

MO 5: Collisions, Energy Transfer

Time: Monday 14:30–16:00

Location: MER 02

MO 5.1 Mon 14:30 MER 02

Scattering of state selected OH and NO — ●MORITZ KIRSTE, XINGAN WANG, HANS CHRISTIAN SCHEWE, GERARD MEIJER, and SEBASTIAAN VAN DE MEERAKKER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

The crossed molecular beam technique is a mature and important experimental method to understand molecular interactions and molecular reaction dynamics. The Stark deceleration technique yields unprecedented control over both the internal and external degrees of freedom of polar molecules in a molecular beam. The combination of both techniques offers new possibilities in scattering experiments. In particular, crossed Stark-decelerated molecular beams allow detailed molecular scattering studies as a function of the collision energy, from low to high collision energies, and with a very high energy resolution. Recently, a new Stark decelerator molecular beam machine has become operational in our laboratory that is dedicated to crossed beam scattering experiments. We will discuss our results on the inelastic scattering of fully state selected OH($X^2\Pi_{3/2}, J=3/2, f$) radicals with hexapole state-selected NO($X^2\Pi_{1/2}, J=1/2, f$), as a function of the collision energy.

MO 5.2 Mon 14:45 MER 02

Reactive scattering of cold OH⁻·(H₂O)_n with CH₃I — ●RICO OTTO¹, JONATHAN BROX¹, SEBASTIAN TRIPPEL¹, MARTIN STEI², THORSTEN BEST¹, and ROLAND WESTER² — ¹Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg — ²Institut f. Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, A-6020 Innsbruck

Chemical reactions in solution are exceedingly different from their gas-phase counterparts [1]. Up to now the role of the solvent molecules is not understood in detail. We investigate the influence of microsolvation in the reaction OH⁻·(H₂O)_n + CH₃I by adding single water molecules to the molecular anion. The combination of crossed beam imaging [2] with a multipole radio frequency ion trap allows us to prepare the anion water clusters in well defined initial states. We present crossed beam imaging studies at low collision energies between 0.2 - 2.5 eV for a different number of solvent water molecules. New reaction channels arising from the water will be discussed.

[1] C. K. Regan, S. L. Craig, J. I. Brauman, *Science* 295, 2245 (2002)
[2] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, *Science* 319, 183 (2008)

MO 5.3 Mon 15:00 MER 02

Rotational dependence of the proton-transfer reaction HBr⁺ + CO₂ → HOCO⁺ + Br — ●LISA PAETOW, FRANZISKA UNGER, BERND BEUTEL, and KARL-MICHAEL WEITZEL — Philipps-Universität Marburg, Fachbereich Chemie, 35032 Marburg

The effects of reactant ion rotational excitation on the proton-transfer reactions of HBr⁺ and DBr⁺ with CO₂ were studied in a guided ion beam apparatus. State selected HBr⁺ (DBr⁺) ions in the ²Π_{3/2}(v⁺=0) and the ²Π_{1/2}(v⁺=0) state were prepared by resonance enhanced multiphoton ionization (REMPI). This process, which results in ions with narrow rotational state distributions, was used to vary the mean rotational energy of the ions from 1 to 66 meV. Cross sections are presented for collision energies E_{c.m.} in the center of mass system in the range of 0.23 to 1.90 eV. *Ab initio* calculations were performed to obtain energetic information about reactants, intermediates, and products [1]. For certain values of E_{c.m.}, a comparison between the experimental results for HBr⁺ and DBr⁺ indicates that the cross section is dominated by effects of rotational energy rather than angular momentum. While the proton transfer is slightly endothermic for HBr⁺(²Π_{3/2}), it is exothermic for HBr⁺(²Π_{1/2}). This allows us to compare the cross sections for an endothermic and an exothermic reaction within the same reaction system [2]. Our results provide information on the relevant bottleneck of the reactions.

[1] L.Paetow, F.Unger, W.Beichel, G.Frenking, K.-M.Weitzel, *JCP* 132, 174305(2010)

[2] L.Paetow, F.Unger, B.Beutel, K.-M.Weitzel, *JCP*, in press

MO 5.4 Mon 15:15 MER 02

Quantum dynamical investigations of the gas phase S_N2 reaction: Cl⁻ + CH₃I — ●MARKUS KOWALEWSKI, REGINA BLEICHNER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwigs-Maximilians Universität München

The class of S_N2 reactions is a fundamental reaction mechanism in chemistry. While its behavior in solution in thermal equilibrium is well understood, the reaction in gas phase is still subject of complex many-body physics with open questions. The experimental studies on the gas phase dynamics of the anion-molecule nucleophilic substitution reaction of chloride and methyl iodine [1] led to interesting results. With our theoretical investigations we want to gain more insight into some outstanding questions.

Our theoretical methods based on quantum chemical *ab initio* calculations involve selected reactive coordinates which are treated with wave function methods in the Schrödinger picture. We can identify a minimal set of two reactive coordinates which are sufficient to qualitatively reproduce the important features of the dynamics. Within this system we can understand the suppressed reactivity of the reaction partners at low collisional energies and investigate the energy redistribution in the molecule. Moreover these results are compared to an enhanced model which additionally includes a spectator mode.

[1] J. Mikosch, S. Trippel, C. Eichhorn, R. Otto, U. Lourderaj, J. X. Zhang, W. L. Hase, M. Weidemüller, R. Wester, *Science* 319, 183 (2008).

MO 5.5 Mon 15:30 MER 02

Mass Effect during the Reaction O(³P)+HD→OH+D and OD+H — ●VICTOR WEI-KEH WU^{1,2} and FUMI KURE² — ¹Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 80782 Kaohsiung City, Taiwan — ²Victor Basic Research Laboratory e. V. Gadderbaumer-Str. 22, D-33602 Bielefeld, Germany

Calculation of O(³P) + HD→OH + D and OD + H at E_{rel} = 0.2 - 1.0 eV on the lowest electronic PES 1³A" of Kuppermann [(*J. Chem. Phys. A* 104, 2308 (2000))] with QCT-PDDCS code has been completed. The reaction threshold for OH molecule (0.4 eV) is located slightly lower than that for OD (0.5 eV). Both profiles of the reaction cross sections dependent upon E_{rel} keep increasing from the threshold energies to 1.0 eV. Curve of branching ratios σ(OD)/σ(OH) shows a maximum of 5.8651 at E_{rel} = 0.6 eV. It runs asymptotically to approx. 2.5 in the region of E_{rel} = 0.8 - 1.0 eV. The value p₂(k·j) of OD shows stronger alignment than OH. The results prefer the isotopic reaction of O(³P) + HD→OD + H comparing with several available theoretical results of Broida et al. in 1984, and Sultanov et al. in 2004. Production of nascent molecule OD prefers linear arrangement or interaction of [O-D-H] in the reaction of O(³P) + HD→OD + H. Provision of QCT-PDDCS code by K.-L. Han, Group 1101 of DICP, CAS, and financial aids by his group and VBR in Bielefeld, Germany are acknowledged. Ref. V. W.-K. Wu, *Chin. J. Chem. Phys.* 23, 149 (2010); *J. Mol. Struct.* 983, 1 (2010).

MO 5.6 Mon 15:45 MER 02

Molecular fluids under thermal gradient — ●FRANK RÖMER and FERNANDO BRESME — Chemical Physics Section, Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

Non equilibrium phenomena play an important role in many processes of relevance in chemistry, biology, physics as well as in material science. Chemical reactions in small compartments (e.g. lab-on-a-chip devices) can result in large thermal gradients.

We have performed non-equilibrium molecular dynamics (NEMD) simulations to study the different contributions to the heat conduction and the influence of the thermal gradient on the non equilibrium response of molecular fluids. We show that anisotropic molecules adopt a preferred orientation with respect to the thermal gradient. We illustrate this notion with diatomic molecules modelled using two Lennard Jones (LJ) sites, so called two centre LJ models (2CLJ), connected by a flexible bond. Using this model we investigate the mechanism of heat transport and the molecular alignment with the temperature gradient as a function of the molecule interaction parameters.