

## O 49: Particles and Clusters

Time: Wednesday 15:15–17:45

Location: MA 005

O 49.1 Wed 15:15 MA 005

**Comparing the sampling efficiency of genetic and basin-hopping algorithms in the structural optimization of Lennard-Jones clusters** — ●VLADIMIR FROLTISOV and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)

Detailed knowledge about structural properties is an indispensable prerequisite en route towards a future exploitation of the intriguing materials properties of small atomic clusters. Crucial for the corresponding global geometry optimization problem is a reliable sampling of the high-dimensional potential-energy surface (PES) to identify the (meta)stable minima. In view of the high computational cost when the PES is evaluated with predictive quality by first-principles methods, utmost efficiency with a minimum dependence on the initial starting configuration is an additional demand on the sampling scheme. With this focus we compare the efficiency of the two prevalent algorithms for PES sampling, namely genetic algorithms (GA) and the basin-hopping (BH) approach, using the determination of the ground-state structure of model Lennard-Jones clusters as criterion. We find an intriguing cross-over between the two approaches, with BH more efficient than GA for cluster sizes up to 65, and GA more efficient for larger clusters. We rationalize this finding with the ability of the population-based GA's to explore in parallel disjoint parts of the PES, which becomes increasingly important for the increasingly high-dimensional PESs of larger clusters.

O 49.2 Wed 15:30 MA 005

**Absorption spectra of small metal clusters** — ●GEORGE PAL<sup>1</sup>, YAROSLAV PAVLYUKH<sup>2</sup>, HANS CHRISTIAN SCHNEIDER<sup>1</sup>, and WOLFGANG HÜBNER<sup>1</sup> — <sup>1</sup>Department of — <sup>2</sup>Institut für Physik,

We present results for the photoabsorption cross sections of small sodium clusters ( $\text{Na}_4$ ,  $\text{Na}_9^+$  and  $\text{Na}_{21}^+$ ) calculated by means of a linear response approach for the electron-hole correlation function. Following Refs. [1] and [2], we compute the electron-hole correlation function as the functional derivative of the generalized density matrix with respect to an external field, which yields an equation of the Bethe-Salpeter type. This procedure is conserving and fulfills important sum rules by construction. The theoretical spectra are in excellent agreement with the experimental results.

[1] L. P. Kadanoff and G. Baym, Phys. Rev. **124**, 287 (1961)[2] N.-H. Kwong and M. Bonitz, Phys. Rev. Lett. **84**, 1768 (2000)

O 49.3 Wed 15:45 MA 005

**Ensemble-modelling of CdSe/ZnS core-shell nanoparticles using x-ray powder diffraction data** — ●FRANZISKA NIEDERDRAENK<sup>1</sup>, CHRISTIAN KUMPF<sup>1</sup>, REINHARD NEDER<sup>2</sup>, and EBERHARD UMBACH<sup>1,3</sup> — <sup>1</sup>Universität Würzburg, Experimentelle Physik II, 97074 Würzburg — <sup>2</sup>Universität Würzburg, Mineralogisches Institut, 97074 Würzburg — <sup>3</sup>Forschungszentrum Karlsruhe GmbH, D-76021 Karlsruhe

Standard methods for the analysis of powder x-ray diffraction data (like e.g. a Rietveld refinement) cannot be used efficiently for heterogenic or imperfect systems like core-shell nanoparticles, since they are usually based on bulk-crystal approaches. In particular, mixed (epitactic) structures, interface-effects, and imperfections like relaxations and stacking faults, that often occur in very small particles (<3 nm), cannot be handled. In order to overcome these limitations we developed a bottom-up approach which models the entire nanoparticle including the shell, and hence takes all structural features implicitly into account. The Debye formula is used to calculate the corresponding diffraction pattern. Furthermore a size distribution for the nanoparticles is considered by applying ensemble averaging.

We present data from CdSe particles with a diameter of  $\sim 4$  nm and a ZnS shell of nominally  $\sim 1$  nm thickness. Different shapes and different shells for the particles were tested, as well as all relevant structural parameters refined. The best model consists of an elliptical CdSe core with a non-epitaxial ZnS shell which does not cover the core-surface completely.

O 49.4 Wed 16:00 MA 005

**Understanding the reversibility of graphene and carbon nanotubes covalent functionalization** — ●ELENA ROXANA MARGINE<sup>1</sup>

and XAVIER BLASE<sup>1,2</sup> — <sup>1</sup>LPMC Université Lyon I, France — <sup>2</sup>Institut Néel, CNRS and Université Joseph Fourier, Grenoble, France

The reversibility of the grafting process of functional groups on the surface of carbon nanotubes is an essential step in the recovery of the ballistic properties of metallic nanotubes after separation or assembling. We use  $\{\text{ab initio}\}$  calculations to explore activation barriers against desorption of aryl radicals from the surface of graphene and nanotubes. We provide evidence for the recently observed partial reversibility of the diazonium salts reaction with carbon nanotubes and discuss the possibility of improving the reversibility using different functional groups.

O 49.5 Wed 16:15 MA 005

**Plasmon-induced chaotic photodesorption of xenon from silver nanoparticles on a thin alumina film** — ●KI HYUN KIM<sup>1</sup>, KAZUO WATANABE<sup>1</sup>, DIETRICH MENZEL<sup>1,2</sup>, and HANS-JOACHIM FREUND<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — <sup>2</sup>Technische Universität München, 85747 Garching, Germany

We have observed a unique action of plasmon excitations in photodesorption of xenon from silver nanoparticles (AgNPs,  $\sim 8$  nm particle diameter) deposited on a thin alumina film. A mass selected time-of-flight method was used to measure the kinetic energy and the total amount of desorbed atoms. The results show that xenon atoms from a xenon monolayer on AgNPs are photodesorbed nonthermally when the laser is tuned to excite the (1,0) mode of the Mie-plasmon of AgNPs (3.5 eV,  $p$ -polarization) at low fluences ( $< \sim 2$  mJ/cm<sup>2</sup>) where laser induced thermal desorption is negligible. Moreover, the photodesorption yield on plasmon resonance showed chaotic behavior with large bursts and intermittences. These effects were suppressed for multilayers of xenon, which indicates that the nonthermal desorption is not due to thermal heating of the AgNPs.

We suggest a new mechanism of plasmonic desorption by accumulated momentum transfer of the repetitive Pauli repulsions between the collectively oscillating surface electrons and the xenon atom in its shallow physisorption well. The chaotic behavior is ascribed to plasmon coupling which creates fluctuating hotspots and decays slowly ( $> 300$  fs) enough to accelerate xenon atoms sufficiently to desorb them.

O 49.6 Wed 16:30 MA 005

**Growth mechanism of group 5 transition metal clusters elucidated by far-infrared spectroscopy** — ●PHILIPP GRUENE<sup>1</sup>, GERARD MEIJER<sup>1</sup>, CARSTEN RATSCH<sup>2</sup>, and ANDRÉ FIELICKE<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>UCLA, Los Angeles, USA

The knowledge of the electronic and geometric structure of clusters is vital for the understanding of their physical and chemical properties. However, the determination of the clusters' geometric structure is an experimental challenge. Recently, we have shown that vibrational spectroscopy in combination with density functional theory calculations can provide information on the geometric structures of free metal clusters.<sup>[1]</sup> The experimental far-infrared spectra of free metal clusters are obtained by multiple photon dissociation (MPD) spectroscopy of their complexes with rare gas atoms, using the intense and tunable radiation of a free electron laser. We have completed the investigations on clusters of group 5 elements of the periodic table, namely vanadium, niobium, and tantalum. For all three elements many cluster sizes show remarkable similarities in their vibrational features, indicating a similar growth mechanism. Furthermore, for niobium clusters both neutral and cationic clusters have been studied, which allows for an understanding of the influence of a single electron both on the vibrational properties as well as on the clusters' geometric structure.

[1] A. Fielicke, A. Kirilyuk, C. Ratsch, J. Behler, M. Scheffler, G. von Helden, and G. Meijer, Phys. Rev. Lett. **93**, 023401 (2004).

O 49.7 Wed 16:45 MA 005

**Ag cluster growth on biaxially oriented PET** — ●GÜNTHER WEDLINGER, LIDONG SUN, JOSÉ MANUEL FLORES-CAMACHO, MICHAEL HOHAGE, DANIEL PRIMETZHOFFER, PETER BAUER, and PETER ZEPPENFELD — Institut für Experimentalphysik, Johannes Kepler Universität Linz, Altenberger Straße 69, A-4040 Linz

Ag was deposited on biaxially oriented polyethylene terephthalate

(PET) by means of Physical Vapor Deposition under UHV conditions up to a nominal Ag layer thickness of 5 nm. Since Ag does not wet the PET surface, Ag clusters are formed on the surface rather than a continuous metal film. The optical properties of these silver clusters were monitored with Reflectance Difference Spectroscopy (RDS) during metal deposition. Morphological studies of the samples reveal that the clusters are embedded in the PET substrate and that the shape of the individual clusters as well as their in-plane arrangement is isotropic. Despite the structural isotropy of the Ag clusters, an in-plane anisotropy of the cluster plasmon resonance can be observed in the RD spectra. This is attributed to the anisotropic dielectric properties of the substrate and its influence on the plasmon response. At low nominal Ag thicknesses ( $\leq 0.3$  nm), the FWHM and the energy position of the plasmon resonance show a  $1/R$ -dependence on the cluster radius  $R$ . A broadening and an accelerated red-shift of the resonance due to retardation effects and cluster-cluster interactions are observed for silver thicknesses above 0.3 nm.

O 49.8 Wed 17:00 MA 005

**Fluorescence yield of optical emitters close to noble-metal nanoparticles** — ●FLORIAN HALLERMANN and GERO VON PLESSEN — I. Institute of Physics (IA), RWTH Aachen University, 52056 Aachen, Germany

The intensity of fluorescence from a fluorescent emitter is modified when placed in close proximity to a noble-metal nanoparticle. This modification is partially caused by a change in excitation efficiency due to the local-field enhancement near the nanoparticle, and partially by additional radiative and non-radiative decay processes due to resonant energy transfer from the emitter to the metal. Here we calculate the total fluorescence yield of fluorescent emitters distributed uniformly around a noble-metal nanoparticle, as a function of excitation and emission wavelengths.

O 49.9 Wed 17:15 MA 005

**Creation of hot electrons below the surface by highly charged ions** — ●THORSTEN PETERS<sup>1</sup>, CHRISTIAN HAAKE<sup>1</sup>, DOMOCOS KOVACS<sup>2</sup>, DETLEF DIESING<sup>3</sup>, ARTUR GOLCZEWSKI<sup>4</sup>, GREGOR KOWARIK<sup>4</sup>, FRIEDRICH AUMAYR<sup>4</sup>, ANDREAS WUCHER<sup>1</sup>, and MARIKA SCHLEBERGER<sup>1</sup> — <sup>1</sup>Universität Duisburg-Essen, Fachbereich Physik, Lotharstrasse 1, 47057 Duisburg, Germany — <sup>2</sup>Experimentalphysik II, Ruhr-Universität Bochum, 44801 Bochum, Germany — <sup>3</sup>Physikalische Chemie, Universität Duisburg-Essen, 45117 Essen, Germany —

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Highly charged ions provide a unique method for creating ultra high energy densities in the surface region of a solid. Thin film metal-insulator-metal junctions are used in a novel approach to investigate the dissipation of the energy of multiply charged ions impinging on a polycrystalline metal surface. The ion-metal interaction leads to Auger electron emission of several ten eV which again leads to excited electrons and holes within the top layer. A substantial fraction of these charge carriers is transported inwards and can be measured as an internal current in the thin film tunnel junction. In Ag-AlO<sub>x</sub>-Al junctions, yields of typically 0.1–1 electrons per impinging ion are detected in the bottom Al layer. The separate effects of potential and kinetic energy on the tunneling yield are investigated by varying the charges state of the Ar projectile ions from 2+ to 9+ for kinetic energies in the range from 1 to 12 keV. The tunneling yield is found to scale linearly with the potential and kinetic energy of the projectile.

O 49.10 Wed 17:30 MA 005

**Structure and properties of Au on nanostructured ceria** — ●MARTIN BARON, DARIO STACCHIOLA, SHAMIL SHAIKHUTDINOV, and HAJO FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

It is well established that oxide supported gold nanoparticles catalyze CO oxidation at temperatures as low as 200 K [1]. Among those reported in the literature, gold catalysts supported on the cerium oxide (CeO<sub>2</sub>) often show a superior activity, in particular when ceria is present as nanoparticles [2]. To date, there are still open questions regarding the reaction mechanism and the nature of active species. In particular, the role of cationic (Au<sup>3+</sup>, Au<sup>+</sup>) species in this reaction remains unclear. Herein, we will present combined STM, XPS, LEED and IRAS studies of gold particles deposited on both extended CeO<sub>2</sub> films and ceria nanoparticles. Well ordered CeO<sub>2</sub> films were grown on Ru(0001) single crystal, and the quality of the films was controlled by XPS, LEED and STM. The ceria nanoparticles were prepared on thin silica films, which are essentially inert towards Au and CO, such that Au was only nucleated on the ceria particles and CO adsorbed only on Au/ceria. The results are rationalized on the basis of highly defective surface of nanoceria, which modifies the electronic structure of gold. [1] M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, *J. Catal.*, 115 (1989) 301 [2] Carrettin S., Concepción P., Corma A., López Nieto J.M., Puentes V.F. (2004) *Angew.*