MO 15: Experimental Techniques 3

Time: Thursday 10:30–12:15 Location: BEBEL SR144

MO 15.1 Thu 10:30 BEBEL SR144

Characterisation of dinuclear transition metal complexes by collision-induced dissociation studies and IRMPD spectroscopy — •Maximilian Gaffga, Joachim Hewer, Johannes Lang, Isabel Munstein, Werner Thiel, and Gereon Niedner-Schatteburg — Technische Universität Kaiserslautern, Deutschland

In extension of previous work [1], a combination of mass spectrometric and spectroscopic techniques was applied to determine the composition and structure of isolated cationic dinuclear transition metal containing complexes in the gas phase. Via the electrospray ionization technique the dinuclear metal complexes could be transferred into the gas phase and then stored in a Paul trap.

Collision-induced dissociation (CID) studies were used to get information about the fragmentation behavior of the complexes. Assignment of vibrational bands and identification of the complex coordination pattern arise from comparison of Infrared Multiple Photon Dissociation (IRMPD) spectra in the range of 1200 - 4000 cm-1 to calculated spectra (B3LYP/cc-pvDZ,ECP). Seemingly surprising fragmentation patterns are well understood on the basis of these investigations.

References: [1] Nosenko, Y.; Menges, F.; Riehn, C.; Niedner-Schatteburg, G. Phys. Chem. Chem. Phys. 2013, 15, 8171.

MO 15.2 Thu 10:45 BEBEL SR144

Photofragmentation imaging of vibrationally excited methyl iodide — •Alexander Dörfler, Martin Stei, Eduardo Carrascosa, and Roland Wester — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

In our group a crossed-beam velocity map imaging setup has been developed to study ion molecule reactions [1]. To study the effect of vibrational C-H symmetric stretch (v_1=1) excitation on the dynamics and kinematics of the reaction $CH_3I + F^-$ a narrowband IR-Laser system has been set up. To characterize and optimize the vibrational excitation in a CH_3I molecular beam, we have applied a probing scheme based on the approach of Zhou and coworkers [3]. The basic idea is, that since the v_1 vibrational excitation is mainly a spectator to the dissociation process, the initially excited CH_3I can be studied by probing CH_3 produced by photodissociation. In this contribution we will be present high resolution velocity images and kinetic energy distribution of the two different CH_3 fragments (v_1=0 and v_1=1) produced by photodissociation at 266 nm ionized using a (2+1) REMPI scheme. We will compare our results to the work of Zhou et al. [2], who applied a different dissociation wavelength. Furthermore, an approach to measure rotational beam temperatures with this scheme will be discussed.

[1] R. Wester, Phys. Chem. Chem. Phys. 16, 396 (2013) [2] Hu, L., Z. Zhou, C. Dong, L. Zhang, Y. Du, M. Cheng and Q. Zhu, J. Phys. Chem. A 117(21): 4352-4357 (2013)

MO 15.3 Thu 11:00 BEBEL SR144

Prediction of Infra-Red spectra of organic liquids within the framework of the cluster model for a substance — Gennady Melnikov[1], •Vyacheslav Verveyko[2], Eugene Postnikov[2], and Marina Verveyko[2] — [1]South West State University — [2]Kursk State University

The distribution function of clusters on particles number is proposed within the frame of the cluster model of a fluid condensed state. The estimations of the most probable, average and root-mean-square number of particles in clusters are obtained using the proposed cluster distribution for simple and organic liquids as a function of the thermodynamic parameters.

The relation for the prediction of frequencies in the infra-red (IR) spectrum of liquids is connected with the presence of rotational and oscillatory motions in clusters structure accordingly to the effective field theory. Verification of the proposed model has been evaluated for inert gases, nitrogen, oxygen, hydrocarbons and water.

The comparison of the calculated results with the experimental data confirms a relevance of the proposed model for the prediction of a number of particles, which form clusters and frequencies of the IR-spectra for liquids.

G.A. Melnikov, V.N. Verveyko et al. Int. J. Therm. 32 (2011), 901.

G.A. Melnikov, V.N. Verveyko et al. High Temperature. 50 (2012), 214.

MO 15.4 Thu 11:15 BEBEL SR144

Methods to simulate light propagation and optical response in small metal cluster aggregates — •Polina Lisinetskaya[1] and Roland Mitric[2] — [1]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Deutschland — [2]Institut für Physikalische und Theoretische Chemie, Universität Würzburg, D-97074 Würzburg, Deutschland

We present a method of the simulation of the optical responce and light propagation in ordered arrays of small noble-metal clusters with discrete electronc structure. The description of the systems is based on the excitonic Hamiltonian constructed employing the TDDFT electronic states of the individual subunits and the dipole-dipole interaction between them. The time evolution of the systems is studied by numerical solution of the time-dependent Schrödinger equation with the excitonic Hamiltonian perturbed by an external laser field. For each subunit the time-dependent dipole moment is calculated using the reduced density matrix formalism. Such quantum-mechanically determined dipole moments are used to simulate the spatio-temporal distribution of the electric field produced by the array. Additionally, we introduce an approximate self-consistent iterative approach to treat arrays consisting of many subunits. The developed methodology is illustrated first on the example of Ag_2 and Ag_8 cluster pairs. Subsequently, light propagation in a triangular-shaped array consisting of six Ag_8 clusters is simulated. Finally, the possibility of optimal control of light propagation in a T-shaped structure formed of seven Ag_8 clusters is demonstrated.

MO 15.5 Thu 11:30 BEBEL SR144

Characterization of metal carbonyls and their release of carbon monoxide using IR absorption spectroscopy — •Moritz Klein[1], Ute Neugebauer[1,2], Ali Gheisari[1], Michael Schmitt[3], and Jürgen Popp[1,2,3] — [1]Leibniz Institute of Photonic Technology, Jena, Germany — [2]Center for Sepsis Control and Care, Jena University Hospital, Germany — [3]Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University of Jena, Germany

Carbon monoxide (CO) is a poisonous gas, but nevertheless, application of low doses of CO in medical treatment has been proven several beneficial effects on health. Novel compounds, mainly metal carbonyl complexes, have been synthesized that liberate CO in a controlled manner. However, their exact mechanism and kinetic of CO release is mostly not known. In this contribution, we applied different techniques of infrared (IR) absorption spectroscopy to study the decay of these metal carbonyls: IR gas phase spectroscopy is used to detect liberated CO in the supernatant gas phase above these compounds and attenuated total reflection (ATR) IR spectroscopy of solutions is applied to directly observe the decay of the carbonyl groups of the solved educt. Molecules with different CO releasing mechanisms were investigated. Following their CO release in a time-resolved manner and analysis of their end products supported by DFT calculations yielded important insights into their reaction mechanisms.

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MO 15.6 Thu 11:45 BEBEL SR144

Characterization of a 6 K Ring-Electrode Ion-Trap used for IR Photodissociation Experiments in a Triple Mass Spectrometer — •Tim Esser[1], Nadja Heine[1], and Knut R. Asmis[1,2] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany — [2]Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstrasse 2, D-04103 Leipzig, Germany

Mass-selective infrared photodissociation (IR-PD) spectroscopy combined with electronic structure calculations, is currently one of the most generally applicable techniques to determine the structure of gas phase cluster ions. To assure that the clusters are in their vibrational ground state they are typically buffer-gas cooled in a cryogenic ion trap. Here, we focus on the characterization of a linear ring-electrode radio-frequency (rf) ion-trap used in a 6K ion trap triple mass spectrometer. Preliminary results on the partially rotationally-resolved IR-PD spectrum of the singly hydrated ammonium ion, $NH_4^+(H_2O)$, allow to determine the rotational temperature as a function of the rf amplitude, buffer-gas pressure and store time. Apart from thermalization, the trap allows for bunching of the continuous ion beam and the attachment of messenger atoms or molecules. A genetic algorithm was developed, in order to automatically optimize the three sets of voltages, which are applied to the 12 pairs of ring electrodes during filling, storing and extraction. We further discuss the influence of the form of the trapping potential as well as the length of the store time on the size, shape and rotational temperature distribution of the ion packages.

MO 15.7 Thu 12:00 BEBEL SR144

Direct imaging of S_N2 pathways in the reaction F^- + CH_3Cl — •Eduardo Carrascosa, Aditya Kelkar, Martin Stei, Thorsten Best, and Roland Wester — Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Innsbruck, Austria

Halogenated hydrocarbons play a very important role in organic synthesis both as solvents and as reaction intermediates. The bimolecular nucleophilic substitution (S_N2) is one of the most common reactions of these compounds. Using a crossed beam setup and a velocity map imaging spectrometer our group has extensively studied exothermic S_N2 reaction systems [1]. The present study focuses on the dynamics of the reaction between fluorine anions, F^-, and methyl chloride, CH_3Cl.

In this presentation velocity distributions of the product Cl^- ion at different relative collision energies ranging from 0.6 eV to 2.5 eV will be shown. The direct S_N2 pathway is the dominant channel at high energies, with an increasingly strong contribution from the complex mediated channel at lower energies. The experimental results will be compared with recent theoretical calculations on this system[2,3]. Moreover, a comparison with previous studies by our group on similar systems like Cl^- + CH_3I and F^- + CH_3I [4], will provide a better understanding of the dynamical factors in S_N2 reactions.

[1] R. Wester, PCCP, **16**, 396 (2014) [2] A.P. Bento and F.M. Bickelhaupt, J. Org. Chem., **73**(**18**), 7290 (2008) [3] M. Mugnai et al., J. Chem. Phys.,**118**, 2767 (2003) [4] J. Mikosch et al., J. Am. Chem. Soc.,**135**, 4250 (2013)