

MO 16: Ions

Time: Thursday 10:30–12:15

Location: MO-H5

Invited Talk

MO 16.1 Thu 10:30 MO-H5

Infrared Spectroscopy of Ionic Hydrogen-Helium Complexes — ●OSKAR ASVANY and STEPHAN SCHLEMMER — I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, Köln

Ionic species consisting of only hydrogen and helium, $H_mHe_n^+$, are of interest in astrophysics (those with small n and m) and in molecular physics (because some of them exhibit a floppy behaviour). Using a combination of cryogenic ion-trap machines, operated at 4 K, and different laser sources, the ionic species HHe_n^+ ($n = 2 - 6$), DHe_n^+ ($n = 3 - 6$), H_2He^+ , D_2He^+ and H_3He^+ have been investigated by low- and high-resolution infrared spectroscopy. This contribution gives an overview about the investigations done in the last couple of years, with an emphasis on HHe_n^+ ($n = 2 - 6$). These species are known to consist of a linear $He-H^+-He$ ($n = 2$) chromophore, with additional helium atoms attached to the central proton ($n = 3, 4, \dots$). The IR results confirm this motif, with $n = 3$ and $n = 6$ being of T-shaped C_{2v} and of D_{4h} symmetry, respectively, while the species with $n = 4, 5$ are suggested to exhibit interesting dynamical phenomena related to large-amplitude motion.

MO 16.2 Thu 11:00 MO-H5

Deuteration effects in the reactive scattering of a nucleophilic substitution reaction. — ●ATILAY AYASLI¹, THOMAS GSTIR¹, ARNAB KHAN¹, TIM MICHAELSEN¹, DÓRA PAPP², GÁBOR CZAKÓ², and ROLAND WESTER¹ — ¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, 6020 Innsbruck, Austria — ²University of Szeged, Szeged, Hungary

Our group studies ion-molecule reactions using a crossed-beam setup with kinematically complete velocity map imaging (VMI). We have investigated reactive scattering of fully deuterated methyl iodide CD_3I with atomic fluorine anions in the energy range from 0.7 to 2.3 eV relative collision energy. The results are compared with the hydrogenated system $F^- + CH_3I$ [1] as well as quasi-classical trajectory (QCT) simulations [2]. The two main reaction channels are nucleophilic substitution (S_N2) and deuteron/proton transfer for both systems. The $F^- + CH_3I$ reaction shows a significant large-impact parameter contribution in the S_N2 channel, a feature that is absent for its deuterated counterpart. While the simulations can fully capture the S_N2 dynamics in the reaction with CD_3I , large-impact parameter events from $F^- + CH_3I$ cannot be reproduced. Such a discrepancy between experimental and theoretical work might hint towards a quantum effect that cannot be captured by QCT simulations.

[1] Michaelsen et al., *J. Phys. Chem. Lett.* 2020, 11, 11, 4331-4336[2] Olasz et al., *Chem. Sci.*, 2017, 8, 3164-3170

MO 16.3 Thu 11:15 MO-H5

Disentangling elimination and nucleophilic substitution dynamics — ●TIM MICHAELSEN¹, JENNIFER MEYER¹, VIKTOR TAJTI², EDUARDO CARRASCOSA¹, TIBOR GYÖRI², MARTIN STEI¹, BJÖRN BASTIAN¹, GÁBOR CZAKÓ², and ROLAND WESTER¹ — ¹Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria — ²Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, University of Szeged, Szeged, Hungary

In the presented study we combine angle- and energy-differential cross sections, obtained in a crossed-beam velocity map imaging experiment, with quasi-classical trajectory (QCT) calculations on an accurate 21-dimensional hypersurface to disentangle the competition of base induced elimination (E2) and nucleophilic substitution (S_N2) in the reaction of F^- with CH_3CH_2Cl [1]. As the detected product ion Cl^- is identical for S_N2 , anti and syn-E2, separating the pathways from experiment alone is very challenging. The QCT calculations quantitatively reproduce the measured total experimental cross section due to their novel accuracy for such polyatomic reactions and allow us to differentiate the competing channels and extract detailed information on the underlying reaction mechanisms. We find that the anti-E2 pathway is dominant, but that S_N2 contributions become more important towards larger collision energies.

[1] J. Meyer, V. Tajti, E. Carrascosa et al., *Nat. Chem.* 13, 977-981 (2021)

MO 16.4 Thu 11:30 MO-H5

Aromaticity and structure variation from cationic cyclopropenyl by varying the number of hydrogen atoms — ●SIMON REINWARDT¹, PATRICK CIESLIK¹, ALEXANDER PERRY-SASSMANNSHAUSEN², TICIA BUHR², ALFRED MÜLLER², STEFAN SCHIPPERS², FLORIAN TRINTER^{3,4}, and MICHAEL MARTINS¹ — ¹Universität Hamburg, Hamburg, Germany — ²Justus-Liebig-Universität Gießen, Gießen, Germany — ³Goethe-Universität Frankfurt am Main, Frankfurt am Main, Germany — ⁴Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Small carbon systems play an important role in the ion chemistry in the interstellar medium [1] and planetary atmospheres [2]. Soft X-ray spectroscopy enables the analysis of these small structures as well as their aromaticity [3]. This allows a comprehensive understanding of the chemical bonding of these hydrocarbon cations and the transition from rings to chains. The smallest aromatic ion, the cyclopropenyl cation ($C_3H_3^+$), is an ideal system for studying the aromaticity in chemical bonds on a fundamental level. Through the production in an ion source and a subsequent mass analysis, the structure and the aromaticity can be selected by controlling the number of attached hydrogen atoms. We present new results on these systems that we have measured on the photon ion spectrometer (PIPE) [4] at PETRA III in Hamburg.

[1] D. Smith *et al.*, *Chem. Rev.*, **92** (1992).[2] C. A. Nixon *et al.*, *A. J.*, **160** 205 (2020).[3] C. Kolczewski *et al.*, *J.Chem.Phys.*, **124** 034302 (2006).[4] S. Schippers *et al.*, *X-Ray Spectrometry*, **49** 11 (2020).

MO 16.5 Thu 11:45 MO-H5

Time-resolved photon interactions of size- and charge-state selected polyanionic tin clusters — ●ALEXANDER JANKOWSKI, PAUL FISCHER, MORITZ GRUNWALD-DELITZ, and LUTZ SCHWEIKHARD — Institute of Physics, University of Greifswald, Germany

Small tin clusters (Sn_n^- of sizes $n \lesssim 50$) are formed by so-called building blocks of Sn_7 , Sn_{10} [1-3] and, in the case of anionic clusters, Sn_{15} [3]. These cluster sizes $n = 7, 10$ and 15 lead to corresponding fragmentation patterns [4,5] which have been confirmed and further investigated [6,7] at the ClusterTrap setup [8]. These previous findings suggested for dianionic tin clusters fission processes into two monoanionic fragments in analogy to the case of lead clusters [9]. Recently, photodissociation experiments have been performed on size- and charge-state-selected polyanionic tin clusters. By delaying the ejection/analysis of the trapped clusters with respect to the pulsed photoexcitation, time-resolved measurements allow the reconstruction of the decay pathways.

[1] C. Majumder *et al.*, *Phys. Rev. B* **64**, 233405 (2001)[2] H. Li *et al.*, *J. Phys. Chem. C* **116**, 231-236 (2011)[3] A. Lechtken *et al.*, *J. Chem. Phys.* **132**, 211102 (2010)[4] E. Oger *et al.*, *J. Chem. Phys.* **130**, 124305 (2009)[5] A. Wiesel *et al.*, *Phys. Chem. Chem. Phys.* **14**, 234-245 (2012)[6] S. König *et al.*, *Eur. Phys. J. D* **72**, 153 (2018)[7] M. Wolfram *et al.*, *Eur. Phys. J. D* **74**, 135 (2020)[8] F. Martinez *et al.*, *Int. J. Mass Spectrom.* **266**, 365-366 (2014)[9] S. König *et al.*, *Phys. Rev. Lett.* **120**, 163001 (2018)

MO 16.6 Thu 12:00 MO-H5

Cryo Kinetics and IR Spectroscopy of Nitrogen on Tantalum Cluster — ●DANIELA V. FRIES, ANNIKA STRASSNER, MATTHIAS P. KLEIN, MAXIMILIAN HUBER, MARC H. PROSENC, and GEREON NIEDNER-SCHATTEBURG — TU Kaiserslautern, Kaiserslautern, Deutschland

As motivated by prior room temperature studies on Ta_2^+ [1] we investigate larger Ta_n^+ clusters ($3 < n < 8$) and their N_2 adsorption and activation abilities by adsorption kinetics and infrared spectroscopy under cryo conditions compared with DFT calculations.

The model system Ta_4^+ appears to be of particular interest with regard to cryo N_2 activation. Experimental results reveal peculiar details for the first and second adsorption kinetics. The absence of any NN stretching signature in $[Ta_4(N_2)_1]^+$ and $[Ta_4(N_2)_2]^+$ indicates cleavage of the first two adsorbed dinitrogen molecules. We unravel a multistep above edge across surface (AEAS) activation mechanism. [2]

In addition to the investigations of these tantalum cations we are interested in the N₂ adsorption on tantalum anions (Ta_n⁻, 4 < n < 10). Initial experiments observe strong size dependencies which are subject of ongoing interpretation.

[1] Proc. Natl. Acad. of Sci. USA, 2018, 115, 11680-11687.

[2] Phys. Chem. Chem. Phys., 2021,23, 11345-11354.