

## MO 21: Photochemie 2

Zeit: Donnerstag 14:00–15:00

Raum: VMP 6 HS-G

MO 21.1 Do 14:00 VMP 6 HS-G  
**Ultrafast bimolecular reactions of benzhydryl cations in the ground state** — ●CHRISTIAN SAILER<sup>1</sup>, JOHANNES AMMER<sup>2</sup>, CHRISTOPH NOLTE<sup>2</sup>, IGOR PUGLIESI<sup>1</sup>, HERBERT MAYR<sup>2</sup>, and EBERHARD RIEDLE<sup>1</sup> — <sup>1</sup>Lehrstuhl für BioMolekulare Optik, LMU München — <sup>2</sup>Department Chemie und Biochemie, LMU München

We investigate the ultrafast reactions of selected benzhydryl cations with different alcohols which are used as solvents. The benzhydryl cations are photogenerated in the electronic ground state from precursor molecules by fs-UV-excitation (270 nm) and sub-ps dissociation and are detected by their characteristic absorption band at about 450 nm. The subsequent reaction of the cation with the solvent to form an ether is observed by quenching of the cation absorption signal. We are able to show that the decay times vary systematically from 2.6 ps for the most reactive educts to several hundred picoseconds for the less reactive pairs. This behavior is in surprisingly good agreement with measurements on longer timescales up to minutes [1]. To the best of our knowledge these extremely short decay times are the fastest measured bimolecular reaction times in the electronic ground state. The ultrafast dynamics suggest that the alcohol molecules are not randomly distributed around the precursor, as the rotational relaxation of alcohols (several picoseconds) is slower than the fastest observed reaction times. It is therefore inferred that the reactants are already suitably aligned before the optical excitation.

[1] S. Minegishi, S. Kobayashi, and H. Mayr, *J. Am. Chem. Soc.* **126** (2004), 5174

MO 21.2 Do 14:15 VMP 6 HS-G  
**Biphasic kinetics in fast ground state chemistry due to vibrational excitation** — ●THOMAS SCHMIERER, WOLFGANG SCHREIER, and PETER GILCH — Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, 80538 München, Deutschland

Internal conversion processes and photo-chemical reactions often result in vibrationally highly excited intermediates. On time-scales which are short compared to vibrational relaxation this excitation can influence chemical kinetics in the electronic ground state.

The photo-chemistry of ortho-nitrobenzaldehyde (NBA) offers an example for such a kinetic. UV-excitation triggers a hydrogen transfer which results in a ketene intermediate within 400 fs [1]. In aprotic solvents, e.g. THF, nanosecond lifetimes for this ketene have been reported [2,3]. Femtosecond UV/Vis and IR experiments show that the decay in THF is biphasic with time-constants of 10 ps and some nanoseconds. The 10 ps constant matches the decay of the vibrational excitation and the rise of a secondary product.

[1] S. Laimgruber et al., *Angew. Chem. Int. Ed.* (2005) 44

[2] R. W. Yip et al., *Res. Chem. Int.*, (1989) 11

[3] S. Laimgruber et al., *Phys. Chem. Chem. Phys.*, (2008) 10

MO 21.3 Do 14:30 VMP 6 HS-G  
**Photodissociation dynamics by means of a revised version of**

**velocity-map ion-imaging** — ●ANDREAS SCHMAUNZ, UWE KENSY, ALKWIN SLENCZKA, and BERNHARD DICK — University of Regensburg, Regensburg

Velocity-map ion-imaging [1] as a refined version of ion-imaging [2] provides the full three-dimensional velocity distribution of an atomic fragment produced via photolysis of a molecule. The velocity distribution reveals the kinetic and internal energy of the counter fragment. Thus, the full dynamic of the photodissociation is obtained. In the case of a molecular fragment the analysis of the full dynamics requires the measurement of an ion-image for each of the energetically accessible internal states. This procedure is extremely time consuming if not impossible due to the spectral overlap. We present a new technique, a hybrid of real-time ion-counting [3] and REMPI spectroscopy. It allows to obtain the angular and velocity distribution for the entire set of internal states of the molecular fragment within the time necessary to record a common REMPI spectrum. The method will be demonstrated for the photolysis of NO<sub>2</sub> by recording the NO fragment. These data provide insight into the dissociation dynamics far beyond conventional data reported on this system so far.

[1] A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3447 (1997). [2] D. W. Chandler and P. L. Houston, *J. Chem. Phys.* **87**, 1445 (1987). [3] B. Y. Chang, R. C. Hoetzlein, J. A. Mueller, J. D. Geiser, and P. L. Houston, *Rev. Sci. Instrum.* **69**, 1665 (1998).

MO 21.4 Do 14:45 VMP 6 HS-G  
**Characterization of the Conical Intersection Seam for Trifluoromethyl-Pyrrolylfulgid, a Highly Substituted Cyclohexadiene Derivative** — ●ARTUR NENOV and REGINA DE VIVIE-RIEDLE — Department Chemie und Pharmazie, Ludwig-Maximilians-Universität München, Butenandt-Str. 11, 81377, München, Germany

Conical intersections of low energy form seams important for photochemical reactions. Different techniques have been developed to determine critical points on these seams [1]. However, quantum dynamical calculations have shown that these points are often not reached during wave packet propagation. A prominent example is the photoinduced isomerisation of cyclohexadiene (CHD) to cZc-hexatriene (HT) [2]. By using linear interpolation methods and constrained gradient difference optimization, we were able to connect three CoIns of minimum energy via a low energy path, thus extending the seam described in previous papers [3]. We applied this approach on trifluoromethyl-pyrrolylfulgid, a highly substituted CHD derivative. The identified conical seam involves molecular motions similar as in case of CHD, however shifted in coordinate space due to electronic and steric effects of the substituents. From the topology of the optimized seams we could locate regions on the PES that lead predominantly either to the educt or to the product state and thus significantly influence the course of the reaction.

[1] M.J. Bearpark, M.A. Robb, *Chem. Phys. Lett.* **223** (1994) 169

[2] A. Hofmann and R. de Vivie-Riedle, *Chem. Phys. Lett.* **346** (2001) 299

[3] M. Garavelli, W. Fuss *J. Phys. Chem. A* **105** (2001) 4458