

MO 11: Photochemistry I

Time: Wednesday 10:30–11:45

Location: MO-H7

MO 11.1 Wed 10:30 MO-H7

UV and Mid-IR Photo-induced Dissociation of Solvated (Bio)Molecular Complexes — ●MUKHTAR SINGH^{1,2,3}, MATTHEW SCOTT ROBINSON^{1,2,3}, HUBERTUS BROMBERGER^{1,2}, JOLIJN ONVLEE^{1,3}, SEBASTIAN TRIPPEL^{1,2}, and JOCHEN KÜPPER^{1,2,3} — ¹Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg — ²Center for Ultrafast Imaging, Universität Hamburg — ³Department of Physics, Universität Hamburg

We present the ultrafast imaging of UV and thermal energy chemical dynamics of micro-solvated (bio)molecular complexes probed with strong field techniques [1]. We produced a pure sample of the molecule of interest in the gas phase by using a combination of a molecular beam and the electrostatic deflector [2]. To study the induced dynamics, we set up the both, an UV and a mid-IR pump-probe experiment, in which a 266 nm and 2.9 μm beam was used to excite the system. A 1.3 μm beam was used for ionising the system. First experiments focused on the ion imaging of the UV and mid-IR triggered system. Future experiments will use laser-induced electron diffraction (LIED) [3,4] to probe the induced dynamics in order to obtain structural information about the system with atomic resolution.

[1] J. Onvlee, et al., *arXiv:2103.07171v1* 12 Mar 2021.

[2] S. Trippel, et al., *Rev. Sci. Instrum.* **89**, 096110 (2018).

[3] J. Wiese, et al., *Phys. Rev. Research* **3**, 013089 (2021).

[4] E. T. Karamatskos, et al., *J. Chem. Phys.* **150**, 244301(2019).

MO 11.2 Wed 10:45 MO-H7

Multiphoton light-induced potentials — ●MATTHIAS KÜBEL — Institut für Optik und Quantenelektronik, FSU Jena

We study the strong-field photodissociation of H_2^+ using Cold Target Recoil Ion Momentum Spectroscopy. Our two-color streaking method allows us to produce a coherent wave packet in the molecular cation and expose it to a phase-controlled mid-infrared laser field. The resulting fragmentation pattern exhibits a strikingly structured angular distribution, which depends on various laser parameters. Using two-color Floquet theory as well as numerical solutions of the time-dependent Schrödinger equation, we show that the pattern arises from an interplay of competing multiphoton fragmentation pathways, as well as forced rotational dynamics. On a qualitative level, the dynamics can be intuitively understood by picturing the light-induced potential energy landscape on which the nuclear motion takes place. Interestingly, our experimental approach allows us to shape these potentials and follow the ensuing molecular dynamics. Our results highlight the complexity of intense matter interaction even in the simplest of molecules.

MO 11.3 Wed 11:00 MO-H7

A Velocity Map Imaging Study of the Photodissociation Dynamics of the Trichloromethyl Radical — ●CHRISTIAN MATTHAEI¹, DEB PRATIM MUKHOPADHYAY^{1,2}, and INGO FISCHER¹ — ¹Institute of Physical and Theoretical Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg — ²Present address: Department of Dynamics of Molecules and Clusters, J. Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, 182 23 Praha 8, Czech Republic

CCl_3 is one of the numerous halogen-containing molecules that contribute to the catalytic destruction of the ozone layer. Here we investigate the photodissociation dynamics of this molecule following the

excitation with light between 250 and 230 nm. We mainly observe the loss of a Cl atom, that is associated with the CCl_2 fragment. However, the generation of CCl could also be observed. Control experiments using CCl_2 as a precursor suggest that the CCl results from the reaction CCl_3 to $\text{CCl} + \text{Cl}_2$.

MO 11.4 Wed 11:15 MO-H7

Mechanistic Studies on a Deracemization Reaction via a Triplet 1,3-Diradical Induced by Energy Transfer from a Chiral Sensitizer — ●ROGER JAN KUTTA¹, XINYAO LI², CHRISTIAN JANDL², ANDREAS BAUER², THORSTEN BACH², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany — ²Lehrstuhl für Organische Chemie I, Technische Universität München, Germany

The photochemical deracemization[1] of spiro[cyclopropane-1,3'-indolin]-2'-ones (spirocyclopropyl oxindoles) was investigated by time-resolved spectroscopies and computational approaches. The corresponding 2,2-dichloro compound is configurationally labile upon direct irradiation and when sensitized by excited achiral thioxanthone-9-one. In the latter reaction the triplet 1,3-diradical intermediate is generated via triplet energy transfer from the photosensitizer.

Deracemization is achieved by using a chiral thioxanthone photosensitizer with a lactam hydrogen bonding site. Here, three factors co-act favorably for high enantioselectivity: i) a factor 3 differing binding constants to the chiral thioxanthone for the two enantiomers. ii) unequal molecular distances in the complexes, presumably lead to differing energy transfer efficiencies. iii) the 1,3-diradical lifetime exceeds the complex lifetime, facilitating a racemic deactivation back to the ground state.[2]

[1] Nature **2018**, 564, 240-243.

[2] Angew. Chem. Int. Ed. **2020**, 59, 21640-21647.

MO 11.5 Wed 11:30 MO-H7

Selenyl Radicals in Solution: Photogeneration and Reactions — ●CARINA ALLACHER¹, ROGER JAN KUTTA¹, ELIAS HARRER¹, DANIEL GREYDA¹, AMIT KUMAR-DUTTA², SOOYOUNG PARK², ALEXANDER BREDER², and PATRICK NUERNBERGER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — ²Institut für Organische Chemie, Universität Regensburg, 93040 Regensburg

Due to the low bond energy of selenium bonds, selenium-centered radicals can be formed photochemically with visible or near-UV light [1], thereby opening up new synthetic strategies based on the versatile reactivity of these radical species. A prominent precursor of the phenylselenyl radical (PhSe^\bullet) is diphenyl diselenide (Ph_2Se_2) which upon irradiation with UV light may dissociate homolytically [2]. In this work, we identify an additional reaction pathway that is pursued after excitation of Ph_2Se_2 with 355 nm light. To quantify the dynamics of these competing photochemical processes, transient absorption studies on a timescale from nano- to milliseconds are performed in various solvent environments. Solely in the solvent hexafluoro-2-propanol, a further intermediate, namely the radical $\text{PhSeH}^{+\bullet}$, can be photogenerated. Beyond Ph_2Se_2 , we present time-resolved studies on further organoselenium compounds as light-triggered sources of PhSe^\bullet and $\text{PhSeH}^{+\bullet}$ radicals.

[1] S. Ji et al., *Angew. Chem. Int. Ed.* **53**, 6781 (2014).

[2] I. P. Beletskaya et al., *J. Chem. Soc., Perkin Trans. 2*, 107 (2007).