

O 36: Particles and clusters

Time: Wednesday 15:00–16:45

Location: SCH A01

O 36.1 Wed 15:00 SCH A01

Nature of Ar bonding to small Co_N^+ clusters and its implications for the structure determination by far-infrared absorption spectroscopy — ●RALF GEHRKE, PHILIPP GRUENE, ANDRÉ FIELICKE, GERARD MEIJER, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Far-infrared vibrational spectroscopy by multiple photon dissociation has proven to be a very useful technique for the structural fingerprinting of small metal clusters [1]. Whereas previous work on cationic vanadium clusters assumed a negligible influence of the adsorbed Ar probe atoms, measured vibrational spectra of small cationic cobalt clusters show an intriguing dependence on the number of adsorbed Ar atoms, which becomes stronger with decreasing cluster size. Focusing on Co_4^+ to Co_8^+ we therefore use density-functional theory to analyze the Ar- Co_N^+ bond and its role for the IR spectra. First, low-lying isomers are identified through first-principles basin-hopping runs. A comparison of their computed spectra with the experimental data then enables in some cases a unique assignment of the cluster structure. Independent of the specific isomer, we obtain a pronounced increase of the Ar binding energy for the smallest cluster sizes, which correlates with the observed increased influence of the Ar atoms on the IR spectra. Further analysis of the electronic structure motivates an electrostatic picture that not only explains this binding energy trend, but also why the influence of the rare-gas atom is much stronger than in the previously studied systems. [1] A. Fielicke, A. Kirilyuk, C. Ratsch, J. Behler, M. Scheffler, G. von Helden, G. Meijer, *Phys. Rev. Lett.* **93** (2), 023401 (2004)

O 36.2 Wed 15:15 SCH A01

Aqueous Suspensions of Detonation Nanodiamond Particles, Investigations of Deaggregation and Deagglomeration with Mechanical Disintegration Methods — ●MARTIN RUDOLPH^{1,2}, JÖRG OPITZ², INGA HANNSTEIN², URS ALEXANDER PEUKER¹, and JÜRGEN SCHREIBER² — ¹TU Bergakademie Freiberg, Institut für Mechanische Verfahrenstechnik und Aufbereitungstechnik, Freiberg, Germany — ²Fraunhofer Institut für zerstörungsfreie Prüfverfahren, Dresden, Germany

Detonation synthesized Nanodiamonds (DND) have been of great interest since their discovery in the mid 1960s. They were first published in 1988. First applications in the fields of Material and Life Sciences are already being established.

This study deals with aqueous suspensions of DND and the possibilities of producing stable colloidal dispersions only by mechanical disintegration methods and electrostatic stabilization. Three methods of disintegration were utilized including a planetary ball mill, a 200 W Ultrasound device with sonotrode as well as the new method of bead assisted sonic deaggregation (BASD) first published by Ozawa et al. A new model of the aggregates before and after mechanical treatment is established showing a difference between the methods of hard and soft disintegration, referring to milling as well as BASD and simple ultrasound, respectively. To the knowledge of the author it was the first time reagglomeration effects have been found to take place while mechanically disintegrating DND particles. A theoretical model for this effect has been developed therefore.

O 36.3 Wed 15:30 SCH A01

Metal-Nanoparticle-Induced Fluorescence Enhancement from a Single Layer of Dye Molecules — ●RENÉ SCHNEIDER, THOMAS HÄRTLING, PHILIPP REICHENBACH, and LUKAS M. ENG — Institute of Applied Photophysics, TU Dresden, Germany

We investigate the applicability of metal nanoparticles (MNPs) to enhance the fluorescence signal of a monolayer of dye molecules. The dependence of the signal strength on the distance between the molecules in the layer and a single MNP is examined by means of a scanning near-field optical microscope (SNOM), the scanning probe of which is equipped with a single gold nanoparticle [1]. This setup allows to change the separation between the particle and the illuminated sample and monitor the optical response of the system under various illumination conditions.

We show that single 80 nm gold particles embedded in immersion oil enhance the fluorescence signal from a layer of molecules when illuminated with a Gaussian focus. By changing the separation between

MNP and sample we observed a modulated fluorescence signal. This modulation is induced by the interference of incoming and scattered light of the particle. The results of analogous investigations using radially polarized light will be presented and compared with the previous measurements.

[1] M. T. Wenzel, T. Härtling, P. Olk, S. C. Kehr, S. Grafström, S. Winnerl, M. Helm, and L. M. Eng, *Opt. Express*, **16**, 12302 (2008).

O 36.4 Wed 15:45 SCH A01

Initial-state effects in X-ray absorption spectra of size-selected transition metal clusters — ●MATTHIAS GRAMZOW, RALF GEHRKE, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

X-ray absorption spectra (XAS) at the $L_{2,3}$ edge of 3d transition metal solids are known to be sensitively affected by the created core hole. The recently reported experimental access to XAS of size-selected cationic transition metal clusters provides therefore a unique possibility to study the evolution of core hole screening from the atomic to the bulk-like limit [1]. While the measured data for the $L_{2,3}$ branching ratio and the L_3 absorption onset for cationic Ti, V and Co clusters containing up to 10 atoms shows indeed pronounced variations, it is unclear how much of this is simply due to the varying atomic coordination in the different isomer geometries (initial-state effects). As a first step towards a detailed interpretation of the experimental spectra we therefore use density-functional theory in conjunction with a basin-hopping sampling algorithm to identify the energetically lowest-lying isomers. On the basis of the obtained structures we disentangle the initial-state effects from the experimental data, and further quantify the amount of core hole screening using a Slater-Janak transition-state approach. [1] J.T. Lau *et al.*, *Phys. Rev. Lett.* **101**, 153401 (2008).

O 36.5 Wed 16:00 SCH A01

Non-IPR isomers of C_{60} on HOPG — ●DANIEL LÖFFLER¹, NOELIA BAJALES¹, PATRICK WEIS¹, SERGEI LEBEDKIN¹, ANGELA BIHLMEIER², WIM KLOPPER², ARTUR BÖTTCHER¹, and MANFRED KAPPES¹ — ¹Institut für physikalische Chemie, Universität Karlsruhe — ²Institut für theoretische Chemie, Universität Karlsruhe

Thin monodisperse films consisting of exclusively non-IPR C_{60} molecules have been generated by depositing vibronically excited C_{60} cations onto HOPG followed by sublimation of the more volatile $\text{C}_{60}(\text{I}_h)$ isomers. A beam of C_{60} cations was generated by the electron-impact mediated heating and ionization of C_{70} . The associated excitation and fragmentation leads to the formation of C_{60}^+ cages with non-IPR sites (in addition to the dominant $\text{C}_{60}(\text{I}_h)$ derived cation). The fabrication of pure C_{60} (non-IPR) films has been achieved simply by heating the film grown up to 600 K which results in the thermal removal of all IPR cages, $\text{C}_{60}(\text{I}_h)$. The topography of the resulting films, is governed by the aggregation of the C_{60} (non-IPR) cages, which is in turn driven by intercage bonds constituted by non-IPR sites (e.g. pairs of adjacent pentagonal rings). These covalent intercage bonds are responsible for the high stability of the C_{60} (non-IPR) films as mirrored by a sublimation temperature of 1100 K - significantly higher than for pure $\text{C}_{60}(\text{I}_h)$. The valence band of the C_{60} (non-IPR) films exhibits a triplet with a well distinguishable additional peak at a binding energy of 2.6 eV. The C_{60} (non-IPR) films exhibit a narrower HOMO-LUMO gap than that found for $\text{C}_{60}(\text{I}_h)$ films.

O 36.6 Wed 16:15 SCH A01

Optical properties of single alkali-earth particles on MgO films — ●PHILIPP MYRACH, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der MPG, D14195 Berlin, Germany

Light emission spectroscopy with an STM is employed to study the optical properties of single Mg and Ca particles deposited on 8 ML thick MgO/Mo(001) films. The particles grow with distinct rectangular shapes due to the strong affinity of the alkali-earth atoms to the O ions in the oxide surface. The overall emission properties are governed by material-dependent plasmon excitations, giving rise to photon peaks at 2.3 and 2.1 eV for Mg and Ca particles, respectively. However, a characteristic fine-structure is superimposed on the optical response that originates from the plasmon excitation mechanism via inelastic electron transport in a double barrier STM junction. High excitation cross sections are observed at photon energies that correspond to the

separation of quantized electron levels in the MgO conduction band, so called Gundlach resonances.

O 36.7 Wed 16:30 SCH A01

Reaction of Cu and Au clusters with single crystalline ZnO surfaces — •MARTIN KROLL, THOMAS LÖBER, and ULRICH KÖHLER — Experimentalphysik IV / AG Oberflächenphysik, Ruhr-Universität Bochum, 44780 Bochum, Germany

As model systems in heterogeneous catalysis metal clusters on single ZnO-crystals grown in UHV are used as a first step to understand the complex reactions under real catalytical conditions. STM and SEM were used to examine nucleation and thermal behaviour of the sys-

tems Cu/ZnO(0001)-Zn, Au/ZnO(0001)-Zn and Cu/ZnO(10 $\bar{1}$ 0) up to 500°C. Cu and Au were deposited using MBE. Additionally a CVD-source was used for Cu-deposition. On the polar ZnO(0001) surface and on the mixed terminated ZnO(10 $\bar{1}$ 0) surface separated clusters are formed at room-temperature and a partial entrenching of Cu into the ZnO substrate at elevated temperatures of $T \geq 400^\circ\text{C}$ was found[1]. In contrast, Au on ZnO initially forms a closed layer at room-temperature and annealing to comparable temperatures shows a pile-up of Au-material into a network of connected island without any reaction with the ZnO-support.

[1] M.Kroll, U. Köhler; Surf. Sci 601 (2007) 2182