

MO 22: Cluster

Time: Friday 10:30–12:00

Location: V38.02

MO 22.1 Fri 10:30 V38.02

Isomer-Selective IR/IR Double Resonance Spectroscopy: Isolating the Spectral Signatures of $\text{H}^+(\text{H}_2\text{O})_6^+$ Isomers —•NADJA HEINE¹, GIEL BERDEN², GERARD MEIJER¹, and KNUT ASMIS¹ — ¹Fritz-Haber-Institut, 14195 Berlin, Germany — ²FOM Institute, 3439 Nieuwegein, The Netherlands

Understanding how protons are hydrated remains an important and challenging research area. The anomalously high proton mobility of water can be explained by a periodic isomerization between the Eigen and Zundel binding motifs, $\text{H}_3\text{O}^+(\text{aq})$ and $\text{H}_5\text{O}_2^+(\text{aq})$, respectively, even though the detailed mechanism is considerably more complex. These rapidly interconverting structures from the condensed phase can be stabilized, isolated and studied in the gas phase in the form of protonated water clusters. The smallest protonated water clusters that exhibits structural isomers related to the Eigen and Zundel motifs experimentally is the protonated water hexamer $\text{H}^+(\text{H}_2\text{O})_6^+$.

Here, we present first results on infrared/infrared (IR/IR) double resonance experiments on $\text{H}^+(\text{H}_2\text{O})_6^+$. Protonated water clusters are formed by electrospray ionization, mass-selected, cooled to cryogenic temperatures, and messenger-tagged (H_2) in a buffer gas filled ion trap. Isomer-selective IR/IR photodissociation spectra are measured from 300–4000 cm^{-1} by combining population-labeling double resonance spectroscopy with the widely tunable IR radiation of the free electron laser FELIX. The results demonstrate that two isomers, an Eigen and a Zundel-type isomer, are indeed present and that their IR spectra can be measured individually over the complete spectral range.

MO 22.2 Fri 10:45 V38.02

Structural Variability in Transition Metal Oxide Clusters: Gas Phase Vibrational Spectroscopy of $\text{V}_3\text{O}_{6-8}^+$ —•CLAUDIA BRIEGER¹, TORSTEN WENDE¹, JENS DÖBLER², ANDRZEJ NIEDZIELA², JOACHIM SAUER², GERARD MEIJER¹, and KNUT R. ASMIS¹ — ¹Fritz-Haber Institut der MPG, Berlin — ²Humboldt Universität Berlin

Vanadium oxides exhibit a high structural variability and redox activity which comes to play into heterogeneous catalysis. Interestingly, the structure of the active sites in vanadium oxide catalysts is often not well known. Infrared photodissociation (IRPD) spectroscopy can be used to obtain structural information on isolated clusters in the gas phase. Here, we study the structures of tri-nuclear vanadium oxide cations. IRPD spectra of $\text{V}_3\text{O}_6^+\text{He}_{1-4}$, $\text{V}_3\text{O}_7^+\text{Ar}_{0-1}$, and $\text{V}_3\text{O}_8^+\text{Ar}_{0-2}$ from 350 to 1200 cm^{-1} are presented. V_3O_7^+ and V_3O_8^+ have a cage-like structure whereas a chain isomer is found to be most stable for V_3O_6^+ . The binding of the rare gas atoms to $\text{V}_3\text{O}_{6-8}^+$ clusters is found to be strong, up to 58 kJ/mol for Ar, and markedly isomer-dependent, resulting in two interesting effects. First, for $\text{V}_3\text{O}_7^+\text{Ar}_1$ and $\text{V}_3\text{O}_8^+\text{Ar}_1$ an energetic reordering of the isomers compared to the bare ion is observed, making the ring-motif the most stable one. Second, different isomers bind different number of rare gas atoms. We demonstrate, how both effects can be exploited to isolate and assign the contributions from multiple isomers to the IR spectrum. The present results exemplify the sensitivity of the structure of vanadium oxide clusters on small perturbations in their environment.

MO 22.3 Fri 11:00 V38.02

Activation of oxygen on small cationic platinum clusters in the gas phase —•CHRISTIAN KERPAL¹, DAN HARDING¹, ALEXANDER HERMES², SUZANNE HAMILTON², ROBERT MOFFATT², STUART MACKENZIE², GERARD MEIJER¹, and ANDRÉ FIELICKE¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin — ²Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK

Small clusters of platinum represent model systems for potentially important industrial catalysts, e.g. for the activation of C-H bonds and for fuel cells. The long term goal of such cluster model studies is to understand the chemistry occurring at specific low coordinated metal sites in heterogeneous catalysis. However, the properties of metal clusters often differ dramatically with particle size. As most of the physical and chemical properties of clusters are directly related to their geometries, the determination of the precise structure is essential. The combination of infrared multiple photon dissociation (IR-MPD) spectroscopy and density functional theory (DFT) calculations provides a means to get detailed knowledge of the structures of both bare metal clusters

and the adsorption geometries of small ligands on the clusters. Here we present IR-MPD spectra of $\text{Pt}_n\text{O}_{2m}^+$ clusters for $n \leq 6$; $m = 1, 2$ and a comparison to DFT calculations, allowing structural determination for the cluster-ligand complexes. These structures give direct information on the activation of the oxygen, showing different types of molecular and dissociated binding and in some cases a mixture of both, depending on cluster size and oxygen coverage.

MO 22.4 Fri 11:15 V38.02

Electronic structure and binding energies of structurally modified diamondoid complexes studied with photoemission spectroscopy —•TOBIAS ZIMMERMANN¹, ROBERT RICHTER¹, DAVID WOLTER¹, TORBJÖRN RANDER¹, PETER SCHREINER², and THOMAS MÖLLER¹ — ¹Technische Universität Berlin, Institut für Optik und Atomare Physik — ²Justus-Liebig-Universität Gießen, Institut für Organische Chemie

While the smallest diamondoids, in particular Adamantane, have been known for some decades as perfectly shape- and mass-selectable carbon clusters, their significant scientific interest has risen only in the last few years. This is due to the fact that now also the larger ones have become more widely available due to new extraction and synthesis possibilities. Adamantane, with only ten carbon atoms, can be seen as the smallest unit of the macroscopic diamond crystal structure. The electronic structure of such nanoparticles can be analyzed with the help of photoemission spectroscopy (PES). In recent experiments we investigated the electronic structure of structurally modified lower diamondoids and lower diamondoid complexes. In particular we focus on lower diamondoid complexes containing sp^2 -impurities. These systems are of interest due to the fact that sp^2 -impurities in bulk diamond are known to enhance luminescence. Recently, it has also been reported that this type of structures possesses some of the longest C-C bonds known, the peculiarities of which may be studied by using PES.

MO 22.5 Fri 11:30 V38.02

Experimental and theoretical Raman analysis of functionalized diamondoids —•REINHARD MEINKE¹, ROBERT RICHTER¹, THOMAS MÖLLER¹, BORYSLAV TKACHENKO², PETER R. SCHREINER², CHRISTIAN THOMSEN¹, and JANINA MAULTZSCH¹ — ¹Institut für Festkörperphysik, Technische Universität Berlin, Germany — ²Institut für Organische Chemie, Justus-Liebig-Universität Giessen, Germany

Diamondoids functionalized with thiol, alcohol and amine groups [1] are investigated by means of Raman spectroscopy. Here we present so-called fingerprint regions in the Raman spectra which can be used for determination of functionalization in diamondoids. Several effects due to functionalization are observed: frequency shift of Raman modes, activation of Raman-inactive modes, and splitting of degenerate modes. We show how to determine the site and the type of the functional group with the help of the fingerprint regions. The Raman modes have been characterized and assigned by supporting DFT computations using Gaussian 09, using the B3LYP functional and the basis set 6-311G(d).

[1] Hartmut Schwertfeger, Andrey A. Fokin, and Peter R. Schreiner, *Angew. Chem. Int. Ed.* 2008, 47, 1022/1036. DOI: 10.1002/anie.200701684

MO 22.6 Fri 11:45 V38.02

Molecular fragmentation and charge redistribution in XeF_2 after K-shell photoionization —ROBERT W. DUNFORD¹, STEPHEN H. SOUTHWORTH¹, DIPANWITA RAY¹, ELLIOT P. KANTER¹, BERTOLD KRAESSIG¹, LINDA YOUNG¹, DOHN A. ARMS¹, ERIC M. DUFRESNE¹, DONALD A. WALKO¹, •ORIOLE VENDRELL², SANG-KIL SON², and ROBIN SANTRA^{2,3} — ¹Argonne National Laboratory, Lemont, IL 60439, USA — ²Center for Free-Electron Laser Science, DESY, 22607 Hamburg, Germany — ³Department of Physics, University of Hamburg, 20355 Hamburg, Germany

The photoionization of an inner-shell electron in a heavy atom by synchrotron radiation sets off a cascade of x-ray and Auger transitions as the atom relaxes and reaches its final charge state. If the heavy atom is embedded in a molecule, the decay is accompanied by charge redistribution and molecular fragmentation processes.

In this work, we investigate the effect of Xe K-shell hole in XeF_2 and compare it to the isolated atomic case, Xe. The average total

charge produced for Xe is +8, whereas it is +9 for XeF₂. Such similarity suggests a model in which the cascade proceeds at the atomic level followed by charge redistribution and Coulomb explosion. Simulations of the decay cascade of Xe, however, indicate that the cascade lasts for about 100 fs, in which case nuclear motion may play a role.

Moreover, energetic considerations based on an independent ion model suggest that it is unlikely that the total charge in XeF₂ is initially produced entirely on Xe. Therefore, a more complex mechanism involving molecular effects is probably at play.