MO 2: Collisions, Energy transfer and ab initio Modelling

Time: Monday 11:00–12:30 Location: f142

MO 2.1 Mon 11:00 f142

Studying competing reaction pathways in F^- + CH_3I using 3D velocity map imaging — •Tim Michaelsen, Eduardo Carrascosa, Jennifer Meyer, Björn Bastian, Martin Stei, and Roland Wester — University of Innsbruck, Austria

We study ion-molecule reactions in a kinematically complete way using velocity map imaging in a crossed-beam setup [1,2]. A major focus of our group are substitution reactions of halide anions with methyl halides. Due to a fruitful collaboration between theory and experiments a lot of insight into the mechanics of these S_N2 reactions was gained [3]. Beyond these, at sufficiently high collisional energies and entrance geometries other reaction channels become available and we will focus on these here. Specifically, we present in this talk the reaction of F^- + CH_3I where we observed three additional reaction pathways: the proton transfer forming CH_2I^-, the formation of IF^- via halogen abstraction and first evidence of a $[FHI]^-$ product ion [4].

Furthermore we report on the latest results on a study of the transition between predominantly substitution (S_N2) driven reactions to elimination (E2) driven ones. This was realized by measuring the energy and angle differential cross sections for reactions between different halide ions (Cl^-, F^-) and methyl halides of subsequent degree of methylation at multiple collision energies.

[1] J. Mikosch et al., Science 319, 183 (2008) [2] S. Trippel, et al., PRL 110, 163201 (2013) [3] R. Otto et al., Nat. Chem. 4.7 534 (2012) [4] E. Carrascosa et al., submitted to JPC (2015)

MO 2.2 Mon 11:15 f142

Incoherent photoelectron scattering in above threshold ionization of dense media — •Martin Wilke, Ruba Al-Obaidi, Igor Yu. Kiyan, and Emad F. Aziz — Institute for Methods for Material Development and Joint Ultrafast Dynamics Lab in Solutions and at Interfaces (JULiq) at Helmholtz-Zentrum Berlin, and Freie Universität Berlin, FB Physik, Berlin, Germany

We report on how the typical cutoff laws of fast electron emission by high-intensity ionization processes of single molecules as above-threshold ionization (ATI) and high-order ATI (HATI) can be substantially violated by laser-assisted electron scattering (LAES) on neighboring molecules. Such collective effects occur during the ionization process on the time scale of few laser cycles (40 fs at 1300 nm) in dense media. Above a certain density threshold electron heating by inelastic scattering even dominates the fast photoelectron emission by strong laser fields. Recording photoemission spectra in UHV and providing gas densities of a few millibars and liquids as target is enabled by the liquid micro-jet technique. A study of strong field ionization for different densities and solvents in gas and liquid phase was performed and supported by numerical calculations.

MO 2.3 Mon 11:30 f142

Autofragmentation of rovibrational excited metal dimer anions — •Jürgen Göck[1], Arno Becker[1], Klaus Blaum[1], Christian Breitenfeldt[1,2], Sebastian George[1], Manfred Grieser[1], Florian Grussie[1], Robert von Hahn[1], Philipp Herwig[1], Jonas Karthein[1], Claude Krantz[1], Holger Kreckel[1], Sunil Kumar[1], Jorrit Lion[1], Svenja Lohmann[1], Christian Meyer[1], Preeti M. Mishra[1], Oldrich Novotny[1], Aodh P. O'Connor[1], Roland Repnow[1], Kaija Spruck[1,3], Stefan Schippers[3], Dirk Schwalm[1,4], Lutz Schweikhard[2], Stephen Vogel[1], and Andreas Wolf[1] — [1]Max-Planck-Institut für Kernphysik (MPIK), Saupfercheckweg 1, 69117 Heidelberg, Germany — [2]Institut für Physik, Ernst Moritz Arndt Universität Greifswald, 17487 Greifswald, Germany — [3]I. Physikalisches Institut, Justus-Liebig-Universität Gießen, 35392 Giessen, Germany — [4]Weizmann Institute of Science, Rehovot 76100, Israel

The autofragmentation of Co_2^- and Ag_2^- ions was investigated over times up to 1000 s in the Cryogenic Storage Ring (CSR) [1] at the MPIK. The 35 m circumference electrostatic storage ring is operated at cryogenic temperature using liquid helium as cooling agent. The cryogenic environment of below 10 K leading to a residual gas pressure of lower than 10^{-13} mbar room temperature equivalent offers perfect conditions for background-free gas phase spectroscopy experiments. The rovibrationally excited anions were produced in a metal ion sputter source, accelerated to 60 keV and stored in the CSR. The neutral and charged fragments of the reaction $X_2^{*-} \rightarrow X^- + X$ were recorded by micro channel plate based detectors [2] . Results and analysis will be presented. A coincidence signal from auto dissociation of the anions was observed as function of the storage time up to 1000 s. The non-exponential nature of the decay will be presented and compared to earlier short-time measurements [3] . [1] R. von Hahn et al., Nucl. Instrum. Meth. B 269, 2871 (2011) - [2] K. Spruck et al., Rev. Sci. Instrum. 86, 023303 (2015) - [3] J. Fedor et al., Phys. Rev. Lett. 94, 113201 (2005)

MO 2.4 Mon 11:45 f142

Theoretical Photoelectron Spectroscopy: Unravelling Ultrafast Spin-Crossover Transitions — •Gilbert Grell[1], Sergey I. Bokarev[1], Saadullah G. Aziz[2], and Oliver Kühn[1] — [1]Universität Rostock, Institut f. Physik, Albert Einstein Straße 23-24, 18059 Rostock, DE — [2]King Abdulaziz University, Chemistry Department, Faculty of Science, 21589 Jeddah, Saudi Arabia

Recently, we have demonstrated the ability of the RASSCF/RASSI method together with a Dyson orbital formalism to accurately predict the L-edge photoelectron spectra (PES) of aqueous transition metal complexes [1]. Key features of this methodology are the account for the multiconfigurational character (RASSCF), the inclusion of spin-orbit coupling (RASSI), as well as the accurate numerical evaluation of the PES intensities. This contribution focuses on the application of the protocol to interpret VIS pump / XUV photoelectron probe experiments that regard the spin-crossover (SCO) transitions on $[Fe(bpy)_3]^{2+}$. We will provide a clear understanding of the actual SCO pathway, thus closing the open questions that arise from contradicting experimental results [2-4].

We acknowledge financial support by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah (Grant No. D-003-435), and the DFG (Grant No. KU952/10-1)

[1] Grell et al., J. Chem. Phys. 143, 074104 (2015)
[2] Zhang et al., Nat. 509, 345 (2014)
[3] Auböck and Chergui, Nat. Chem. 7, 629 (2015)
[4] Sousa et al., Chem. Eur. J. 19, 17541 (2013)

MO 2.5 Mon 12:00 f142

Natural extension of Hartree-Fock through extremal 1-fermion information — •Carlos L. Benavides-Riveros — Martin-Luther-Universität Halle-Wittenberg, 06120 Halle (Saale), Germany

Fermionic natural occupation numbers (NON) do not only obey Pauli's exclusion principle but are even stronger restricted by so-called generalized Pauli constraints. Whenever given NON lie on the boundary of the allowed region the corresponding N-fermion quantum state has a significantly simpler structure. By employing this structure a variational optimization method for few fermion ground states is elaborated. We quantitatively confirm its high accuracy for systems with the vector of NON in a small distance to the boundary of the polytope. In particular, we derive an upper bound on the error of the correlation energy given by the ratio of the distance to the boundary of the polytope and the distance of the vector of NON to the Hartree-Fock point. As a consequence, the proposed method is the computationally cheapest covering the leading order correlations for systems exhibiting the recently found quasipinning phenomenon. Moreover, these geometric insights shed some light on the concept of active spaces, correlation energy, frozen electrons and virtual orbitals.

MO 2.6 Mon 12:15 f142

Mechanism of Forward and Backward Scattering and Modification of the Polanyi rule for reaction A+BC→AB+C and AC+B — •Victor Wei-Keh Chao — Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan, R.O.China — Group 1101, State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R.China — Victor Basic Res. Labor. e.V. 33602 Bielefeld, Germany

The Polanyi rule - The reactive cross sections can be enhanced with transl. and vibr. prepared BC on the early and late barrier PESs, respectively, has contributed immensely over 60 years. Results of H+FCl(v,j)→HF+Cl and HCl+F at E_{rel}=0.5-20 kcal/mol show, con-

siderations of 1. Mass combination of A, B and C, 2. Width and steepness of the entrance channel, 3. Space on the barrier top, are necessary. The entrance channel is very steep and narrow (For HCl is ca.3 times wider), and barrier top for HF (For HCl is ca.5 times wider) is very small compared with the bond length of FCl, whatever cause both transl. and vibr. enhancement on the early barrier PESs. Appearance of max. of curvature σ_{AB}-v$_{BC}$ can be similarly explained. The forward and backward scattering mechanism can also be clarified. The nascent, light AB (HF) and heavy C (Cl) will be forwards and backwards scattered, respectively, on the barrier top because of the exoergicity and mass ratio AB/C $<$ 1; heavy AC (HCl) and light B (F) backwards and forwards, with AC/B $>$1. Support of financial aids by Section 11, DICP, CAS (KF-2013-01, KF-2014-01), and VBR are acknowledged.