISCHER<sup>1</sup>** — <sup>1</sup>Institut für Physikalische Chemie, Universität Würzburg, Am Hubland D-97074 — <sup>2</sup>CEA Saclay, Bâtiment 522, 91191 Gif sur Yvette

The photophysics of the 3s and 3p state of the *t*-Butyl radical, C<sub>4</sub>H<sub>9</sub>, were investigated by femtosecond time resolved pump probe experiments in the gas phase. The radicals were produced by flash pyrolysis of Azot-butane. Three detection methods were used to elucidate the dynamics of the radical: Time of flight mass spectroscopy, photoion imaging and photoelectron imaging. Interestingly the lifetime of the 3<sup>2</sup>A<sub>1</sub> (3p) state at 255 nm is longer than the lifetime of the lower lying 2<sup>2</sup>A<sub>1</sub> (3s) state at 330 nm (1.9 ps vs. 110 fs).

MO 42.3 Mi 14:30 H12

**Xanthone in Water — Fast Intersystem Crossing and Intense Fluorescence — ●BJÖRN HEINZ<sup>1</sup>, BERNHARD SCHMIDT<sup>1</sup>, CHRISTOPHER ROOT<sup>1</sup>, HELMUT SATZGER<sup>1</sup>, FRANZ MILOTA<sup>2</sup>, BEAT FIERZ<sup>3</sup>, THOMAS KIEFHABER<sup>3</sup>, WOLFGANG ZINTH<sup>1</sup>, and PETER GILCH<sup>1</sup>** — <sup>1</sup>Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany — <sup>2</sup>Institut für Physikalische Chemie der Universität Wien, Währingerstraße 42, A-1090 Wien, Austria — <sup>3</sup>Division of Biophysical Chemistry, Biozentrum, University of Basel, Klingelbergstraße 50/70, CH-4056 Basel, Switzerland

Due to their efficient intersystem crossing (ISC) aromatic carbonyl compounds are of great importance in photophysics and photochemistry. They, for instance, serve as triplet sensitizers and thereby allow to access triplet states of molecules with low inherent ISC yields. Because of its rigid and symmetric structure the carbonyl compound xanthone has been thoroughly studied by various spectroscopic techniques. In most solvents (non-polar and polar) the fluorescence quantum yield is very low ( $\sim 10^{-4}$ ) in accordance with short ISC times. In water this yield is as high as 0.05. Still, a fast ISC process is observed. We propose a delayed fluorescence scheme to account for these observations. The scheme will be underscored by time resolved fluorescence and absorption measurements. The schemes allows to extract energetic information on the triplet states not accessible heretofore.

MO 42.4 Mi 14:45 H12

**Molecular mechanisms of fluorescence quenching of organic pigments — ●LISA LORENZ, VICTOR MATYLITSKY, KARSTEN NEUMANN, and JOSEF WACHTVEITL** — J.W. Goethe Universität, IPTC, Marie-Curie-Str. 11, 60439 Frankfurt/Main

The occurrence of fluorescence of crystalline pigments is often explained by their intermolecular distance, which is thought to be the main parameter determining fluorescence quenching. In a recent study of the organic pigment P.Y.101 we found that in contradiction to common rules for solid

state fluorescence, the radiationless deactivation of the excited state is a property of the individual molecule rather than a cooperative one.

In time resolved experiments on P.Y. 101 and three of its derivatives (one fluorescent and two non-fluorescent di-naphthyl-bisazomethin-based pigments), which are very similar in structure, we were able to show the dynamics and reaction pathways of deactivation. By embedding P.Y. 101 in a polyethylene matrix it was possible to compare dynamics in solution and in the microcrystalline state. It was found that the dynamics are slowed down by a factor of four in the solid state. For the non-fluorescent pigments a long-lived intermediate was observed which decays via internal conversion.

These results are in excellent agreement with time-dependent DFT[1,2] studies of the excited state properties of P.Y. 101 and its derivatives.

- 1.) A. Dreuw et al. *Angew. Chem. Int. Ed.*, 44, 7783, 2005
- 2.) J. Ploetner and A. Dreuw Solid-state fluorescence of Pigment Yellow 101 and derivatives: a conserved property of the individual molecules *Phys. Chem. Chem. Phys.*, 2006, in press

MO 42.5 Mi 15:00 H12

**Anisotropie nicht entarteter und (quasi)-entarteter Systeme - dynamische und statische Eigenschaften — ●OLIVER SCHALK und ANDREAS-NEIL UNTERREINER** — Universität Karlsruhe (TH), Lehrstuhl für Molekulare Physikalische Chemie, Kaiserstr. 12, 76128 Karlsruhe

Die transiente Anisotropie ist eine wichtige Methode der Ultrakurzzeitspektroskopie zur Charakterisierung von Moleküleigenschaften. Sie liefert u. a. Informationen über die Rotationsbewegung von Molekülen in flüssiger und gasförmiger Phase. Eine wichtige Größe ist dabei die Anisotropie zum Zeitpunkt  $t = 0$  (Anfangsanisotropie). Es ist bekannt, dass dieser Wert im Falle zweier elektronisch entarteter, angeregter Zustände den Wert 0,7 erreichen kann - im Gegensatz zu 0,4 für einen nichtentarteten Zustand. Gänzlich unbekannt ist jedoch das Verhalten bei quasi-entarteten Zuständen. Ein von uns weiterentwickeltes Modell kann sowohl die Rotationsdynamik als auch die Dynamik in Systemen mit entarteten angeregten Zuständen beschreiben. Ferner erhält man neue Erkenntnisse bzgl. des bekannten gaußförmigen Abklings der Anisotropie durch Rotation sowie der Multiphotonenspektroskopie und der Dynamik im entarteten System. Eine Beschreibung der Anfangsanisotropie eines Systems mit quasi-entarteten Zuständen ist ebenfalls möglich. Als Anwendungsbeispiel dient Cycloheptatrien, welches eine unerwartet hohe Anfangsanisotropie von etwa 0,6 zeigt, was als quasi-Entartung zweier Zustände gedeutet werden kann, die z.B. über eine konische Überschneidung gekoppelt sein können.

MO 42.6 Mi 15:15 H12

**Ultrafast proton transfer and vibrational coherence in the gas phase — ●CHRISTIAN SCHRIEVER, STEFAN LOCHBRUNNER, and EBERHARD RIEDLE** — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

The ultrafast excited state intramolecular proton transfer (ESIPT) is a prototype photoinduced chemical reaction that strongly couples electronic and nuclear motion. It has recently been studied by means of transient absorption measurements with sub-30-fs resolution. From these measurements a novel model of the ESIPT mechanism was derived that emphasizes the importance of the slow skeletal modes [1]. Typically, the wavepackets that are observed in the keto form after the ESIPT dephase on a time scale of 1 ps. It is not yet known whether this dephasing is mainly due to intramolecular vibrational coupling or due to the influence of the solvent. Neither is it known, whether the ESIPT and its irreversible nature depend on the solvent for a given molecule. We will decide these questions by comparison of the solution phase and the gas phase ultrafast behavior. The measurement in the gas phase is quite challenging due to the low vapor pressure that necessitates a collinear pump probe arrangement with matching of the beam sizes over a long range. To maximize the transient signal, we have recorded time resolved spectra from 310 to 700 nm. These reveal very large absorptions in the near UV that render a fivefold larger signal than the stimulated emission in the visible.

- [1] S. Lochbrunner, A. J. Wurzer, and E. Riedle *J.Phys.Chem. A* 107, 10580 (2003)

MO 42.7 Mi 15:30 H12

**Quantum interference oscillations of fs-photoionization of heavy alkali-doped Helium nanodroplets** — ●MARCEL MUDRICH<sup>1</sup>, OLIVER BÜNERMANN<sup>1</sup>, GEORG DROPPPELMANN<sup>2</sup>, PATRICK CLAAS<sup>2</sup>, CLAUS-PETER SCHULZ<sup>3</sup>, and FRANK STIENKEMEIER<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg — <sup>2</sup>Physikalische Fakultät, Universität Bielefeld — <sup>3</sup>Max-Born-Institut, Berlin

Quantum interference (QI) oscillations of the ion yield obtained from fs pump-probe photoionization of K, Rb, and Cs attached to He nanodroplets are recorded. All three heavy alkalis are found to form alkali-helium exciplexes which also show QI [1,2,3]. The observation of QI of RbHe photoionization over tens of picoseconds demonstrates that laser induced coherence persists even when a new molecular bond is formed. Analysis of the QI frequency spectrum allows to determine the vibrational level structure of the exciplex molecule. Moreover, the change in vibrational energies and vibrational cooling can be followed in real time during exciplex formation.

[1] C.P. Schulz, P. Claas and F. Stienkemeier, *Phys. Rev. Lett.* **87**, 153401 (2001)

[2] G. Droppelmann, O. Bünermann, C.P. Schulz, and F. Stienkemeier, *Phys. Rev. Lett.* **93**, 023402 (2004)

[3] O. Bünermann, M. Mudrich, M. Weidemüller, and F. Stienkemeier, *J. Chem. Phys.* **121**, 8880 (2004)

MO 42.8 Mi 15:45 H12

**Vibrational relaxation and wavepacket motion in electronically excited perylene dyes in solution** — ●PATRIZIA KROK, IDA Z. KOZMA, STEFAN LOCHBRUNNER, and EBERHARD RIEDLE — LS für BioMolekulare Optik, Ludwig-Maximilians-Universität München

We study the S<sub>1</sub> state vibrational dynamics of perylenbisimid dyes in solution. The absorption spectrum and the emission spectrum show a well structured progression that is mainly due to a single vibration. By selective excitation of the first three vibronic levels and probing at suitable wavelengths, we find a time constant of about 2 ps for the vibrational reorganization in the nonyldecyl bisubstituted dye S-19. We attribute this time constant to internal vibrational redistribution as well as relaxation to the solvent, i.e. the population decay of the optically excited vibrational level.

A complementary experiment investigates the ultrafast wavepacket motion in S-19 and related dyes to identify the Franck-Condon active modes and their dephasing and decay mechanism. We create a superposition of vibronic states with spectrally broad 11-fs pulses at 510 nm and detect oscillations at about 500, 1300 and 1500 cm<sup>-1</sup> with 10-fs probe pulses centered in the emission region. The vibrational frequencies are compared to calculations and measurements in helium nano droplets [1]. The decay of the wavepacket motion allows us for the first time to decide whether pure vibrational dephasing is a significant contribution in addition to the population decay.

[1] M. Wewer and F. Stienkemeier, *Phys.Chem.Chem.Pys.* **7**, 1171 (2005)