



XV INTERNATIONAL SYMPOSIUM ON SMALL PARTICLES AND INORGANIC CLUSTERS



Book of Abstracts

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September 19-24, 2010

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Edited by Alfredo Tlahuice, Dulce Aguilar, Luis Pérez, Cecilia Noguez,
Gabriela Díaz, and Ignacio L. Garzón
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PREFACE

This Book of Abstracts contains a compilation of contributions presented at the XV International Symposium on Small Clusters and Inorganic Clusters - ISSPIC XV, held at Oaxaca City, Mexico on September 19-24, 2010. Contributions include plenary, progress reports (invited), and selected (hot topics) talks, as well as poster presentations. The scientific program also includes two Memorial talks in honor to Professors Tomotsu Kondow and Eckehard Recknagel, who were distinguished scientists in the field of Cluster and Nanoparticle Science. All the talks (plenary, invited and hot topics) are arranged chronologically according to the Program. The poster contributions have been classified into different topics, listed below. Topics A-01 to A-07 belong to Poster Session A, and topics B-01 to B-06 to Poster Session B. A code has been assigned to each poster abstract (for example, Poster B-03-10 is the tenth poster within topic B-03). An author index is provided at the end of the Book. We acknowledge support from Consejo Nacional de Ciencia y Tecnología (CONACyT-Mexico) and Universidad Nacional Autónoma de México (UNAM) for the edition of this Book of Abstracts.

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- A-03. Carbon nanostructures
- A-04. Nanoparticles in biology and medicine
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- A-06. Nanoparticles in environmental science
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MONDAY SEPTEMBER 20

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Photo-induced processes in metallic clusters and fullerenes

From atoms to clusters supported on oxide surfacesHans-Joachim Freund¹

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Metal-atoms, -dimers, -chains, -two-dimensional and three-dimensional metal nanoclusters are prepared by physical vapor deposition on oxide supports and investigated with respect to their electronic properties as well as their reactivity applying a variety of experimental techniques including local scanning tunneling microscopy and spectroscopy as well as ensemble averaging techniques such as Infrared-Fourier-Transform, electron spin resonance spectroscopy and electron spectroscopies. Thin oxide films grown epitaxially on appropriate metal ~ metal alloy supports are used to either model a bulk oxide or to provide a support where the deposited metal interacts with the underlying metal-oxide interface. The latter system may exhibit designable properties as far as their electronic structure and morphology is concerned.

The experimental findings are compared with results from calculations using a variety of approaches including local cluster and slab calculations from different collaborating theory groups.

Exotic structures of oxide-supported metallic nanoparticles

R. Ferrando

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Oxide-supported nanoparticles are widely studied for their applications in catalysis and magnetism. The computational prediction of their low-energy structures is a challenging task, due to the great variety of possible structural motifs.

Here we show that the interplay between metal-metal and metal-oxide interactions can lead to the stabilization of exotic geometries, which, in some cases, have no counterpart in gas-phase nanoparticles. Three metallic systems adsorbed on MgO(001) are considered: pure Ni and Au nanoparticles and PtCo nanoparticles. The most stable structures range from hcp nanodots for nickel [1], to leaflets and empty cages for gold [2,3], to polyicosahedra for PtCo [4].

[1] R. Ferrando, G. Rossi, F. Nita, G. Barcaro, A. Fortunelli, ACS Nano 2, 1849 (2008)

[2] R. Ferrando, G. Barcaro and A. Fortunelli, Phys. Rev. Lett. 102, 216102 (2009)

[3] R. Ferrando, G. Barcaro and A. Fortunelli, in preparation

[4] G. Barcaro, R. Ferrando, A. Fortunelli, G. Rossi, J. Phys. Chem. Lett. 1, 111 (2010)

Small gap effects in SERS: going beyond conventional classical electrodynamics

George C. Schatz

Northwestern University

This talk will describe my recent collaborative work with Richard Van Duyne, Chad Mirkin and others concerned with the role of small gaps between nanoparticles in SERS. The talk begins with a presentation of recent experimental results and related theoretical simulations which show that SERS is often dominated by small gaps where there is little relationship between the extinction properties of the nanoparticle clusters and the corresponding SERS excitation spectra. In some cases it is possible to use classical electrodynamics to provide a quantitative interpretation of the observed behavior, however for <1 nm gaps or for fused particles, classical electrodynamics breaks down and it is necessary to develop theories which go beyond this in some sense. Two approaches are described: (1) a top-down theory in which nonlocal dielectric functions are included into classical electrodynamics, thereby incorporating quantum effects in some sense, and (2) a bottom-up theory in which real-time time-dependent density functional theory is combined with classical electrodynamics to describe portions of the structure, such as the junction, with quantum mechanics, and then the rest with classical electrodynamics. Predictions of both theories for junction structures are described.

Optical absorption and fluorescence spectra of small size selected neutral noble metal clusters

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We present optical absorption spectra in the UV-Visible range for size selected neutral Ag_n ($n=1-9$), Cu_n ($n=1-9$) and Au_n ($n=1-9$) clusters embedded in solid Neon. Fig.1 shows as an example the optical spectra of Au. The influence of electronic transitions having d-electron character increases the complexity of the absorption spectra. Bunching of the oscillator strength in a narrow energy window which develops into a plasmon like transition for larger cluster sizes is only distinguishable in Ag. Comparison to TDDFT calculations allow for a clear assignment of the optical spectra to specific isomers of all Ag and some selected Cu and Au clusters.

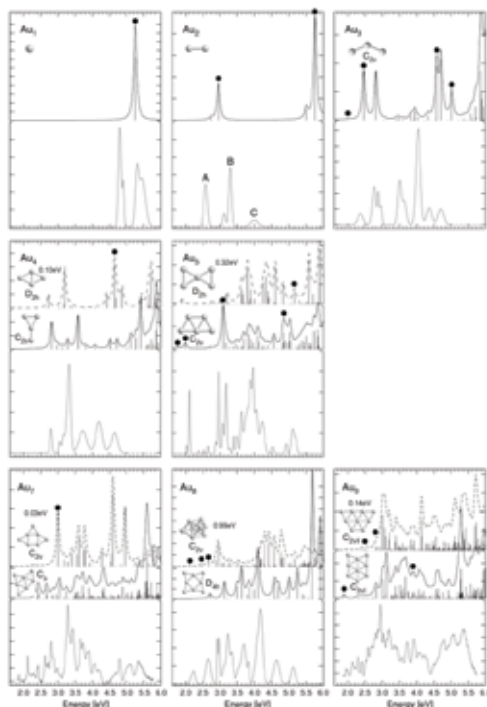


Fig.1: The optical UV Visible spectra of neutral Au clusters in Ne compared to TDDFT calculations

Fluorescence spectra of mass selected neutral clusters of the same size are collected either via optical excitation (LIF) or electron impact induced fluorescence over the energy range from 1.5 eV to 5 eV.

Monitoring of the plasmon resonance of gold nanoparticles in Au/TiO₂ catalyst under oxidative and reducing atmospheres

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Au nanoparticles supported on oxides display remarkable catalytic properties, e.g. in the reaction of oxidation of CO at low-temperature. Despite numerous studies performed on powders or on model catalysts, the mechanism of the activation of oxygen in these reactions is not yet completely understood, and only few methods of characterization can be used in real-condition, at atmospheric pressure.

We present a UV-visible optical investigation performed on Au/TiO₂ powder catalysts at atmospheric pressure [1]. The Au nanoparticles (NPs), with an average size of 4 nm as shown by TEM (figure a), are prepared by deposition-precipitation with urea [2] on a TiO₂ powder, then calcined in air. Diffuse optical reflectance shows an intense absorption around 550 nm, due to the excitation of plasmon resonances in the NPs. Its location, intensity and width are reproduced theoretically by using a distribution of shapes of the NPs. The changes of the reflectance upon exposure of the Au/TiO₂ catalyst to different atmospheres (O₂/He, H₂/He, CO/He) are measured in real-time by use of a home-made differential diffuse reflectance (DDR) spectrometer. The derivative-like DDR spectra show that the exposure to oxygen leads to the adsorption of oxygen species at the surface of the Au NPs (figure b). We analyze different processes that could occur during the oxygen exposure, and we find that the main effect is a charge transfer from gold to the adsorbed oxygen species, combined with a slight flattening of the Au NPs. The exposure to CO gives a similar but much smaller effect. Real-time optical measurements performed during the exposures to gas indicate that two different sets of particles are probably present in the catalyst, and react with different kinetics (figure c), slightly flat 3-dimensional NPs and very flat almost 2-dimensional NPs.

In order to investigate these two kinds of NPs, we also monitor the formation of the Au NPs during the reduction of the Au salts dispersed on TiO₂ just after the deposition-precipitation procedure, by heating the powder around 100°C under hydrogen atmosphere.

[1] Y. Borensztein, L. Delannoy, A. Djedidi, R.G. Barrera, C. Louis, *J. Phys. Chem. C*, in press

[2] R. Zanella, L. Delannoy and C. Louis, *Appl. Catal. A* 291, 62 (2005)

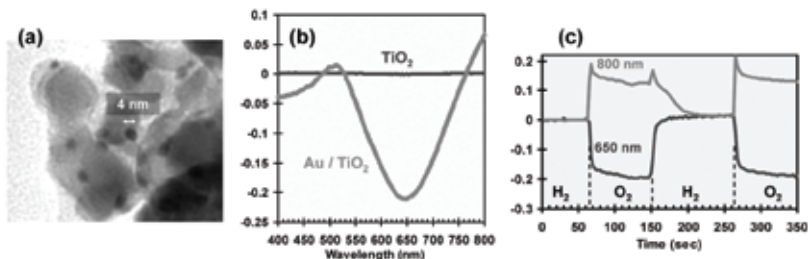


Fig. (a): TEM of Au NPs; (b): Au NPs Plasmon change in O₂; (c): Kinetics of change in O₂ or H₂

Simulation of Palladium clusters supported on graphene and hydrogen adsorption/dissociation in those clustersM.J. López¹, I. Cabria¹, S. Fraile², J.A. Alonso¹*Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, 47011 Valladolid, Spain*²*Departamento de Física Aplicada-LATUV, Universidad de Valladolid, 47011 Valladolid, Spain**maria.lopez@fta.uva.es*

Palladium might enhance hydrogen storage in carbon porous materials by surface reactions [1], especially by hydrogen spillover which consists in the dissociation-storage-recombination of hydrogen in the material. To gain some insight on the possible structures formed by palladium on nanoporous carbons and on the role played by palladium in the storage of hydrogen, we have investigated the adsorption of palladium on a graphene surface and the adsorption/dissociation of molecular hydrogen on those clusters. Our density functional calculations show that [2], even at the earlier stages of Pd deposition on the graphene surface, the Pd atoms have a strong tendency to form clusters. Three-dimensional clusters are more stable than planar clusters and the transition from planar to three-dimensional Pd clusters adsorbed on graphene occurs very early as a function of cluster size, at Pd₄. This tendency is a consequence of the strong Pd-Pd interaction. We have also investigated the adsorption-and/or-dissociation of molecular hydrogen on the deposited Pd clusters as a function of cluster size. The mechanism for the activation of the hydrogen molecule and its possible subsequent dissociation is discussed. We also discuss the implications for the hydrogen storage capacity of Pd-doped nanoporous carbon materials.

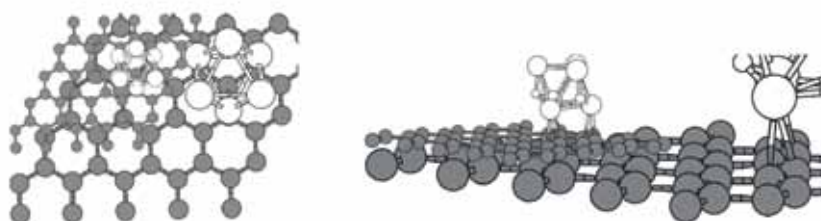


Figure 1: H₂ dissociated on a Pd₆ cluster adsorbed on graphene.

[1] C.I. Contescu, C.M. Brown, Y. Liu, V.V. Bhat and N.C. Gallego, *J. Phys. Chem. C* **2009**, *113*, 5886 ; A. Lueking and R.T. Yang, *Appl. Catal. A--Gen.* **2004**, *265*, 259.

[2] I. Cabria, M.J. López, and J.A. Alonso, *Phys. Rev. B* **81**, 035403 (2010)

XMCD spectroscopy on mass-selected transition metal clusters using a Penning ion trap

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B. Hofferberth², F. Menges², G. Niedner-Schatteburg²

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An experimental setup has been installed at the BESSY II synchrotron storage ring which is intended to record X-ray absorption spectra of free mass-selected clusters using bright soft X-ray radiation. The goal of the unique setup is to provide XMCD spectra of mass-selected cluster ions in order to extract the spin and orbital magnetic moments of the clusters. For this a Fourier-Transform-Ion-Cyclotron-Resonance mass spectrometer (FT-ICR) has been installed which provides a strong axial magnetic field for ion trapping. The photoabsorption signal is obtained by recording the fragmentation pattern produced after X-ray absorption and subsequent Auger decay of the core-excited parent cluster ion. The experimental setup and first X-ray absorption spectra will be discussed. Upon collisional cooling of small Co clusters a clear dichroic signal is observed when circular polarisation is used.

Controlled strong-field laser ionization

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Atomic clusters in intense laser fields are a nice playground to study the coupling of strong radiation into matter. In particular, non-stationary plasma effects lead to pronounced dynamics in the optical response [1]. In the case of dual laser pulse excitation, experimental angular-resolved photoelectron spectra on silver clusters yield a significant directional asymmetry which can be adjusted by the laser pulse timing. From corresponding microscopic real-time simulations we deduce a dynamical electron acceleration mechanism based on the strong laser-induced polarization fields. This ‘surface plasmon-assisted resonant electron acceleration in clusters’ (SPARC) opens a route towards nanometer-sized sources for extremely short and energetic electron bursts, triggered on the femtosecond time scale [2].

Another interesting observation concerns the ionization threshold intensities leading to a given atomic charge state. They exhibit steplike behaviour as we have recently shown in the ionization of laser-driven Xe clusters [3]. In these studies, laser intensity resolved measurements reveal that the high- q ion generation starts at an unexpectedly low threshold intensity of about 10^{14} W/cm². Above threshold, the Xe ion charge spectrum saturates quickly and changes only weakly for higher laser intensities. Good agreement between these observations and a molecular dynamics analysis allows us to identify the mechanisms responsible for the highly charged ion production and the surprising intensity threshold behaviour.

The modern tools of laser pulse shaping go beyond timing of two or more femtosecond pulses. They allow creating laser fields tailored in time and phase nearly at will. Optimal control techniques combined with femtosecond laser pulse shaping are suited to steer and enhance the strong-field induced emission of highly charged atomic ions. This will be shown with silver clusters embedded in helium nanodroplets [4], see Fig. 1.

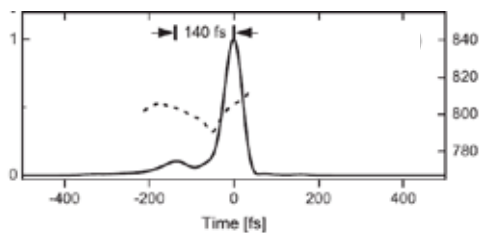


Figure 1: Pulse shape (solid line) and evolution of the carrier wavelength (dashed) of the laser field corresponding to light field fully optimized to the generation of the highest charge states [4].

- [1] Th. Fennel, K.-H. Meiwes-Broer, J. Tiggesbäumker, P.-G. Reinhard, P. M. Dinh and E. Suraud, *Rev. Mod. Phys.* 82, in press (2010)
- [2] Th. Fennel, et al., *Phys. Rev. Lett.* 98, 143401, 2007
- [3] T. Döppner et al., *PRL.*, in press, 2010
- [4] N. X. Truong et al., *PRA* 81, 013201, 2010

Ultrafast spectroscopy of single metal nanoparticles

Natalia Del Fatti, Aurélien Crut, Paolo Maioli, and Fabrice Vallée

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Ultrafast electron interactions, i.e., electron-electron and electron-lattice, and their modifications by size reduction play key roles in the properties of metal nanoparticles. In this context, time-resolved optical spectroscopy has been shown to be an efficient and versatile tool for their investigation in nanoparticles embedded in different environments [1]. Using the same time-resolved approach, the vibrational properties of metal nanoobjects have been studied down to the one nanometer range [2], also permitting analysis of the acoustic and thermal energy exchanges at the nanoscale.

However, almost all of these time-resolved optical investigations were performed on large ensembles of nanoparticles dispersed in a liquid or solid matrix, with an unavoidable dispersion of the size, shape and environment condition of the nanoparticles. This is making difficult detailed comparison of the experimental results with theoretical model, a difficulty that has been partly circumvented by using high quality samples with weak size and shape dispersions, and performing experiments in environment-independent conditions [1]. Single metal nanoparticles can now be optically detected, in particular using the far-field spatial modulation spectroscopy technique, which also permits their optical in-situ characterization [3,4]. Coupling this approach with a high sensitivity pump-probe femtosecond setup, it has been shown that time-resolved spectroscopy of a single metal nanoparticle can be performed [4]. We will discuss applications of this method to the investigation of the ultrafast nonlinear optical response of a single metal nanoparticle: a gold nanorod of known size and geometry, determined via its optical response. The results can then be quantitatively compared to a theoretical model, permitting detailed identification of the physical origin of the optical nonlinearity in a metal nanoobject. Extension of this approach to the investigation of the vibrations of single nanoobject and of local energy exchanges at the nanoscale will also be discussed.

1. C.Voisin, N.Del Fatti, D.Christofilos and F.Vallée, *J. Phys. Chem B* **105**, 2264 (2001).
2. V. Juvé, A. Crut, P. Maioli, M. Pellarin, M. Broyer, N.Del Fatti, and F.Vallée, *Nano Letters* **10**, 1853 (2010).
3. O. L. Muskens, P. Billaud, M. Broyer, N. Del Fatti, and F. Vallée *Phys. Rev. B* **78**, 205410 (2008).
4. O. L. Muskens, N. Del Fatti, and F. Vallée *Nano Letters* **6**, 552 (2006).

Photo-induced processes in metallic clusters and fullerenesA.V. Korol¹, A.V. Solov'yov¹, R.G. Polozkov², and V.K. Ivanov²¹ *Frankfurt Institute for Advanced Studies, Germany*² *St. Petersburg State Polytechnical University, Russia**korol@fias.uni-frankfurt.de*

Our work is focused on the analysis of several peculiar phenomena, occurring in various photo-induced processes involving metallic clusters and fullerenes, which currently are subjects of intensive theoretical and experimental investigation. We present clear theoretical explanations of a variety of experimentally obtained results as well as predict new phenomena which can be verified in experiments. The following issues will be addressed at the Conference.

- Angle-resolved photoelectron spectra of metal clusters. A consistent many-body theory has been applied for the description of angular resolved photoelectron spectra of various metal clusters [1]. The results of calculations demonstrate the dominant role of the many-body effects in the formation of angular distributions of photoelectrons and do explain recent experimental data [2]. We also demonstrate that for a strongly polarizable target (e.g., a cluster) the angular distribution is noticeably modified due to the action of the field of alternating dipole moment induced at the residue by the laser field [3]. Strong modification can be achieved by applying laser fields of comparatively low intensities $\sim 10^{10} - 10^{11}$ W/cm².
- Confinement resonances in photoionization of endohedral systems, A@C_n. We demonstrate [4] that the structure of confinement resonances in the photoionization of an encapsulated atom is very sensitive to the mean displacement $\langle a \rangle$ of the atom from the cage center. The resonances are suppressed if $2\langle a \rangle$ exceeds the photoelectron half-wavelength. We explain the results of recent experiments [5] which contradict the earlier theoretical predictions on the existence of confinement resonances in particular endohedral systems.
- Dynamical screening of endohedral complexes. The fullerene cage screens the endohedral atom from external electromagnetic fields and, thus, influences the photoabsorption rate of the atom. We demonstrate that this effect is strongly dependent on the photon energy. It was found that in the vicinity of the plasmon resonances of the fullerene, the photoabsorption of the confined atom is strongly enhanced from that of the free atom [6,7].
- Modification of the Auger decay of endohedral atoms. The Auger decay in an encapsulated atom strongly depends on its displacement from the cage center [8]. We explain dramatic broadening of the peaks in atomic photoionization measured recently [9] for Sc₃N@C₈₂.

[1] A.V. Solov'yov, R.G. Polozkov, V.K. Ivanov. Phys. Rev. A **81**, 021202(R) (2010).[2] B. von Issendorff *et al.* Science **323**, 1323 (2009).[3] A.V. Korol, A.V. Solov'yov. J. Phys. B **42**, 015002 (2009).

[4] A.V. Korol, A.V. Solov'yov. arXiv:0912.2690 (2009).

[5] A. Müller, S. Schippers *et al.*, Phys. Rev. Lett. **101**, 133001 (2008).[6] J.-P. Connerade and A.V. Solov'yov. J. Phys. B **38**, 807 (2005).[7] S. Lo, A.V. Korol, A.V. Solov'yov. Phys. Rev. A **79**, 063201 (2009).

[8] A.V. Korol, A.V. Solov'yov. In preparation (2010).

[9] A. Müller, S. Schippers *et al.* J. Phys.: Conf. Ser. **88** 012038 (2007).

TUESDAY SEPTEMBER 21

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.....
In honor to T. Kondow
- Memorial 2
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In honor to E. Recknagel
- Invited 5
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T. Tsukuda
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Aerobic Oxidation of Alkanes by Size-Controlled Au Clusters (n=10, 18, 25, 39) on Hydroxyapatite
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S. Vajda
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R. Zanella
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O. López-Acevedo
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P. Pyykkö
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Derivatives of WAu₁₂
- Invited 8
A. Fielicic
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- Oral 10
G. Markovich
.....
Inducing chirality in metal nanoparticles - interaction of chiral molecules with metal nanostructures

Tamotsu Kondow

In memory of great Pioneer in nano-material science

Koji Kaya, RIKEN, Wako, Japan



Our colleague Tamotsu has passed away in May 25, 2009 after long term struggle against the heavy heart disease at the age of 72. Tamotsu was the professor at the chemistry department of University of Tokyo until 1997. After the retirement from Tokyo University, he moved to Toyota automobile company as a Director of the Cluster Research Laboratory. Throughout his research career, Tamotsu's research covered a wide area of physical chemistry from the solid state chemistry of organic charge transfer materials and their catalytic activity, to the dynamical properties of atomic and molecular clusters as studied by molecular beam method. Because of his excellent achievement in this field, he was honored recipient of an Alexander Humboldt Research award in 2004 entitled "Structure and reactivity of clusters studied by mass spectrometry and laser spectroscopy".

In addition to his great scientific achievements, he is the person who opened a door to Japan widely for many nano material scientists from abroad. His efforts resulted in a significant number of international research collaborations. As many of the foreign scientists point out, Tamotsu was an ambassador.

In this talk, we will talk about his brilliant science and his warm personality.

In Memory of Ekkehard Recknagel

O. Echt

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Ekkehard Recknagel, a distinguished scientist with contributions in nuclear physics, hyperfine physics, and cluster science, died on June 8 2009 in Konstanz after a long battle with cancer.

Ekkehard was born on April 7, 1931, in Halberstadt, Germany. In 1957 he earned his Diploma in Physics under the supervision of Prof. Hans Kopfermann; three years later he was awarded the doctoral degree for his Ph.D. Thesis *The Hyperfine Structure of the $^2S_{1/2}$ Ground State and the Nuclear Magnetic Dipole Moment of ^{197}Au* . He conducted postdoctoral research at the University of Karlsruhe under Prof. Helmut Friedberg, and at Harvard University under Prof. Norman Ramsey. In 1963 Ekkehard joined the Hahn Meitner Institute in Berlin. The central topic of his research was the measurement of lifetimes and magnetic dipole and electric quadrupole moments of isomeric nuclei formed in nuclear reactions, but his group also developed methods to apply nuclear techniques to the investigation of radiation damage in solids.

In 1975 Ekkehard became Professor of Physics at the newly founded University of Konstanz. A 350 kV accelerator became the cornerstone of his research in nuclear solid state physics; the accelerator was used to implant radioactive nuclei into solids, to irradiate solids with particles, and to study ion channeling in crystals. Members of his group also performed experiments at the Swiss Institute of Nuclear Physics in Switzerland (now the Paul Scherrer Institute) where muons were implanted into solids to study diffusion, magnetic ordering and radiation damage. The second focus of Ekkehard's research in Konstanz was cluster science. Among the early accomplishments of his group were the synthesis of metal clusters in the gas phase, the discovery of "magic numbers" in mass spectra of xenon and other van der Waals clusters which revealed geometric shell closings, and the identification of "Coulomb explosion" of multiply charged cluster ions. In 1990 he chaired ISSPIC V in Konstanz.

Ekkehard will be remembered by his many friends for his warmth, hospitality, and enthusiasm with which he would celebrate achievements by his students and research assistants.

Bonding in Thiolate-Protected Gold Clusters & Self-Assembled Monolayers:**What Happens When a “Good Metal” Meets Some “Satisfied Molecules”**

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The recent total structure determinations (*TSDs*) of several distinct thiolated gold clusters, along with enhanced STM-imaging of low-coverage thiolate-on-*Au(111)* monolayers, have already afforded an opportunity to analyze their electronic structure and stability in a rigorous way, via high-level electronic-structure theory (*EST*). We offer here a bonding interpretation consistent with these *TSDs* & *EST* results: A set of saturated anionic Au(I)thiolate complexes are bound by electrostatic (ionic plus polarization) interactions to a positive metallic core, characterized in the most favorable cases by filled shells of delocalized orbital's and near charge-neutrality. In this lecture, the consistency of this simplified picture with observed chemical, optical, and electrical phenomena will be critically summarized.

Ligand-protected gold clusters as "molecular metals"H. Häkkinen*Departments of Physics and Chemistry, Nanoscience Center, University
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This talk will review the fast recent progress in theoretical understanding of ligand-protected gold clusters. This area has attracted considerable interest due to experimental breakthroughs in solving for the atomic structure of thiolate-protected $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{102}(\text{SR})_{44}$ clusters via single-crystal X-ray crystallography. A useful concept for analyzing the electronic structure and the degree of "metallicity" is the so-called superatom complex model that accounts for the "available" delocalized electrons in the metal core, responsible for, e.g., optical and chemical properties. The improved understanding of stability, structure, and properties of ligand-protected gold clusters should provide guiding principles for molecular-precision-design and functionalization of these exciting building blocks of nanomaterials that are finding applications in diverse fields of biolabeling, photonics, sensing, and nanocatalysis.

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Aerobic Oxidation of Alkanes by Size-Controlled Au_n Clusters (n=10, 18, 25, 39) on Hydroxyapatite

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Supported gold nanoparticles (diameter > 2 nm) have gained much attention as promising catalysts for a variety of oxidation reactions using molecular oxygen O₂ as an oxidant. We aimed to develop active Au catalysts utilizing intrinsic chemical activity of small (diameter < 2 nm) Au clusters to O₂. To this end, it is essential to develop an experimental method to synthesize gold clusters whose size (“number of Au atoms”) is controlled with atomic resolution. The method we developed utilized ligand-protected Au clusters with well-defined size as precursors.[1,2] In this work, we synthesized the Au_n clusters with n=10, 18, 25 and 39 on hydroxyapatite (HAP; Ca₁₀(PO₄)₆(OH)₂) using glutathionate-protected Au clusters.[3] Then we tested the catalytic activity of these size-selected clusters (0.2wt% Au_n-HAP) for the aerobic oxidation of cyclohexane (**1**). As summarized in Table 1, cyclohexanol (**2**) and cyclohexanone (**3**) were obtained as primary products in all cases. The total selectivity of **2** and **3** is nearly 100% and does not depend on the cluster size. In contrast, the conversion of **1** gradually increases with increase in the Au clusters size; from 11.6% to 14.9% for n=10 to 39 (entries 1-4). This result clearly shows the difference in the cluster size by few atoms affects the catalytic activity.

Table 1. Solvent-free oxidation of cyclohexane

C1CCCCC1 $\xrightarrow[150\text{ }^\circ\text{C, 4h}]{\text{O}_2, \text{Au-HAP}}$ C1CCCC(O)C1 + O=C1CCCCC1

1
2
3

Entry	Catalyst	Conv. [%]	TOF / h ⁻¹	Selectivity [%]	
				2	3
1	0.2Au ₁₀ -HAP	11.6	660	58	41
2	0.2Au ₁₈ -HAP	12.9	730	49	50
3	0.2Au ₂₅ -HAP	14.2	800	50	49
4	0.2Au ₃₉ -HAP	14.9	840	50	49

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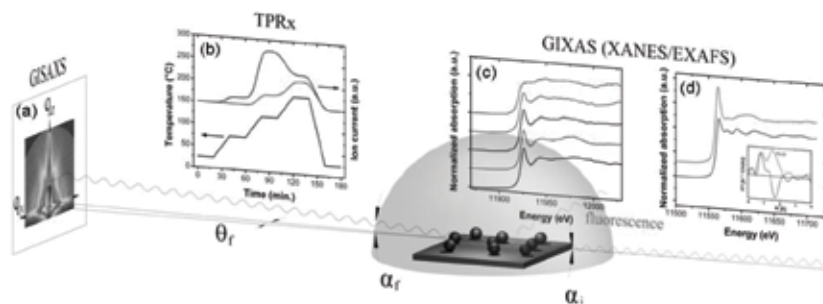
Coupling Studies of Model and Practical Nanocatalysts under Realistic Reaction Conditions and Bridging the Sub-Nanometer to Nanometer Gap

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Using precious metal and transition metal-oxide clusters deposited on technologically relevant oxide and carbon-based supports, in this overview presentation examples will be given on bridging the size gap between the sub-nm and nm cluster size regime as well as on coupling studies of model size-selected [1-3] and "practical" – with wet methods prepared [4-5] nanocatalysts. Select reactions will include Fischer-Tropsch synthesis and other for industry central processes, where new classes of highly selective and active catalyst systems performing at low temperatures were identified for dehydrogenation, epoxidation and other reactions. The effect of cluster size along with the effect of support composition and pretreatment is studied under realistic conditions of pressure and temperature. The experiments are based on *in situ* synchrotron X-ray characterization of clusters under working conditions, combined with mass spectroscopy analysis of reaction products. Accompanying density functional theory calculations are used to understand the activity of clusters and the underlying reaction mechanisms.



Schematic of the combined temperature-programmed reaction, grazing-incidence X-ray scattering and X-ray absorption approach.[4] The insets illustrate the capabilities offered by this combination of techniques: a) two-dimensional GISAXS pattern enabling the determination of particle size and shape b) monitoring of product evolution with temperature/time, c) series of XANES spectra collected during *in situ* reduction, and d) a quick EXAFS scan

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[5] in preparation

Au-Ag/TiO₂: More active and stable catalysts for CO oxidation

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Since the discovery in the late eighties that gold is catalytically active when dispersed as small particles on an oxide support, the preparation of gold-based catalysts has been widely studied [1,2]. They are particularly interesting in many reactions of both industrial and environmental importance. The most remarkable catalytic properties of supported gold have been obtained for the reaction of CO oxidation at ambient temperature [3,4]. The catalytic activity strongly depends on the particle size and is the highest in the range of 1-3 nm. However it decreases during the catalytic run [5]. This could be due to the sintering of the nanoparticles or to the adsorption of carbonates on the reactive sites of the catalysts. Hence, in spite of their good initial catalytic activity, these catalysts have still very few commercial applications. A way to overcome this drawback, i.e. catalytic deactivation, is to prepare bimetallic catalysts. Bimetallic combinations such as Au-Ag could exhibit significantly improved activity and stability for several reasons. Silver is known as a catalyst for CO oxidation at higher temperatures than gold. Compared to gold which is the most electronegative metal, Ag has a larger electron donating ability and could modify the electronic properties of gold. Moreover the presence of a second metal can induce geometric modifications of the surface of the gold particles. In general in bimetallic nanoparticles, the interactions between the two metals are complex and largely unknown.

In this contribution we studied the effect of adding Ag, to gold catalysts supported on TiO₂ and CeO₂. The variation of the ratio of metals, the final temperature and the atmosphere used in the thermal treatment were studied. The catalysts were characterized by electron microscopy (HRTEM and Z-contrast), XRD, DRIFTS, UV-vis and XAS. The catalytic test showed that the catalytic activity varies with the Au/Ag ratio, the temperature and the atmosphere used for the thermal treatment. Au-Ag catalysts deactivate less than the monometallic gold catalysts. Moreover these bimetallic catalysts show a synergetic effect i.e. a higher activity than gold and silver (Ag is inactive at RT) when they are thermally treated at the optimum temperature. It is proposed that Ag plays a key role in the activation of oxygen. It was shown by TEM that the metal particles formed were small (2-3 nm) in all the synthesized catalysts, which helps to increase their efficiency. The XANES results showed variations in the reduction temperature of gold and silver when they are present in a monometallic or in a bimetallic catalyst. EXAFS data clearly demonstrate that the reduction treatment led to the formation of the Au-Ag particles. The phase composition and the particle structure changed with reduction temperature. The increase in the reduction temperature provokes enrichment with Ag atoms of the surface of bimetallic nanoparticles.

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Quantum size effects in ambient CO oxidation catalysed by ligand-protected gold clustersO. Lopez-Acevedo¹, K. A. Kacprzak¹, J. Akola¹, H. Häkkinen^{1,2}¹ *Department of Physics, Nanoscience Center, University of Jyväskylä, Finland*² *Department of Chemistry, University of Jyväskylä, Finland**lopez@phys.jyu.fi*

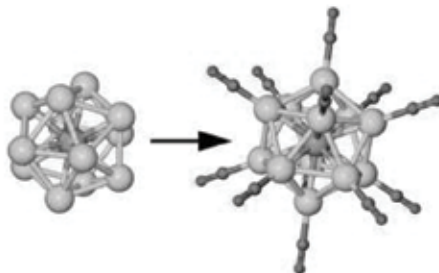
Crystal structure determination of two members of the family of gold Monolayer Protected Clusters opened the unique possibility to obtain via Density Functional Theory their precise electronic structure [1-5]. The super-atom model we have derived [4] and recent extensions have shown that electronic shell models not only apply to bare clusters but also to gold clusters protected by either gold-thiolate oligomeric semi-rings, halide atoms [4], iron-carbonyl units [6] and chlorinated methyl protections [7], and is still valid even for bi-metallic gold-transition metal cores [8]. Various physico-chemical properties directly related to the electronic structure have been simulated and explained including electrochemical gap, optical absorption spectrum, and catalytic reactivity. In addition, new ligand effects like modification of the cluster redox properties and chiroptical activity have also been addressed in recent joint theory-experiment studies. The success of the electronic model, a good understanding of the role of the protective layer and the particularity of having several crystal determined structures makes the possibility of model catalytic reactions of high interest.

It is known that finely dispersed nanometre-scale gold particles catalyse several oxidation reactions in aerobic, ambient conditions. The catalytic activity has been explained by various complementary mechanisms, including support effects, particle-size-dependent metalinsulator transition, charging effects, frontier orbital interactions and geometric fluxionality. We show [9], by considering a series of ligand-protected gold clusters with diameters between 1.2 and 2.4 nm, that electronic quantum size effects, particularly the magnitude of the so-called HOMO-LUMO energy gap, has a decisive role in binding oxygen to the nano-catalyst in an activated form. This can lead to the oxidation reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ with low activation barriers. Binding of dioxygen is significant only for the smallest particles with a metal core diameter clearly below 2 nm. Our results suggest a potentially viable route to practical applications using ligand-protected gold clusters for green chemistry.

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Derivatives of WAu₁₂M. P. Johansson¹, P. Pyykkö¹¹ *Department of Chemistry, University of Helsinki, POB 55 (A. I. Virtasen aukio 1), FI-00014 Helsinki, Finland**Pekka.Pyykko@helsinki.fi*

The possible existence of the cluster WAu₁₂ was predicted by Pyykkö and Runeberg[1] and its stability was attributed to the three complementary reasons of relativistic strengthening of the radial covalent bonds, the 18-electron principle and the 'aurophilic' dispersion-type attraction between the 5d¹⁰ cores. The species was almost immediately observed [2]. We have now considered the possibility of protecting the cluster surface by carbonyls and found that, indeed, each of the surface gold atoms accepts a -CO group whose binding energy is about 100 kJ mol⁻¹, up to the last one. This opens the possibility for a new family of systems that has a potential of existing in the bulk [3].

Figure 1: The predicted I_h structure of WAu₁₂(CO)₁₂ [3].

This work was inspired by the previous experimental observation of an isoelectronic and isostructural platinum carbonyl structure in the solid state by the Bologna group [4].

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- [4] S. Zacchini, *Int. Symp. on Metallophilic Interactions*, Mittelwihir, France, 4-6 February 2010, lecture 4.

**Vibrational spectroscopy of metal cluster complexes:
investigating the chemistry on a small surface**

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Transition metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of heterogeneous catalytic reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behavior. Vibrational spectroscopy of gas-phase clusters can provide insights into the clusters' structure and the behavior of adsorbed species.

In the last years we have intensively utilized mass-selective vibrational spectroscopy of neutral and charged cluster complexes by multiple photon dissociation (MPD) spectroscopy down to the far-infrared ($<100\text{ cm}^{-1}$). This technique requires an intense and widely tunable IR light source, in our experiments the Free Electron Laser for Infrared eXperiments (FELIX), which generates IR light between $\sim 40\text{--}3500\text{ cm}^{-1}$ and is therefore well suited to induce resonant photodissociation by excitation of ligand vibrations as well as of internal cluster modes.

In the first part of my talk I will focus on the far-IR MPD spectroscopy on weakly bound complexes between metal clusters and rare gas atoms that can provide the unique vibrational fingerprints of the metal clusters. The comparison with IR spectra calculated using density functional theory allows determination of the clusters' structures and provides insights into the growth mechanism. The capabilities of structure determination via far-IR MPD spectroscopy are demonstrated for cationic rhodium [1] and neutral gold [2] clusters.

A second topic will be an overview on recent experimental studies on the interaction of single CO molecules with transition metal clusters in the gas-phase, typically in the size range of 3 to more than 20 atoms, emphasizing specifically the insights gained from vibrational spectroscopy [3]. Trends across the transition metals for C—O bond activation, eventually leading to a transition from molecular to dissociative chemisorption [4], as well as for adsorption geometries are discussed and compared with the behaviour of CO adsorbed on extended surfaces.

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- [2] P. Gruene, D. M. Rayner, B. Redlich, A. F. G. van der Meer, J. T. Lyon, G. Meijer, and A. Fielicke, *Science* **674**, 321 (2008).
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Inducing chirality in metal nanoparticles - interaction of chiral molecules with metal nanostructures

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In recent years several groups have demonstrated the synthesis of chiral metal clusters of < 100 atoms where chirality was induced by the preparation of the clusters in the presence of chiral surfactant molecules. However, this chiral templating effect is limited to very small clusters and vanishes as metal core size increases. We aim at producing larger metal nanostructures by wet chemical techniques with enhanced chiroptical properties. One of the major candidates to achieve this is DNA templating of the growth of chiral nanoparticles. Other, unpublished ideas will be presented as well.

WEDNESDAY SEPTEMBER 22

Plenary 2 M. T. Bowers	<i>Alzheimer's Disease, Type 2 Diabetes and Amyloid Formation</i>
Invited 9 P. Milani	<i>Cluster-assembled systems for efficient clinical screening of onco-hematological malignancies</i>
Oral 11 J. S. Martinez	<i>Oligonucleotide-templated silver nanoclusters for DNA and protein detection</i>
Oral 12 D. Grandjean	<i>Thermooptical Properties of Branched Gold Nanoparticles Unraveled by In situ EXAFS</i>
Oral 13 H. Chacham	<i>Doped assemblies of Au nanoparticles: structural and electronic properties</i>

Alzheimer's Disease, Type 2 Diabetes and Early Amyloid Oligomer States

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Many important diseases are characterized by the appearance of amyloid plaques. In recent years it has been determined that in most of these diseases the proximate toxic agents are located in the early oligomer states not in the plaques themselves. These states are very difficult to study due to the flexibility of the monomer species in vitro/vivo and their rapid oligomerization making observation of the oligomer distribution and individual oligomer structures inaccessible to traditional spectroscopic methods. Here we will apply Ion Mobility based Mass Spectrometry coupled with high level theoretical modeling to attack this problem. The talk will briefly outline the methods and give recent results on the peptides responsible for Alzheimer's Disease and Type 2 Diabetes. Results on model systems will also be presented where the detailed mechanism of amyloid formation can be more readily probed.

CLUSTER-ASSEMBLED SYSTEMS FOR EFFICIENT CLINICAL SCREENING OF ONCO-HEMATOLOGICAL MALIGNANCIES**Paolo Milani**

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Deposition of clusters from the gas phase is becoming an enabling technology for the production of nanostructured devices. Among different experimental approaches, supersonic clusters beam deposition (SCBD) has been shown as a viable route for the production of nanostructured thin films. By using SCBD and by exploiting aerodynamical effects typical of supersonic beams it is possible to obtain very high deposition rates with a control on neutral cluster mass distribution, allowing the deposition of thin films with tailored nanostructure. Due to high deposition rates, high lateral resolution, low temperature processing, SCBD can be used for the integration of cluster-assembled films on micro- and nanofabricated platforms with limited or no post-growth processing [1].

Cluster-assembled nanostructured titanium oxide film (ns-TiO_x), synthesized by SCBD has recently emerged as a biocompatible substrate in different biological assays [2-4]. The ns-TiO_x surface is characterized by a morphology at the nanoscale that can be tuned to modulate specific biomolecule-material interactions and, in particular, protein binding [5, 6].

Here I will present the use of cluster-assembled ns-TiO_x coatings as active material in a microfluidic device promoting hematopoietic cell immobilization in conditions of shear stress. This allows the analysis of chromosomal aberrations in cancer by miniaturized fluorescence in situ hybridization (FISH). We developed the protocol on tumor cells and bone marrow from normal donor using commercially sex-specific and onco-hematology probes. Miniaturized FISH based on ns-TiO_x showed a robust performance demonstrating that it is suitable for genetic screenings, in research and in clinical settings, for the diagnosis of samples from onco-hematological malignancies [7].

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- [7] A. Zanardi et al., *BioTechniques* 49, 497 (2010)

Oligonucleotide-templated silver nanoclusters for DNA and protein detection

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Fluorescent metal nanoclusters (<1 nm) are collections of several to tens of atoms of gold or silver. While for gold nanoclusters, the fluorescence emission is thought to scale as a function of the number of atoms within the cluster, for silver nanoclusters, the relation of atom number to fluorescence emission is less clear, as is the nature of the complex/cluster. Nevertheless, “fluorescent metal nanoclusters” are gaining much interest because of their desirable photophysical properties, smaller size than quantum dots, and inherent biocompatibility. As a compliment to quantum dots and molecular fluorophores, fluorescent metal nanoclusters have been produced using templates of dendrimers and polymers, small molecular ligands, or within biological materials of interest, such as DNA. Recently, we have synthesized and photophysically characterized Ag-nanoclusters (AgNCs), which were templated on DNA under one reaction condition (near physiological pH), with distinct, and narrow, excitation and emission profiles tuned to common laser lines. We have taken those clusters and developed an intrinsically fluorescent recognition ligand based on a DNA aptamer-templated AgNC for specific and sensitive protein detection. Our intrinsically fluorescent recognition ligand combines the strong fluorescence of oligonucleotide templated AgNCs with the specificity and strong binding affinity of DNA aptamers for their target proteins, to develop a new strategy for detection of specific proteins. Here the AgNC-aptamer assembly serves as both a fluorescent label and a specific binding ligand. Our *in situ* method is a single-step that requires no covalent attachment of aptamer, nor protein, to fluorophore, and is thus simple, inexpensive, and a facile detection method. Additionally, we find that the red fluorescence of oligonucleotide-templated silver nanoclusters can be enhanced 500 fold using a proximity technique. Based upon this newly observed phenomenon, we have designed a DNA detection probe (NanoCluster Beacon, NCB) that “lights up” upon target binding. In a separation-free assay, a signal-to-background ratio of 76 was demonstrated for the detection of a human oncogene target (*Braf*). In addition to eliminating the need to purify DNA nanocluster probes that do not bind targets, there is no need to remove the silver nanocluster precursors used during nanocluster formation.

Thermo-optical Properties of Branched Gold Nanoparticles Unraveled by *In situ* EXAFS

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Gold nanoparticles (Au NPs) have immense potential for biomedical applications due to their localized surface plasmon resonance (LSPR) enhanced light absorption. Under optical illumination they efficiently convert the strongly absorbed light into localized heat, which can be exploited for the selective laser photothermal therapy of cancer [1]. Notwithstanding the successful initial demonstrations of the use of immunotargeted Au NPs in hyperthermia therapy, a number of parameters and thermo-optical properties need to be better understood and optimized [2]. As most of the temperature evaluations at the surface of NPs are still based on theoretical calculations involving numerous assumptions, the experimental determination of the actual NP temperature increase appears to be a crucial objective for current applications of heated NPs in nanomedicine [3]. Branched Au NPs featuring a very promising hyperthermia potential due to their strong LSPR [4] have been investigated with *in situ* extended X-ray absorption spectroscopy (EXAFS) under illumination with a wavelength close to their plasmon frequency. The individual NP temperature could be measured experimentally in remarkable agreement with the NP suspension temperature measured with a thermocouple located next to the laser beam. Concomitantly, a strong NP concentration variation has been clearly observed and quantified, showing that the heating process originates from a complex interaction of parameters.

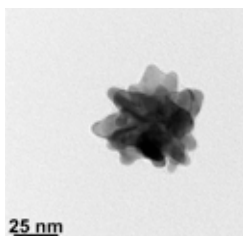


Figure 1: TEM image of a branched Au NP

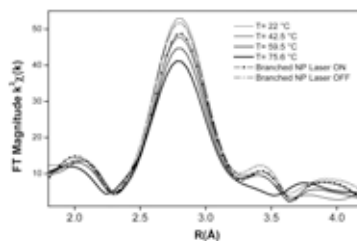


Figure 2: Fourier transforms of the Au L3-edge EXAFS of the Au NPs during calibration and laser test

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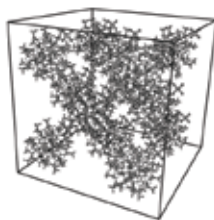
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Doped assemblies of Au nanoparticles: structural and electronic properties

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Assemblies of ligand-stabilized metal nanoparticles can present peculiar properties that differ from those of bulk materials. The large interstitial voids in these assemblies allow them to be permeated by dopant molecules in a reversible and controllable way, inside electrochemical cells. This latter property has been recently used to produce a tunable Schottky barrier between a Au nanoparticle film and a semiconductor surface [1], which is an example of the technological potential of this new class of nanostructured materials. In this work, we apply ab initio methods to study the changes in the properties of a periodic assembly of Au nanoparticles due to the addition of either donor or acceptor dopant molecules. As a model for the assemblies, we consider methylthiol-capped nanoparticles periodically assembled in a face-centered cubic (fcc) structure, as shown in the Figure 1. As models for the nanoparticles, we consider methylthiol-covered Au₃₈ and Au₂₅ clusters. As dopants, we consider the donor tetrabutylammonium (C₄H₉)₄N molecule and the acceptor hexafluorophosphate (PF₆⁻) molecule. These dopant molecules have been used in the experiments [1]. To our knowledge, this is the first ab initio investigation for this new type of material. We obtain structural and electronic properties, in particular the dependence of the Fermi level with the dopant concentration. We find a linear dependence of the Fermi level with dopant concentration, consistent with recent experiments, up to a critical concentration. For larger concentrations, a new regime is predicted. These features are well reproduced by a simple, analytical model for the material.

Figure 1: Fcc assembly of methylthiol-capped Au₃₈ nanoparticles doped with PF₆⁻.

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THURSDAY SEPTEMBER 23

Plenary 3 O. Cheshnovsky	<i>Seeking critical sizes in clusters, using photoelectron spectroscopy</i>
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Seeking critical sizes in clusters, using photoelectron spectroscopyO. Cheshnovsky

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Photoelectron spectroscopy (PES) of mass selected anionic clusters is a well established technique in studying the electronic structure of clusters. Its appeal stems from its general ability of mass selected assignment of energy levels in the neutral cluster generated during the photodetachment process, and very often its lowest excited state. It also allows access to relatively deep energy levels due to the low values of electron affinities. Finally it is highly compatible with ultrafast laser techniques for monitoring the dynamics of electronic states in mass selected clusters.

The evolution of versatile pulsed cluster sources and pulsed lasers at the Vacuum UV together with the advent of the high efficiency Magnetic bottle Time of Flight PES has promoted this technique as a highly versatile tool in cluster research. The advent of velocity-map imaging and impulsive deceleration of the detached electrons, over the last decade, have further improved the quality and usability of PES. This talk will focus mainly of critical size effects in clusters, as investigated in our research group.

First, we will highlight the issue of critical size for the insulator to metal transition. We will argue that the strict criterion for metallicity, a finite density of states (DOS) at the Fermi energy (EF), cannot be applied to clusters because energy levels are always discrete in a system of finite size. We propose an alternative definition whereby clusters can be considered metallic when the gap between occupied and unoccupied states at EF is consistently smaller than or equal to the Kubo band gap δ . We use the experimental findings of photoelectron spectroscopy of anionic clusters to analyze band gaps of various cluster families. Monovalent clusters (alkali and noble metals) grossly follow the shell structure pattern, producing band gaps smaller than δ for most cluster sizes, with some exceptional sizes exhibiting electronic shell closure or symmetry-induced band gaps. Among the bivalent metals, only mercury shows consistent band gap closure with increasing cluster size that is a simple insulator-metal transition. Other bivalent elements such as Zn, Mg and Sr or transition metals exhibit a much more complicated behavior.

We will then refer to electron solvation in clusters. We show that by using 2P PES from an intra-cluster impurity state the binding energy of excess electrons can be monitored in noble gases. This approach is very relevant to the characterization of impurity states in clusters. We will show how PES combined with dynamic Time resolved PES measurements shed light on the nature of the solvated electron in water clusters.

We will then highlight recent studies on critical sizes pertaining to reactivity in clusters. The critical size for proton transfer in ground state clusters is interrogated by monitoring the spectroscopic fingerprints of their PES. Finally, we will discuss the evidence for a critical size in the formation and the reactivity of two electron solvation in water clusters.

Probing the structural isomers, structural transitions, and O₂ reactivity of gold clusters using photoelectron spectroscopy

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Gold clusters have attracted significant attention in nanoscience because of emerging new catalytic, electronic, and optical properties discovered for gold at the nanometer scale. The structures of gold clusters up to 20 atoms have been extensively studied. However, structural isomers and structural transitions have been less well understood. Using a combination of O₂-titration [1], Ar-tagged clusters [2], and isoelectronic substitution by Cu and Ag [3,4], we have been able to discover low-lying isomers for a number of gold cluster anions and definitive information on structural transitions from 2D to 3D at Au₁₂⁻ [2], and from cage to pyramid at Au₁₈⁻ [5]. For Au₇⁻, we found a new isomer built from the D_{3h} Au₆ to be competing for the global minimum [3]. For Au₁₀⁻, we discovered three low-lying isomers in addition to the triangular global minimum (Figure 1) [4]. The triangular Au₁₀⁻ is unreactive with O₂, whereas the three low-lying isomers are reactive and can be all titrated out of the cluster beam [1].

O₂-activation by gold clusters is of paramount importance to understanding the catalytic mechanisms of nanogold. Previous studies showed that only even-sized Au_{*n*}⁻ clusters react with O₂, whereas odd-sized Au_{*n*}⁻ clusters are not reactive. New photoelectron spectroscopy data on O₂ complexes of odd-sized Au_{*n*}⁻ clusters showed that they are van der Waals complexes, confirming the inertness of odd-sized Au_{*n*}⁻ toward O₂. New data on O₂ complexes of even-sized Au_{*n*}⁻ clusters led to fresh insight into how neutral even-sized Au_{*n*} clusters interact with O₂ [6].

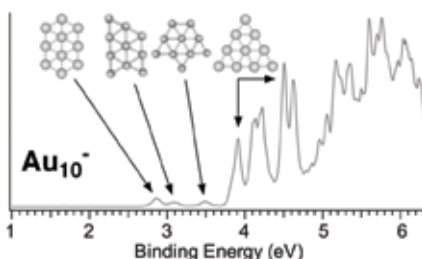


Figure 1: The photoelectron spectrum of Au₁₀⁻. Spectral contributions and structures of the triangular global minimum and three low-lying isomers are shown.

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Dynamical Properties of Metal Clusters

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Research on metal clusters is strongly motivated by the goal to characterize, understand and explore their extraordinary dynamic properties as a function of size, structure and environment. Size-selected silver tetramers, for example, were identified already rather early as the latent image spec of the photographic elementary process. Later it was found, that supported gold clusters with few atoms up to nanometer size exhibit pronounced catalytic properties. In order to tackle the problem and to obtain detailed insights into the underlying dynamic processes, experiments and advanced calculations were performed on corresponding systems in the gas phase, which allowed to interrogate these particles at a specific mass, charge and structure and in a very simple and well controlled environment.

The particles were produced by state of the art cluster sources, which allowed to synthesize a rich variety of neutral as well as negatively and positively charged pure and mixed metal clusters and their oxides. The produced particles were also combined to form new architectures like "clusters on clusters", mimicking in the well defined gas phase the situation of an active site deposited on a surface element. These charged cluster assemblies were then injected into a tandem mass spectrometer with a temperature-controlled ion trap inserted in between. This allowed - when introducing non-reactive and reactive target gases into the trap - to perform energetically well-controlled collision experiments, allowing to study the fragmentation behavior and bonding capabilities of the trapped particles. Interesting conclusions on their geometric structure and their pronounced reactive behavior could be drawn from these results. For example, the investigation of the CO-combustion reaction on small gold clusters revealed a catalytic activity even for negatively charged gold dimers. In contrast to that and affirmed by theory small atomic silver clusters were not found relevant for catalytic oxidation processes so far. Feeding laser beams into the trap allowed to study photo-dissociation, -association, charge transfer and ionization processes. Among these infrared absorption experiments performed with free electron lasers (FEL) provided the richest harvest, allowing the systematic comparison with theoretically predicted cluster structures of catalytically relevant transition metal oxides.

The experimental approach also served for time-resolved investigations in the femtosecond (fs)-regime. Since these particles exhibit pronounced absorption bands, which are well located within the tuning range of the available fs-laser sources; their detachment and photo-ionization energies are well within their reach, and the vibrational frequencies can also be resolved with the available fs-pulse lengths. Further the influence of internal vibrational redistribution processes (IVR), which depend upon the amount of internal degrees of freedom, can simply be adapted to the experimental requirement by the right choice of the cluster size. For this reason we have performed systematic pump&probe experiments on different metal clusters in order to study the evolution of wave packet dynamics, vibronic couplings, geometrical rearrangements, and fragmentations as a function of cluster size. We have further developed schemes for observing wave packet and reaction dynamics also in the electronic ground state by means of charge reversal spectroscopy (NeNePo).

The photo-induced intra-molecular dynamics of a system critically depends upon the employed pulse parameters. We have, therefore, carried out active control experiments, in which we excited differently branching fragmentation and ionization pathways of the photo excited system and its corresponding fragments. By employing evolutionary algorithms for optimizing phase, amplitude and polarization of the applied laser fields, the yields of the resulting parent and fragment ions could significantly be improved and significant features about the investigated system and the irradiated photochemical process could be withdrawn from the obtained optimum pulse shapes.

In recent experiments we have extracted the white light emitted from fs-plasma channels by optimally shaping the 60 fs-input pulses. This allowed us to shorten the pulse durations of the generated white light down to 6.5 fs. These white light pulses were then optimally shaped in order to maximize the yield of multi-photon charge reversal processes. The experiment opens new fascinating perspectives to perform optimally controlled white light photochemistry with phase-, amplitude- and polarization-shaped light fields in the fs-regime.

Confinement effects on the structural and adsorption properties of small molecular systemsR. A. Guirado-López¹

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We present extensive pseudo-potential density functional theory calculations dedicated to analyze the confinement effects on the structural properties and adsorption behavior of small molecular systems. We consider, as representative systems, the encapsulation of molecular nitrogen as well as of hydrated K, Cl, and H atoms on various types of spheroidal carbon fullerenes. First, we will show how with increasing the gas pressure, encapsulated N₂ molecules spontaneously aggregate within the carbon cavities forming molecular clusters of different sizes and symmetries. Interestingly, by analyzing the N—N bond length distribution we found that they correspond to the one obtained in polymeric nitrogen. We will show how the appearance of attractive interactions near the carbon inner-wall plays a fundamental role in the observed N₂ adsorption behavior. In a second part, we will analyze the influence of the confinement effects on the hydration properties of small atomic species. We will show how the encapsulation of hydrated $M+(H_2O)_n$ molecular structures ($M=K, Cl, \text{ and } H$) leads to i) dehydration events, ii) various types of reorientation transitions of the adsorbed water species that changes the structure of the hydration shells, as well as to iii) the inhibition of (the well known) diffusion process of atomic hydrogen through the surrounding water species. We believe that the previous results must be taking into account in order to better understand the transport as well as the adsorption behavior in biological systems.

Structure and Electroluminescence of CdS Nanoparticles Formed on Carbon Nanotube Surface

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Semiconducting properties CdS nanoparticles are promising for elaboration of effective converters of light to electricity, luminescent marks, and electroluminescent screens. A simple and effective method for synthesis of the hybrid material from the CdS nanoparticles (NP) on carbon nanotubes (CNTs) is proposed. CNT arrays were grown on silicon substrates using aerosol assistant chemical vapor deposition (CVD) method. The size and the shape of the CdS NP formed on CNT were found to depend on the temperature of a solution containing CdCl_2 , $(\text{NH}_2)_2\text{CS}$, and NH_3 . Electron microscopy study revealed a direct contact between CdS nanoparticles and CNT surface. X-ray photoelectron spectroscopy examination of the CdS/CNT hybrid material detected surface oxidation of the grown nanoparticles. The synthesis conditions allow preserving alignment of CNTs in the array and uniform decorating the CNTs with CdS nanoparticles. Formation of the continuous CdS/CNT interface indicates that nucleation and growth of the NP take place directly on the nanotube surface. Electroluminescent properties of synthesized materials were studied on a set-up elaborated for measurement of field electron emission characteristics. To observe electroluminescence from CdS NP deposited on the CNT cathode, surface the phosphor screen was replaced by transparent glass coated with ITO. Image luminance of individual radiation centers is more homogenous than that observed on the phosphor screen. Furthermore, the radiation centers can have different spectrum, which is independent on the applied voltage. We suggest that the luminous spots on the cathode surface correspond to individual CdS NP located in regions characterized by a high enhancement of local electric field. It is more likely that these NP are attached to the CNT tips. The difference in color of the luminescent centers could be caused by different size of CdS NP. Color spectrum corresponds to radiation in a region 400-550 nm that is related to change of CdS NP size in an interval 5-30 nm.

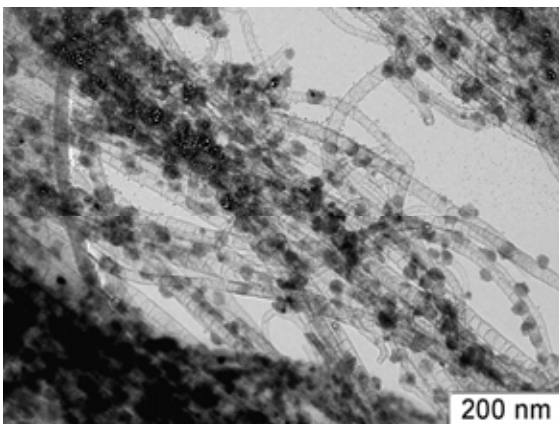


Figure 1: TEM image of nitrogen-doped CNT with CdS NP.

Models and simulations of the growth of carbon nanotubesD. Schebarchov¹, A. Awasthi², S. C. Hendy^{1,2}¹ *MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington 6140, New Zealand.*² *Industrial Research Ltd, Lower Hutt 5040, New Zealand*shaun.hendy@vuw.ac.nz

Despite almost twenty years of endeavour, it is still not possible to grow single-walled carbon nanotubes with selected chirality. Unfortunately, there are few clues from theory to guide experiments in this area, which have largely relied on a trial and error approach. The growth process is difficult to simulate computationally, due to the complex chemistry and thermodynamics involved, and the long timescales associated with growth. Furthermore, there have been few attempts to develop quantitative models that provide insight into chiral selectivity. Here we report on the development of a model that focuses on the lift-off of the carbon nanotube cap after nucleation. We test the model using atomistic molecular dynamics simulations and discuss the implications of the model for understanding growth processes that may control chirality. The modelling also provides insights into how carbon nanotubes can be used as pipettes, allowing one to fill and unfill tubes with non-wetting liquids, something which has recently been demonstrated experimentally.



Figure 1: Snapshots showing the simulated lift-off of a graphite cap from a metal nanoparticle undergoing surface fluctuations.

Surface Plasmon Coupling Effects in a GaN-based Light-emitting Diode with a Silver Nanoparticle On-top Layer

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Light-emitting diodes(LEDs) are the subject of considerable interest for a wide range of applications from displays to optical communications. Recently, high-efficiency GaN-based LEDs have gained much attention because of their importance in the white LED lighting which is expected to replace the fluorescent lamps in the near future. The efficiency of LEDs has important consequences on such applications. Several techniques are being investigated to enhance both their internal quantum efficiency and their light extraction efficiency. An approach that is attracting a lot of attention is the use of surface plasmons (SPs)[1-3].

Here we present a systemic study of the SP coupling effects on the efficiency of the GaN-based LEDs. A layer of silver nanoparticles is deposited on the top of the InGaN/GaN quantum wells(QWs). A dielectric spacer is fabricated between the QWs and the metal nanoparticle layer with different thickness. With a specially designed glancing cluster beam deposition scheme[4], gradient silver nanoparticle array strips with tunable particle sizes and number densities are generated through the graded deposition mass. Across the gradient, the surface plasmon resonance band of the nanoparticle arrays can be widely tuned, from 400nm to about 600nm. With a thinner spacer layer of about 10nm, the coupling of spontaneous emission from InGaN QWs into the SP modes of silver nanoparticle layers is investigated. A systemic change of the photoluminescence(PL) intensity with the deposition mass is directly observed. In the coupling process, excited dipole energy inside the QW is transferred into the SP modes. The radioactive emission of the semiconductor can be enhanced or suppressed, depending on the matching condition for SP radiation. Time-resolved PL measurements confirm that the recombination rate in QWs can be significantly changed due to the coupling. With a thicker dielectric spacer layer of about more than 200nm, the effect of the SPs of the silver nanoparticle arrays on the extraction efficiency of the emitted light is also investigated. A SP-enhanced light scattering mechanism is proposed. A quantitative measurement of such process is performed on an analogous system by fabricating gradient silver nanoparticle arrays on a spectro-prism surface. The result shows that the interaction of the SPs of metal nanoparticles with the evanescent field near the dielectric medium/air interface induced by the total internal reflection of the light can effectively extract the light outside the medium.

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**Imaging supported nanoclusters at atomic-scale with HAADF-STEM:
Recent Achievements and Future Prospects**

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Nanoclusters can have striking different physical and chemical properties when their size changes. To elucidate these properties and to explore their potential technological applications, one needs to know how atoms are bonded in these small aggregates as compared to the bulk. Currently, we have very limited systematic experimental data on the atomic-scale structures of nanoclusters. On the other hand, theoretical investigations have led to various structure models and predicted size-evolutionary patterns, although often with lively debates with, to date, no consensus or resolution. It is hoped that structural investigation of size-selected clusters in a systematic way will be highly useful in this regard.

Direct imaging in three-dimension of all atoms in a supported nanocluster with unknown structure is a challenging task. This is not only that there are many experimental variables involved in the processes of cluster formation, deposition and imaging, but also small clusters are intrinsically unstable. With the help of latest advancement of aberration-corrected optics in a scanning transmission electron microscopy (STEM), we have demonstrated recently that, when the number of atoms within the cluster is known, it is possible to identify their structure through ‘single shot’ technique using high-angle annular-dark field (HAADF) detector when coupled with image simulation [1].

In this talk, I will first introduce the basics behind the technique and describe some of the practicalities of nanoclusters imaging and data analyzing. I will then present a few examples of our recent advancements: counting the number of atoms in a cluster on surfaces and determining its atomic structure; using size-selected clusters to weigh nanoparticles with unknown size. Our current goal is to obtain accurate and statistically representative structure information on such clusters. To this end, we are working towards automation of identifying structures of clusters through digital image processing and analysis. Finally, I will discuss the opportunities and challenges for the use of HAADF-STEM in imaging surface-supported clusters at atomic-scale.

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Clusters on surfaces, embedded in matrices or in interaction with biomolecules

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The low energy deposition of clusters produced in the gas phase is an interesting route for synthesizing nanostructures with specific properties^[1]. We have developed a new and versatile apparatus for the deposition of size selected clusters^[2]. Firstly, this allows us to explore the auto-organization of size selected metal clusters as a function of the kind of metal and of the surface reactivity. We will compare and discuss the different behavior of gold and platinum clusters deposited on HOPG in Ultra high vacuum. For gold clusters large ramified fractal structures are observed while platinum clusters deposited in the same conditions are self-organized in a regular hexagonal pattern

Secondly, the size selected clusters may be also embedded in transparent matrices to study their optical properties as a function of the size. The production and deposition of very small nanoparticles is an issue of fundamental interest to investigate precisely the size evolution of cluster properties from the atom (or molecule) to the bulk phase and especially to highlight the transition from the regime of “quantum size effects” to the regime of the so-called “scalable size effects”. For metal clusters, this roughly corresponds to particle diameters of the order of 1 to 2 nm (typically 30 to 250 atoms). Results in this size regime will be discussed concerning the electron-lattice energy exchanges and the acoustic response^[3].

Finally complexes of small metal clusters with biomolecules can be generated in ESI source and size selected in Ion traps. This allows us to study their optical properties and the influence of the biomolecule on the absorption spectrum^[4]. The biomolecule may also stabilize small doubly charged silver clusters.

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From Superhalogens to Hyperhalogens: Unusual Properties of $Au_n(BO_2)_m$ clusters

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Charged clusters and particles play an important role in a wide variety of areas, such as building groups in inorganic salts, nucleating centers of aerosols in the atmosphere, and the acidification of ocean waters. The chemical reactivity of these anionic species is strongly dependent on the electron affinity (EA) values of their corresponding neutral counterparts. Systems possessing anomalously large EA values (larger than that of chlorine) have been predicted longtime back and are termed as “superhalogens” [1]. However, superhalogens have been so far mostly binary systems, such as metal-halides and metal-oxide clusters.

We have recently discovered unusually stable $Au_n(BO_2)_m$ clusters which formed during the oxygenation of gold clusters, when BN was used as insulation in PACIS. PES measurements and DFT calculations revealed that these ternary clusters have superhalogen properties with EA values greater than 4.5 eV [2]. In addition, we propose a mechanism to create an entirely new-class of highly electronegative species, called “*Hyperhalogens*”, whose EA values are even larger than those of the superhalogens, thus opening the door to the synthesis a new-class of materials.

In this talk, I will first discuss our results on highly stable $Au_n(BO_2)$ clusters ($n = 1-5$). Using DFT based calculations we understand the origin of the unusual stability and the superhalogen properties of these clusters. Then, I will discuss our strategy for creating the hyperhalogens and demonstrate their feasibility by presenting our recent success in generating $Au_n(BO)_m$ clusters with hyperhalogen characteristics. In conclusion, our recent efforts towards designing magnetic superhalogens will be discussed briefly.

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FRIDAY SEPTEMBER 24

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.....
Fcc supracrystals of 7 nm Co nanocrystals: a super-spin glass system

Mass Spectrometry of Atmospheric Aerosol: 1 nanometer to 1 micron

Douglas R Worsnop

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Despite much effort in the past decade, uncertainties in both climate impacts and health effects of atmospheric aerosols are still significant. This reflects both the complexity of suspended aerosols – size, composition and morphology – and the lack of fundamental understanding of many chemical and physical details of the atmospheric aerosol system, from particle formation (nanoparticles) to growth to sub-micron (fine) particles, which have the largest impact on climate – as well as human health [1]. During the last ten years, the application of mass spectrometry has enabled measurement of sub-micron chemical composition worldwide [2] and more recently the composition of atmospheric ions and cluster ions [3,4].

Most recently, the CLOUD (Cosmics Leaving Outdoor Droplets) experiment [5] at the CERN Proton Synchrotron is focused on distinguishing the chemistry of ion and neutral induced nucleation, with the goal of understanding the possible influence of cosmic rays on aerosol particles and clouds. CLOUD utilizes exceptionally clean (near UHV) experimental conditions in a 26 m³ chamber, together with the capability to simulate cosmic rays “on demand” with the synchrotron particle beam.

When a gas mixture of SO₂ and O₃ is exposed to UV light and muons/pions, producing H₂SO₄ vapor and ion concentration of a ~10⁴/cm³, the trimer cluster ion HSO₄⁻(H₂SO₄)₂ dominates observed negative ions. Nucleation and growth of nanoparticles (>2nm diameter) is coincident with appearance of larger sulfuric acid (SA) anion clusters. This is the first observation of SA cluster ion/nanoparticle nucleation and growth under controlled atmospheric pressure and temperature conditions. All larger SA cluster ions (n>4) contain one or more NH₃ molecules, despite the fact that no NH₃ was added to this “clean” chamber.

These observations are very consistent with molecular orbital calculations that indicate that NH₃ cannot add to small SA anion clusters but does stabilize larger clusters [6]. The ultimate aim of these experiments is to understand both neutral and ion-induced nucleation and to connect nanoparticle growth to the ubiquitous presence of oxygenated organic species which dominate aerosol growth and composition in much of the atmosphere [7].

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Calorimetry on free water nanoparticles

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Small-particle thermodynamics often strongly deviates from the bulk limit. Many examples in different materials have been theoretically predicted, experimentally found and interpreted. Reasons are cluster-specific geometries and electronic configurations. Furthermore, nanoparticles do not fulfill the thermodynamic limit.

The melting of ice is the most common example for phase transitions. We study this phase change experimentally on isolated, size selected ice particles. The measured caloric curves are bulk-like at low temperatures, but show well-defined, cluster-size specific transitions, which are characterized by abrupt changes of the heat capacity at temperatures less than 1/3 of the melting point of bulk ice [1].

These temperatures are close to glass transitions observed on one hand in low-density amorphous ice [2] and on the other hand in water confined in nano-pores [3]. Is our observation related? To what transforms melting or a glass transition in a small cluster? What means crystalline or amorphous in this context?

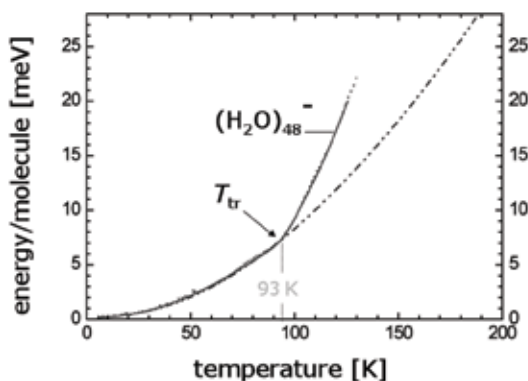


Figure 1: Dots with spline (solid line): The caloric curve of a cluster of 48 water molecules and an excess electron. The dot dashed line represents bulk ice.

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The hydrated electron in new experiments

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In water solutions the hydrated electron plays a prominent role in many fields of solution chemistry and biology such as electron transfer, biological activity and charge-induced reactivity. To elucidate the microscopic behavior of the underlying dynamics, the corresponding properties of clusters have been investigated as function of their size. These include the solvation of the valence electron of alkali metals in doped water clusters and negatively charged water cluster anions. In spite of numerous experiments in these directions some crucial questions remained open like the binding energy of the solvated electron in the liquid to which the cluster results should converge and the constant behavior of the ionization potential of $\text{Na}(\text{H}_2\text{O})_n$ clusters as function of the size in contrast to the behavior of the water clusters anions.

Here we present three different experiments which shed new light on these questions:

- 1) We measured the vertical detachment energy of the hydrated electron in liquid water for the bulk and the surface positions using extreme ultraviolet photoelectron spectroscopy in a liquid micro jet with different precursors [1]. The results of 3.3 eV and 1.6 eV allow us to verify the different extrapolation procedures and the numerous theoretical calculations.
- 2) The measurement of the ionization potential (IP) of $\text{Na}(\text{H}_2\text{O})_n$ clusters revealed a new class of isomers with a lower ionization potential of 2.8 eV for $n \geq 15$ compared to the 3.2 eV found previously for $n \geq 4$ [2]. The theoretical interpretation shows that the distance between the counterion Na^+ and the electron distribution is much larger for the lower IP indicating the existence of a solvent separated and a contact ion pair.
- 3) By means of a new double resonance technique we extended the infrared spectroscopy of completely size selected hydrogen bonded clusters to large Na doped water clusters. By measuring the OH stretch vibration we observe the direct interaction of the H-atoms of the solvent molecules with the delocalized electron distribution [3, 4]. This provides complementary information compared to the other experiments. Again the results differ from those obtained for water cluster anions.

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Electron-induced reactions in helium droplets doped with fullerene and water

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Novel molecular complexes may be grown within ultracold helium droplets. Furthermore, the unusual electronic properties of helium affect the way in which energetic electrons interact with the dopants. Here we describe reactions induced by electrons in helium droplets that are doped with C₆₀, C₇₀, or C₆₀ and water clusters.

- Electron ionization of helium droplets doped with C₆₀ and H₂O clusters primarily results in C₆₀(H₂O)_n⁺ ions, in contrast to pure water clusters that lead to protonated ions, (H₂O)_nH⁺. The autoprotonation reaction within water is suppressed by charge localization on C₆₀⁺.
- Dehydrogenated C₆₀(H₂O)_nOH⁺ ions are observed as well. They are caused by charge transfer from He⁺ to C₆₀ which may, via Penning ionization, result in doubly charged C₆₀-water complexes. Charge separation within [C₆₀(H₂O)_m]²⁺ leads to C₆₀(H₂O)_nOH⁺ + (H₂O)_{m-n-1}H⁺. We also find evidence for multi-ionization via multiple excited He* atoms within one droplet.
- C₆₀(H₂O)_n⁺ ions spontaneously shed all their water molecules if n = 3, 4 or 6. Ab-initio Hartree-Fock calculations indicate that, indeed, fission-like desorption of the entire water complex favorably competes with evaporation of a single water molecule.
- Under suitable expansion conditions many helium atoms remain attached to the fullerene ion X⁺, demonstrating its extremely low vibrational temperature. The ion series XHe_n⁺ exhibits abrupt drops in the abundance at n = 32 and 37 for C₆₀ and C₇₀, respectively. These values indicate a layer of localized helium that fills when one helium atom sits above the center of each carbon ring. C₆₀He_n⁺ shows another shell closure at n = 60, suggesting a structural transition in the helium layer such that one helium atom sits above each carbon atom.

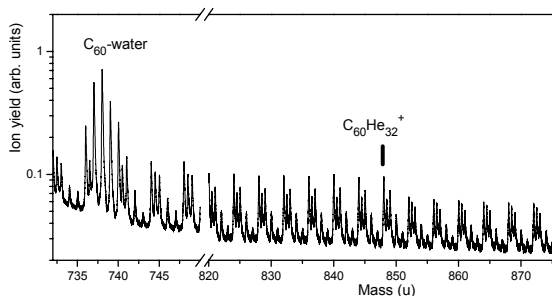


Figure 1: A mass spectrum showing several C₆₀-water complexes and shell closure at C₆₀He₃₂⁺.

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Static polarizability of Ar-AuX complexes (X = F, Hg) and Au_n clusters. DFT calculations with a non local correlation van der Waals functional compared to GGA results.

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Quantum mechanical van der Waals (vdW) dispersion forces are long-range forces arising from an induced-dipole-induced dipole term in the correlation energy. The vdW interactions between atoms and molecules play an important role in many chemical systems, whose accurate description requires expensive *ab initio* quantum chemistry methods [1]. As an alternative, the DFT problem for vdW interactions has now become a very active field of research. A promising step in this direction is the non local vdW functional of Dion et al [2]. An efficient numerical approach to that vdW functional has been implemented recently in the context of Siesta code [3]. In this work we test that vdW implementation in order to compare its performance against the usual PBE (GGA) functional [4] for the calculation of the dipole polarizability of typical van der Waals complexes (Ar-Au⁺, Ar-AuF, Ar-CuF, Au⁻-O₂), as well as mixed Au₂Hg₂ and pure gold clusters Au_n (n = 1-13, 20, 32). The basis set superposition error (BSSE) for binding energies was estimated under the geometries optimized without such corrections.

For the binding energy and bond length of Ar-Au⁺ and Au⁻-O₂ molecules our results using vdW improve largely the GGA results comparing with accurate CCSD(T) calculations in the complete-basis-set (CBS) limit [5]. Similar improvements are found for Ar-AuF and Ar-CuF molecules compared to CCSD(T) calculations in reference [1], as well as for Au-Ar [6] and Au₂Hg₂ [7]. The vdW and PBE polarizability of these molecules is also calculated, although there are not accurate quantum calculations available to compare with. Concerning the polarizability of pure gold clusters we obtain that the vdW values are larger than those obtained with GGA [8] and LDA [9] functionals, as a consequence of the larger Au-Au bond distances obtained using the vdW functional.

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Fcc supracrystals of 7 nm Co nanocrystals: a super-spin glass system

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Fcc cobalt nanocrystals of 7 nm diameter and coated with dodecanoic acid are obtained via soft chemistry route involving micellar system. These particles self-organize over a large distance when deposited on a highly oriented pyrolytic graphite (HOPG) substrate to give rise to fcc supracrystals consisting of several hundred Co layers [1]. In these artificial solids where the individual nanocrystal anisotropy is low, super-spin glass behavior is observed [2]. The dynamic behavior shows a critical slowing down and the characteristic relaxation time is found to diverge to a finite static glass temperature. The collective nature of the glass state is supported by the existence of a memory effect. By adjusting the substrate temperature during the solvent evaporation, control of the structural order of Co three-dimensional assemblies is achieved [3]. Thus, with the same particle population, we form either disordered or fcc ordered 3D assemblies. The magnetic investigations indicate that the organization of Co nanocrystals in an fcc supra-crystal induces a significant change in the magnetic response with respect to a disordered sample. Namely, we observe a narrowing of the zero field cooled (ZFC) magnetization versus temperature peak and an increase in the coercive field (H_c) for the supra-crystal compared to that of the disordered sample [4].

By annealing these supracrystals at 350°C, a phase conversion of the cobalt nanoparticles from a poorly crystallized fcc structure to a pure hcp structure is obtained [5,6]. Neither oxidation nor coalescence of the nano-material occurs. After annealing, we see a drastic increase in both the blocking temperature and magnetization arising from the higher anisotropy and crystallinity associated with the pure hcp structure.

These results are the first examples of the order influence on the physical properties of metallic nanocrystals.

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POSTER SESSION A

A-01 *Structure and thermodynamics of clusters and nanolloys*

A-02 *Clusters on surfaces*

A-03 *Carbon nanostructures*

A-04 *Nanoparticles in biology and medicine*

A-05 *Spectroscopy and dynamics with short laser pulses*

A-06 *Nanoparticles in environmental science*

A-07 *Molecular electronics and transport*

The quest for inorganic fullerenes: a progress report

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The most famous cluster C_{60} is a hollow cage and it is formed from a graphene monolayer shaped into a sphere, this is the system's way to avoid the dangling bonds at the edges of the graphene sheet. There might be other materials forming such hollow spheres. In principle, all layered bulk materials should form similar clusters for the reason to avoid the dangling bonds. We applied a method for the generation of $(MoS_2)_n^-$ and $(WS_2)_n^-$ clusters which is well known from the effective production of carbon. The mass spectra show a bimodal distribution similar to the case of carbon clusters. With this encouraging first result we started an extensive effort to reveal the structure of the clusters in the second maximum with masses up to 50000 amu. We recorded photoelectron spectra with a high photon energy (7.9eV), but the spectra show no distinct feature and do not allow an assignment to a certain structure. Furthermore, we deposited these clusters on a substrate and recorded high-resolution scanning transmission electron microscopy images (HR-STEM). These pictures can be compared to the pioneering work of Kneset et al, who identified octahedral multiwall $(MoS_2)_n^-$ clusters using STEM. However, STEM pictures recorded from our samples show no correlation with the mass spectra in the gas phase. It seems likely that the clusters are not stable on the substrate and coalesce. Further work is in progress to overcome these problems.

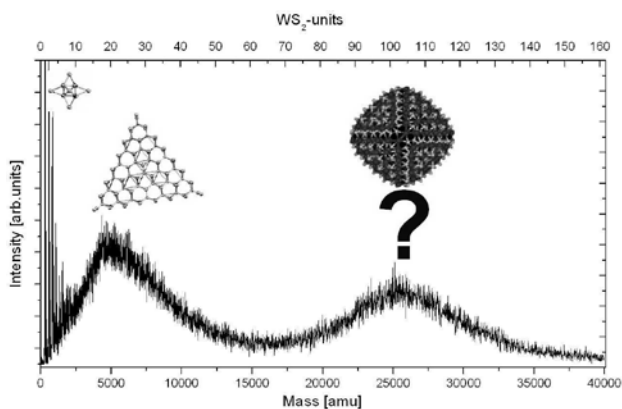


Figure 1: Bimodal mass distribution of annealed $(MoS_2)_n^-$ cluster anions.

Interaction between short alkanethiols from ab initio calculationsY. Wang¹, J. G. S. Canchaya², M. Alcamí¹, F. Martín¹, H. F. Busnengo^{2,3}¹*Departamento de Química C-13, Universidad Autónoma de Madrid, Spain*²*Instituto de Física de Rosario (CONICET-UNR), Argentina*³*Facultad de Ciencias Exactas, Ingeniería y Agrimensura, Universidad Nacional de Rosario, Argentina*

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The structural aspects and formation kinetics of self-assembled monolayers (SAMs) of alkanethiols on surfaces is of great interest due to their potential applications in areas such as corrosion prevention, wear protection and sensor devices [1]. Theoretically, a very important issue is the accurate description of long range dispersion (vdW) interactions among SAMs. Due to the well-known weakness of density functional theory (DFT) in describing vdW interactions and the infeasibility of high-level ab initio calculations for large-scale or extended (periodic) systems, it is highly demanding to develop accurate force fields to allow large-scale molecular dynamics (MD) and Monte Carlo (MC) simulations for these systems.

We present here our newly developed force field to describe the interaction of alkanethiols HS(CH₂)_n-CH₃ (C_n for short) by fitting a set of ~220 interaction energies for dimers of C_n (with n=1,2,...,6) and CH₄ molecules obtained from second-order Møller-Plesset perturbation theory (MP2) calculations. In order to validate the accuracy of the MP2 binding energies (BEs) used in the database, BEs obtained from CCSD(T) method at the complete basis set (CBS) limit were estimated for a few dimers and gave values close to the MP2 results. Also, the comparisons between the ab initio and the DFT (PW91, PBE and B3LYP functionals) methods demonstrate unsurprisingly the failure of DFT in properly describing chain-chain interactions between alkanethiols. Then by using these ab initio BEs as the input data, we performed a weighted least squares fitting to develop a force field which has the form of a sum of exp-6 pairwise potentials and effective Coulomb interaction between the HS-heads.

The developed force field predicts very well the interaction energies for dimers and trimers of alkanethiols not included in the input database for the fit. Also the calculated minimum energy tilt angle ($\theta = 32-35^\circ$) of the alkyl chains for an hexagonal arrangement of alkanethiolates with nearest neighbor distance of 5 Å is in good agreement with available experimental data for a $\sqrt{3} \times \sqrt{3}$ SAM on Au(111) [3]. Thus, the derived force field could be suitable for large-scale MD and/or MC simulations to predict structure, stability and/or kinetics of SAMs on other surfaces.

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**ON THE ELECTRONIC PROPERTIES OF THE TWO DIMENSIONAL
HONEYCOMB GaInN and GaAlN ALLOYS**^{1,A}E. Chigo-Anota, and H. Hernández Cocoltzi¹*Cuerpo Académico Ingeniería en Materiales-Facultad de Ingeniería Química
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The discovery of graphene opened the investigations on two dimensional honeycomb nanostructures. For example, in 2005 Novoselov and coworkers reported the stability of the boron nitride sheet. More studies on nitrides have been done in order to comprehend the nature and applications of this kind of systems. Main results have been obtained on binary compounds and the principal results can be found in references [1,2]. On the other hand, it is well known that bulk GaN, InN and AlN can form a set of ternary alloys which can cover all the visible of the electromagnetic spectrum. It is natural to think that something similar can be done with nitrides sheets, searching for an increase on the efficiency of the devices based on this structures. Motivated on the former reasoning, in this work we study the structural and electronic properties of the $\text{Ga}_x\text{In}_{1-x}\text{N}$ and $\text{Ga}_x\text{Al}_{1-x}\text{N}$ ternary alloys in their two dimensional honeycomb geometry. The study is done employing the Density Functional Theory; the exchanged-correlation term is treated within the GGA. The alloys are modeled with a coronene like cluster, $\text{Ga}_x\text{In}_{1-x}\text{NH}_{12}$ and $\text{Ga}_x\text{Al}_{1-x}\text{NH}_{12}$; the bond length, gap energy and dipole moment are calculated for different values of the concentration x . It is observed that the structural stability depends on the concentration in the case of the GaInN alloy; moreover, there is a decrease on the gap from GaN (3.67 eV) to InN (2.11 eV), and the biggest polarity is observed for $x=66.6\%$. For the GaAlN alloy the gap increases when the value of x increases and the biggest polarity happens for $x=33.3\%$.

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Isomer-selected dissociation of small carbon cluster cations

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Carbon cluster cations (C_n^+) have isomers such as linear, cyclic, and fullerene structures, depending on their sizes, and the isomers coexist in the size range occurring structural transition [1]. Their size-dependent reactivity of dissociation and other reactions have been suggested to be also attributed to their structural variance. In this study, we have applied ion mobility spectrometry to separate different isomers of C_n^+ generated by laser vaporization method. We measured photodissociation (PD) and collision induced dissociation (CID) reaction for $n = 7-11$, in which predominant isomer structures change from linear to cyclic ones.

We have found that fragment ion distribution is characteristic for each isomer of parent ion. Figure 1 shows fragment-ion mass spectra from linear and cyclic isomers of C_n^+ ($n = 9$ and 10) by CID. Dissociation from linear isomers of C_9^+ (a) and C_{10}^+ (c) is dominated by C_3 -loss processes. The C_3 -loss agrees well with previous results of PD [2] and CID [3] without isomer-separation. Dissociation from cyclic isomers of C_9^+ (b) and C_{10}^+ (d), on the other hand, reveals C_2 -loss processes as well as the C_3 -loss. Thus the C_2 -loss from C_9^+ can be attributed to dissociation from cyclic isomers, as well as in our previous report on PD at 355 nm [4].

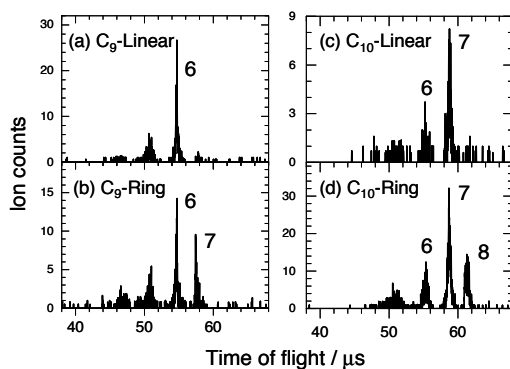


Figure 1. Fragment-ion time-of-flight spectra of C_n^+ ($n = 9$ and 10) by collision-induced dissociation. A number represents a size of fragment ion.

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Temperature dependence of ion mobility of carbon cluster cations

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Ion mobility spectrometry has been established for analysis of gas-phase ions. This method has also been applied to isomer separation of cluster ions [1–3]. Theoretical backgrounds have been developed to describe the correlations between ion mobility of cluster ions experimentally measured and their geometric structures. Ion mobility (K) is defined as eq. (1), where v_d is “drift velocity”, which is a velocity of an isomer passing through a drift-cell, and E is an electric field applied to the cell.

$$K = \frac{v_d}{E} \quad \dots (1)$$

We aim at UV photodissociation (PD) measurement of each separated isomer, and we explore a condition for the improvement of resolution of separation, keeping the intensity of separated cluster ions high enough for PD. Higher resolution of isomers requires the increase of collision frequency with He, and thus the increase of number density (N) of He in the cell. This condition is achieved by lowering cell temperature with a constant electric field. In this study, we have investigated temperature dependence of ion mobility of carbon cluster cations (C_n^+) generated by laser vaporization method. Figure 1 shows arrival time distribution for C_n^+ ($n = 7-9$) measured at three temperatures, showing increase of arrival times of each peak and thus improvement of the resolution of isomer separation.

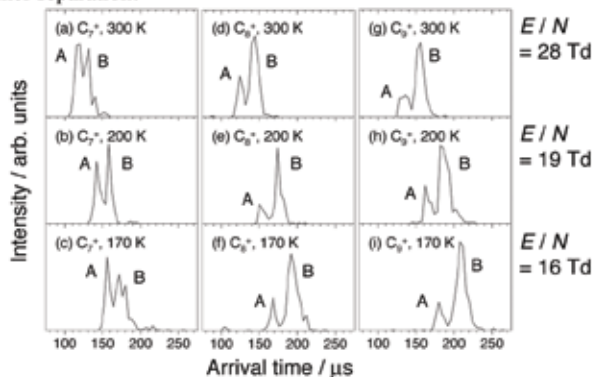


Figure 1. Arrival time distributions of C_n^+ ($n = 7-9$) measured at 300–170 K. Each spectrum shows two peaks; peak A corresponds to a mono-cyclic isomer and B corresponds to a linear isomer. The values of E/N are also presented (E/N is an important parameter for the ion mobility measurement; Td = 10^{17} V cm²).

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Isomers, polarizability and spectrum of Ga_mAs_n clusters

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Isomers of semiconductor clusters of Ga_nAs_n, Ga_{n-1}As_n and Ga_nAs_{n-1} (n= 8-12) have been carefully searched, which was based on genetic global optimization approach and gradient-corrected density functional theory. The genetic algorithm (GA) combined with an empirical Stillinger-Weber potential was used in this work. Candidate structures for each size were searched twice. For the first search, the initial atomic configurations were set up by random selections of atomic positions within a three-dimensional sphere of real space. As for the second search, the initial atomic positions were randomly selected within a spherical shell, and the structures after every mating were optimized confined in the spherical shell. The lowest-energy structures of these cluster isomers were finally obtained and their stability were investigated. Our results showed that the lowest-energy structures for each size cluster were mainly cage structures or fullerene-like structures. The stoichiometric lowest-energy structures were compared to the previous work and our lowest-energy structure for Ga₁₀As₁₀ was energetically preferred over that in Ref. 1 by 0.21 eV.

The electronic properties of the lowest-energy structures among the Ga_nAs_n, Ga_{n-1}As_n and Ga_nAs_{n-1} cluster were investigated and compared. The static dipole moment, polarizability, IR and Raman spectra for above clusters were further calculated with a hybrid density functional theory. The calculation results were approximately consistent with the experimental data [2], and the difference between the theoretical and experimental results were discussed.

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Understanding the superheating of gallium clustersN. Gaston¹, A. J. Parker², K. G. Steenbergen²¹ *MacDiarmid Institute for Advanced Materials and Nanotechnology,
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The experimental discovery of superheating in gallium clusters [1] contradicted the clear and well-demonstrated paradigm that the melting temperature of a particle should decrease with its size [2]. However the extremely sensitive dependence of melting temperature on size also goes to the heart of cluster science, and the interplay between the effects of electronic and geometric structure [3]. In the case of gallium, the extreme polymorphism displayed by the bulk metal introduces additional complications. We use our understanding of the dimeric bulk structure of gallium to elucidate the patterns of bonding in the clusters, which also display dimeric structural motifs for small sizes. In particular, the extremely general linear relationship of melting temperature and cohesive energy for elemental solids (cf. Fig. 1) demonstrates that the low melting temperature of gallium corresponds to the melting of a molecular solid. We explore the nature of both inter- and intra-molecular bonding of the Ga₂ dimer and relate this to structures of the small clusters, and their melting behaviour. We also examine the effect of charge on the cluster structures.

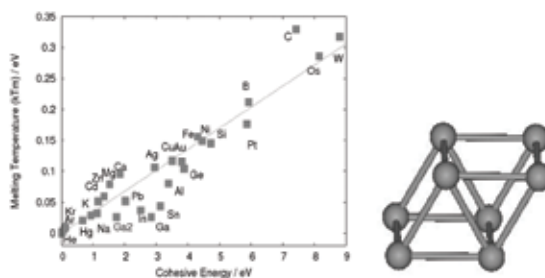


Figure 1: Left: the linear relationship between melting temperature and cohesive energy for the elemental solids, Right: Ga₈.

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Study of 40-atom Pt-Au clusters using a combined empirical potential-density functional approachD. T. Tran¹, R. L. Johnston²¹*School of Metallurgy and Materials, University of Birmingham, UK*²*School of Chemistry, University of Birmingham, UK**r.l.johnston@bham.ac.uk*

This work is a theoretical study of 40-atom Pt-Au clusters which are interesting due to the electronic shell closure of 40-atom noble metal clusters and the current focus on bimetallic clusters containing Pt as catalysts in fuel cells. Here, low-lying energy structures are found using a genetic algorithm [1] with the Gupta many-body empirical potential [2] and then high-accuracy DFT geometrical reoptimizations are carried out using NWChem 5.1 [3], as well as calculations of electronic energy gaps, and Mulliken charge distributions. Structures based on truncated-octahedral (TO), Mackay-icosahedral, decahedral and 5-fold pancake geometries are found to be energetically favored for different composition regions at the empirical-potential level and this is partially confirmed at the DFT level. The HOMO-LUMO gaps calculated in this work are generally sensitive to cluster geometry: high symmetry structures generally exhibit relatively large gaps, while low-symmetry structures present small gaps. Segregation tendencies, including Pt@Au core-shell and phase separation, are observed at both empirical-potential and DFT levels as the most stable chemical configurations.

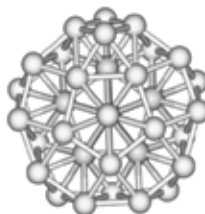


Figure 1: DFT-reoptimized incomplete Mackay-icosahedral structure of Pt₇Au₃₃.

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The effect of potential parameterisation on the structures and chemical ordering of bimetallic nanoclusters

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The semi-empirical many-body Gupta potential has been finely tuned by modifying the bimetallic potential parameters (A , ξ , p , q and r_0). The effect on different type of metals (p -block, and 1st-3rd row transition metals) have been studied using a genetic algorithm global optimization technique. Observation of the energetics, structures and segregation show that the heteronuclear bonding in the bimetallic clusters studied (Palladium-Platinum, Palladium-Gold, Nickel-Aluminium) are strongly dependent on the potential parameters. Specific parameterisations can produce very similar results to those obtained using higher levels of theory (e.g. Density Functional Theory). Structural analysis shows competition between several structural families and this study allowed us to identify five main types of chemical ordering: core-shell, spherical cap, ball-and-cup (intermediate between the first two types), onion-like and mixed.

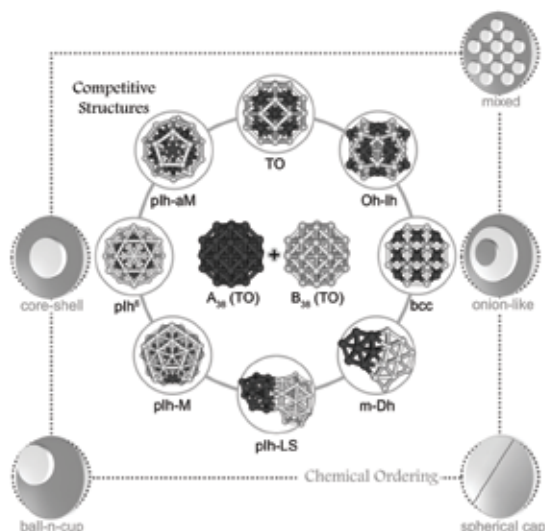


Figure 1: (Inner) Global Minimum structure variation of 38-atom clusters found for PdAu, PdPt and NiAl nanoclusters. (Outer) Five main types of chemical ordering that have been observed.

Size-controlled alloy nanoclusters and their influence on carbon nanotube synthesisD. Belić^{1,5}, K. Edgar^{2,5}, S. C. Hendy^{3,5}, V. B. Golovko^{4,5}, N. J. Ke^{4,5}, S. A. Brown^{1,5}¹ Department of Physics and Astronomy, University of Canterbury, New Zealand² School of Chemical and Physical Sciences, Victoria University of Wellington, New Zealand³ Industrial Research Limited, Lower Hutt, New Zealand⁴ Department of Chemistry, University of Canterbury, New Zealand⁵ MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

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To date alloy nanoclusters have been investigated mainly by computational modeling (e.g. see [1] and references therein) and the relatively rare experimental papers have focused on chemically synthesized nanoclusters. Here we report on using a different approach – AgAu, NiCu, and FeCr nanoclusters have been fabricated from alloy sputter targets by means of inert gas aggregation, using an ultra-high vacuum sputtering system [2]. In addition, it has been predicted [3] that, when used as catalysts in CNT growth, nanoclusters could play an important role in determining the properties of the CNTs, which would be highly advantageous. In order to study this, samples of different cluster sizes and shapes have been produced by varying the experimental parameters - aggregation length, Ar/He ratio in the inert gas mixture, plasma generator power, and inert gas flow. The clusters have been characterized *in situ* by mass spectrometry [4] and *ex situ* by SEM, TEM, EDX, EELS, and synchrotron XPS. We have produced faceted 3-10 nm clusters with composition very similar to the one of the starting alloy targets. In the case of AgAu clusters there is an indication of a surprising phase separation. Furthermore, alloy nanoclusters have successfully been used to grow CNT(F)s. The results suggest the production yield and outer CNT(F) diameter are correlated with the type and diameter of the nanoclusters used as catalysts.

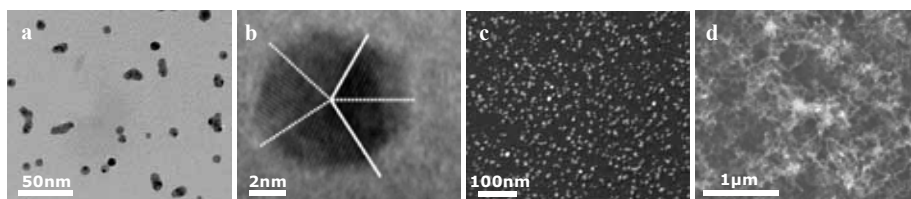


Figure 1: (a) TEM micrograph of 8 nm AgAu clusters and (b) HRTEM micrograph of the same sample: clusters appear to be of a fivefold symmetry with the inner contrast indicating a phase separation. (c) SEM image of 6 nm NiCu clusters deposited onto SiN_x substrate; this sample was later used for CNT(F) synthesis with the results presented on (d).

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**How Does a Nanocrystal Grow?
Shape and Structural Evolution of Metallic Nanoparticles**

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Shape and structure of metallic nanoparticles (NPs) has been one of the subjects of major and intense research in nanostructured materials science, because besides multiple applications that NPs have nowadays in fields such as nanocatalysis, photocatalysis, biomedicine, etc., there still persist fundamental questions that their answer would have impact in the applications. For example, the knowledge of how does electromagnetic radiation is influenced by the shapenot only by the sizeof the nanoparticles is crucial in current biomedical applications.

Thus, inquiries such as why NPs tend to adopt non-crystallographic symmetries in the small size range, or the more intriguing aspect of why there are observed NPs with so called prohibited symmetries, *i.e.*, fivefold symmetry in the size-range of hundreds of nanometers; or how different is the structural phase diagram of, say Au vs. other metal?, and ultimately the fundamental question of how does a crystal grow? are questions that keep nanoparticle research scientists (physical-chemists, computational physicists, etc.) into a continuous search for answers.

In this work we face such problem and present structural and energy stability results for metallic (Au & Ag) nanoparticles from the small (1-2 nm) to the big (\approx 45 nm) size-ranges. We have found that among factors like structural defects (kinks and twins), truncations and strain energy accumulation; at some given clusters sizes the energy strain release due to surface reconstruction is one of the principal factors that influences the growth of metallic NPs with still non-crystallographic symmetries beyond expected nanocrystal sizes. We have identified also structural transitions as a function of the cluster size; an outline for a grow path transformation from the regular tetrahedra (T_h) to the decahedral (D_h) to the icosahedral (I_h) symmetry structures, as well as experimental evidence of this grow path, and particular decahedral motifs in metallic nanoparticles is also presented.

Acknowledgements: Financial support from IPICYT is acknowledged, as well as grants for the use of high performance computational resources from the supercomputer centers CNS-IPICYT, and the TACC-UTexas, at Austin, Tx, USA.

Metal Cluster Structures and Properties from Born-Oppenheimer Molecular Dynamics

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Density functional theory (DFT) Born-Oppenheimer molecular dynamics (BOMD) simulations of metal clusters are presented. The calculations have been performed with the deMon2k [1] code employing all-electron basis sets and local and non-local functionals. The capability of reasonable long (~ 100 ps) first-principle BOMD simulations to explore potential energy landscape of metallic clusters will be presented [2-4]. The evolution of the cluster structures and properties such as minima, transition states, polarizability and heat capacity, at different temperatures, will be discussed.

[1] A.M. Köster, P. Calaminici, M.E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J. Martin del Campo, S. Patchkovskii, J.U. Reveles, A. Vela and D.R. Salahub, deMon2k, The deMon Developers, Cinvestav, 2006; [2] G.U. Gamboa, P. Calaminici, G. Geudtner, A.M. Köster, *J. Phys. Chem. A*, **112**, 11969 (2008); [3] J.M. Vásquez-Pérez, G.U. Gamboa-Martínez, A.M. Köster, P. Calaminici, **131**, 124126 (2009); [4] P. Calaminici, J.M. Vásquez-Pérez, A.M. Köster, to be submitted.

Temperature dependence of optical absorption spectrum of the silver dimer ion measured by photodissociation and photon-trap spectroscopy

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Optical absorption spectra of clusters provide experimental evidence indispensable for elucidation of their electronic structures and properties. We have developed a high-sensitivity technique for spectroscopy of size-selected free cluster ions employing a linear RF ion trap [1,2]. The ion trap is cooled by liquid helium to suppress metastable isomers by reducing internal energies of the clusters via buffer-gas cooling. However, it is not trivial to know the temperature of the clusters from that of the gas cell of the trap. This study presents an attempt to evaluate the cluster temperature from its absorption spectrum.

Figure 1 shows absorption spectra of the silver dimer cation, Ag_2^+ , measured by photodissociation spectroscopy. The spectra exhibited pronounced temperature dependence. At room temperature, the spectra showed a long tail extending more than 0.2 eV towards the low-energy side. The spectrum became significantly sharper when the ion trap was cooled to reach the buffer-gas-cell temperature, T_{cell} , of 10 K, although a vibrational progression is still to be resolved. We simulated these spectra on the basis of the simplest model assuming harmonic potentials for both the ground and the excited electronic states. For the ground state, the vibrational frequency and the bond length are calculated to be 128.2 cm^{-1} and 2.850 \AA , respectively [3]. The parameters for the excited state were found by our spectrum simulation to be 75 cm^{-1} and 3.35 \AA , respectively, which reproduced the experiment reasonably well but not perfectly; more sophisticated analysis based on realistic potentials is certainly needed. The simulated spectra are superimposed in Fig. 1 for cluster-ion temperatures, T_{ion} , of 10, 100, and 300 K. It is concluded that T_{ion} is less than 100 K for $T_{\text{cell}} = 10 \text{ K}$. We could draw only the upper bound because the spectrum was insensitive to the temperature below $T_{\text{ion}} = 100 \text{ K}$. A spectrum of light extinction measured directly by photon-trap spectroscopy will be reported as well.

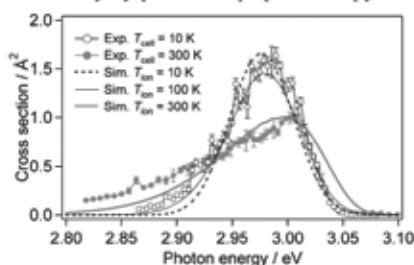


Figure 1: Photodissociation spectra of Ag_2^+ at buffer-gas cell temperature of 10 K (open circles) and 300 K (solid circles) as well as simulated ones assuming internal temperatures of 10 K (broken line), 100 K (thin line), and 300 K (thick line).

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Spatial ordering in multiple element nanostructuresJ.M. Montejano-Carrizales¹, F. Aguilera-Granja¹, J.L. Morán-López²¹ *Instituto de Física, Universidad Autónoma de San Luis Potosí, México*² *Facultad de Ciencias, Universidad Nacional Autónoma de México, México**jmmc@ifisica.uaslp.mx*

The determining factor for the physicochemical properties of multiple element clusters is the chemical ordering within the structure. Here we report a study the total number of different configurations for binary clusters with $N=13$ atoms using a direct enumeration technique. For our study, we consider the ground state geometrical structure of 13-atom pure transition metal clusters (Fe, Co, Ni, Ru, Rh, Pd and Pt) as obtained within the SIESTA code with in the GGA approximation, including exchange and correlation. In this report, we assume that the geometrical structure is preserved, independent of the chemical composition. We considered all the possible pair distribution that in the cluster for all the neighbors in the system. This characterization is necessary to calculate any physical property of the nanosystem. We also, present some preliminary results for ternary alloys with icosahedral geometry.

On the geometrical characteristics of stellated and tentacled clusters

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Cubo-octahedral and icosahedral cluster symmetries are well known in the theory of clusters, and have been already used as cores of stellated structures for modelling star-like gold nanoparticles imaging results (SEM, TEM, and HRTEM) reported recently[1]. In this work we present a detailed geometrical description of how these structures and their main basic units are used in the cluster modelling of these star-like gold nanoparticles. We also present a geometrical description of similar structures that are used for modelling other novel tentacled nanoparticles non-reported yet. Defects such as stacking faults, twinings, and other crystal defects are also enhanced in such description. By using energy minimization by the steepest descent method and the Gupta potential model, results on the structural stability competition for the stellated, non-stellated, and tentacled structures are also presented and discussed.

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Identifying Cluster Geometries from HAADF-STEM Images: A Kinematic Model coupled with Structural SearchesA. J. Logsdail¹, D. S. He², D. Pearmain², Z. Y. Li², R. E. Palmer², R. L. Johnston¹¹ *School of Chemistry, University of Birmingham, UK*² *School of Physics and Astronomy, University of Birmingham, UK**ajl340@bham.ac.uk*

Clusters are of continuing scientific interest due to their unique properties when compared to those of bulk structures. A good example is the differing catalytic properties witnessed due to changes in cluster structure. Scanning transmission electron microscopy (STEM) is an important technique for defining cluster structural characteristics, but it is still difficult to attain high resolution images. However, use of aberration corrected STEM with a high-angle annular-dark field (HAADF) detector has demonstrated that it is possible to achieve atomic resolution. Recent work has shown that HAADF-STEM images of size-selected structures can be rationalised using a simple kinematic model for Au₃₀₉ clusters [1].

In this work we review the development of a kinematic model for simulating HAADF-STEM images, and its use in identifying structures. After the creation of minimised theoretical structures from idealised high-symmetry coordinates, and also genetic algorithm searches for low-symmetry alternatives [2], the kinematic model is coupled with search algorithms in order to automate the comparison of experimental and simulated STEM images; the overall goal being to couple accuracy with computation efficiency. Experimental images of Au₈₈₇ and Pd₈₈₇ clusters are used to demonstrate current progress.

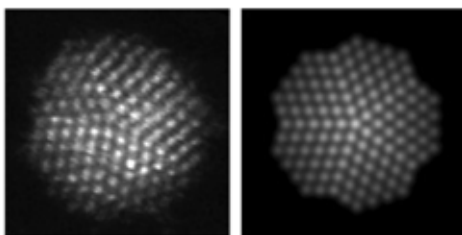


Figure 1: Experimental (left) and simulated (right) HAADF-STEM images of Au₈₈₇.

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Microhydration of methylene blue cations in an electrospray ion source

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Dye molecules are well suitable probes for studying solvent effects on the molecular structures and electronic states, through photoabsorption spectra observed in the visible region. To investigate microscopic hydration structure of molecular ions, we have measured mass spectra of hydrated methylene blue cations, $\text{MB}^+(\text{H}_2\text{O})_n$, at different ion source temperatures.

Molecular ions were produced by electrospray ionization of MB dissolved in a water-acetonitrile mixture (3:7) with 0.5 mM. The ions were introduced into a vacuum chamber through a temperature controlled heated capillary. The capillary temperature, T_{cap} , was varied in the range between 25 and 80°C. Extracted ions were mass selected with a quadrupole mass spectrometer, and detected by an electron multiplier (Ceratron).

A typical mass spectrum observed at $T_{\text{cap}} = 25^\circ\text{C}$ is shown in Fig. 1. A series of peaks of $\text{MB}^+(\text{H}_2\text{O})_n$ ions is observed up to $n \sim 60$. With increasing temperature, the average number of hydrated molecules decreases monotonously. Hydrated ions almost disappear at $T_{\text{cap}} = 80^\circ\text{C}$. Two distinctive features were found in the mass spectra. First, the series of hydrated ions started at $n = 4$; intensities of $n = 1-3$ are extremely suppressed. Second, a magic peak at $n = 24$ is observed clearly. It is well-known that a $(\text{H}_2\text{O})_{20}$ cluster has a pentagonal dodecahedral cage structure. Thus, these results imply that the $\text{MB}^+(\text{H}_2\text{O})_{24}$ ion is formed by attachment of a neutral $(\text{H}_2\text{O})_{20}$ cage to a $\text{MB}^+(\text{H}_2\text{O})_4$ ion with a rigid stable structure.

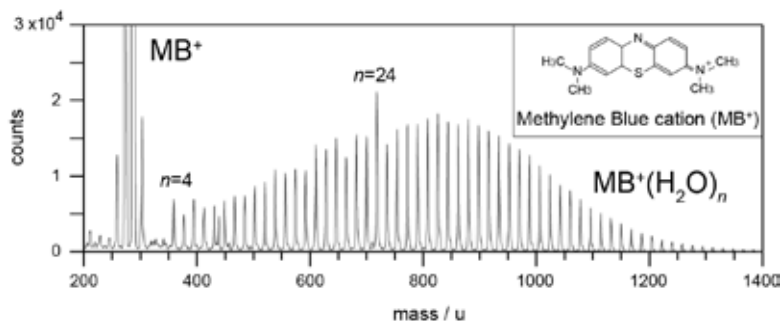


Figure 1: Mass spectrum of hydrated methylene blue cations at $T_{\text{cap}} = 25^\circ\text{C}$.

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Electron detachment of gold cluster anions in an electrostatic ring

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The recent development of ion storage techniques allows us to access slow reactions of ions with the rate constants down to the order of 10^{-1} s^{-1} . In the present study, we have generated hot Au cluster anions and stored them in an electrostatic ring (TMU E-ring [1]) to observe electron detachment reactions. The anions produced in a Cs sputter source were injected to the ring with the energy of 20 keV and were mass-selected in the ring applying the high-voltage kick-out pulses [2]. Neutral particles produced by the auto-detachment and collision-induced reactions were detected with microchannel plates. A typical time spectrum of the neutral-particle yield during storage of Au_2^- is shown in Fig.1, where the fast non-exponential decay is due to auto-detachment and the slow exponential decay is collisional. The non-exponential decay is well fitted by the $1/t$ curve as reported for Cu_2^- and Ag_2^- [3].

Although the Cs sputter source is useful for generating small cluster anions such as Au_2^- and Au_3^- , generation of larger cluster anions is needed to study how the decay depends on the electronic shell structure of clusters. For this purpose, a laser ablation ion source was employed without using cooling gases. The ablation targets were prepared from colloidal gold solutions [4], and irradiated by the 4th harmonic of pulsed Nd:YAG laser (266 nm). A time-of-flight mass spectrum is shown in Fig.2. The peaks of cluster anions up to Au_{13}^- are identified, of which even-odd alternation is attributed to the electronic shell effect. Storage experiments of anions formed in the laser ablation source is now underway.

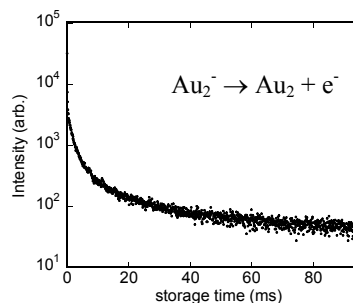


Fig.1 Time spectrum of neutral particles produced from stored Au_2^- .

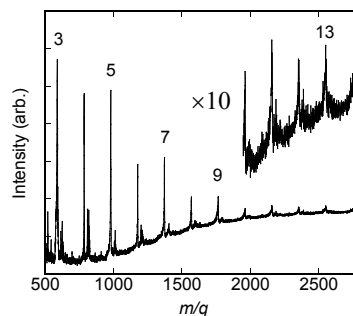


Fig.2 Mass spectrum of anions produced in laser ablation source.

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Isomer Identification and Resolution in Gold Clusters

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A variety of experimental techniques have been used to resolve energetically-close isomers of Au_n^- ($n = 7-15$) by combining photoelectron spectroscopy and *ab initio* calculations. New structurally distinct isomers are confirmed to exist in the cluster beam for a number of these clusters. Populations of the different isomers in the cluster beam are probed using Ar-tagging, O_2 -titration, and isoelectronic atom-substitution by Cu and Ag. The latter is found to be particularly effective in identifying isomers because photoelectron spectra of MAu_n^- are observed to be similar to those of the bare gold cluster Au_{n+1}^- , i.e., substitution of a Au atom by a Ag or Cu atom does not significantly alter the geometric and electronic structures of the clusters in most cases. New low-lying isomers have been observed for Au_7^- , Au_9^- , Au_{10}^- , Au_{11}^- , Au_{13}^- , and Au_{15}^- . The new isomer for Au_7^- consists of a triangular Au_6 unit with a dangling Au atom (Fig. 1). A low-lying isomer was known for Au_8^- before. Using O_2 -titration, we obtained isomer-specific photoelectron spectra of Au_8^- . Three low-lying isomers are identified for Au_{10}^- , whereas one minor isomer is observed each for Au_{11}^- , Au_{13}^- , and Au_{15}^- . The global minimum of Au_{15}^- is a 4-layer structure, which is different from that reported previously. The global minimum and low-lying structures of Au_{n+1}^- and MAu_n^- ($n = 6-14$; $M = \text{Ag}, \text{Cu}$) are obtained through basin-hopping global minimum searches. The results demonstrate that the combination of well-designed photoelectron spectroscopy experiments (including Ar-tagging, O_2 -titration, and isoelectronic substitution) and *ab initio* calculation is not only powerful for obtaining the electronic and atomic structures of size-selected clusters, but also valuable in resolving structurally- and energetically-close isomers of nanoclusters.

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J. Chem. Phys. **132** 054305 (2010)

[2] Lei-Ming Wang, Rhitankar Pal, Wei Huang, Xiao Cheng Zeng, and Lai-Sheng Wang
J. Chem. Phys. **132**, 114306 (2010)

[3] Rhitankar Pal, Lei-Ming Wang, Wei Huang, Lai-Sheng Wang and Xiao Cheng Zeng
manuscript in preparation.

Ionization potentials and structures of lithium stabilized silicon and germanium clusters

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There is evidence that germanium and silicon agglomerates are composed of stable building blocks with six to eleven atoms. These building blocks are dianionic deltahedra, reminiscent of borane and carborane, which follow Wade's rules. The units can be stacked, functionalized with organo-metallic groups, or doped with interstitial atoms to tailor the chemical and physical properties of what can be conceived as promising nanomaterials.

We report on a combined experimental and theoretical study of the structures, stability, and ionization potentials of Si_nLi_m and Ge_nLi_m ($n=5-12$ and $m=1-5$). Mass spectrometry experiments show a strong stabilization upon lithium doping. Mass spectra for doped silicon and doped germanium reveal a striking similarity with enhanced abundances for particular sizes that relate to the building blocks of larger agglomerates. The structures of those stable sizes are studied with density function theory. It is shown that Ge_9 building blocks are stabilized by lithium doping [1] and that lithium has a dual role. It can either be a simple charge donor, e.g., as capping atom, or can take substitutional positions in the cluster frame. Additional information is obtained from threshold photoionization efficiency curves measured in the 4.68 – 6.24 eV range. The deduced adiabatic and vertical ionization potentials are compared with theoretical values and allow for assignment of specific isomers.



Figure 1: The structures of the 8-atom clusters S_7Li_1 , S_6Li_2 , and S_5Li_3 ($S = Si, Ge$), which are pentagonal bipyramids that are charge balanced by a single capping Li atom. The other Li atoms (light spheres) take substitutional positions in the S_7 frame.

Acknowledgments - This research is supported by the Research Foundation – Flanders (FWO) as well as by the Belgian Interuniversity Attraction Poles (IAP) and the Flemish Concerted Action (GOA) research programs.

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Electronic Properties and Structures of $\text{Ni}_5\text{Nb}_3\text{Zr}_5$ Clusters as a Local Structural Unit of Ni-Nb-Zr Ternary Glassy Alloys

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Ternary glassy alloys $(\text{Ni}_{0.6}\text{Nb}_{0.4})_{100-x}\text{Zr}_x$ ($x=30-45$) storing hydrogen atoms exhibit remarkable properties, the superconductivity and the quantum coulomb oscillations.[1] Oji *et al.* investigated the local atomic configuration of the Ni-Nb-Zr alloys with/without hydrogen atoms by XAFS methods and proposed a distorted icosahedral cluster, $\text{Ni}_5\text{Nb}_3\text{Zr}_5$ as a unit of the glassy alloys.[2]

In the present paper, we calculate electronic states of various $\text{Ni}_5\text{Nb}_3\text{Zr}_5$ clusters and those interpenetrated, and optimize the atomic structures of them by the first principles calculation with the GGA scheme. We discuss the local structures of the $\text{Ni}_{36}\text{Nb}_{24}\text{Zr}_{40}$ glassy alloys, and construct the medium range structure consisting of the clusters.

Figure 1 shows results of the total energy calculation for various $\text{Ni}_5\text{Nb}_3\text{Zr}_5$ clusters classified by their center atoms: (a) Ni-centered, (b) Nb-centered and (c) Zr-centered clusters. The results indicate that the Ni-centered clusters are generally stable more than the Nb- and Zr-centered clusters. Figure 1 is also shown as the function of Nb-Ni coordination number (CN). The CN-dependence of the total energy, especially for Ni-centered clusters, suggests that a Nb atom surrounded Ni atoms is energetically unfavorable, and agrees with the experimental estimation of the CN, 0.9 that is interestingly very small value.

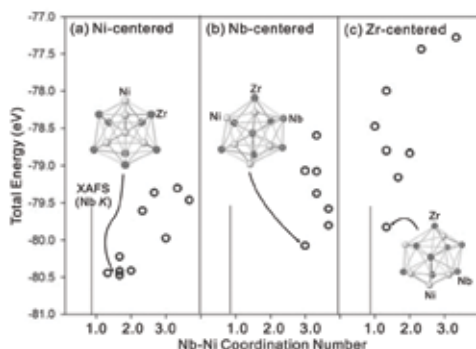


Figure 1: Total energies of various $\text{Ni}_5\text{Nb}_3\text{Zr}_5$ clusters as a function of Nb-Ni coordination number for (a) Ni-centered, (b) Nb-centered and (c) Zr-centered clusters.

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Structural and vibrational properties of gold nanorods

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In recent years we have seen tremendous progress in the study of gold nanorods (GNR) because of their possible applications in cancer diagnostics and therapeutics [1], data storage [2], etc. The GNR of major interest in applications have an aspect ratio (AR) in the range 3-7. Several research groups have reported plasmonic properties of these GNR [3], but not yet the vibrational spectrum.

In this work, we present a structural and vibrational analysis of several gold nanorods with tens to hundreds of atoms and with different ARs. A Gupta n-body potential was used to model the metallic bonding in the GNR. The molecular-dynamics method combined with the simulated quenching technique was used to perform the cluster structure optimization. The analysis of the vibrational density of states (VDOS) was made for all the structures studied.

Our results show that the GNR structures stabilized in compact structures with low aspect ratio, and in most cases the low symmetry structures are energetically more stable. The calculated distribution of normal frequencies for GNR with high AR, display a gap between highest energetic transverse vibrational modes and the less energetic transverse and longitudinal modes. Also, we found that increasing the AR, of a given structure, does not produce more energetic vibrational modes, but creates longitudinal modes with small energy.

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Reactions of small noble metal clusters with CO and N₂O: Implications for selective CO oxidation

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The adsorption of CO, N₂O and mixtures thereof on small pure and binary silver-gold cluster cations was investigated in a temperature variable octopole ion trap experiment under multiple collision conditions. The carbon monoxide adsorption showed size and composition dependent trends concerning the saturation coverage at low temperatures. The evaluation of gas phase reaction kinetics and equilibrium thermodynamics permitted the determination of quantitative CO binding energy data [1,2].

N₂O molecules were found to only weakly interact with silver and gold cluster cations. Molecular adsorption of N₂O was found for the case of Ag₃⁺ below 200 K. At higher temperatures, reaction products could be observed which indicated the immediate dissociation of N₂O on the silver clusters upon adsorption. Reaction kinetics measurements showed that the initially formed cluster oxides were transformed into Ag₃O_x(N₂O₂)_y⁺ (x, y = 1-3, x ≥ y) complexes with time.

When mixtures of N₂O and CO gases were present in the trap, the formation of CO₂ was observed for both silver and gold cluster cations. However, whereas product mass spectra and reaction kinetics measurements indicated the metal clusters to be the catalytically active centers in the case of gold, for silver the pre-oxidation of the metal clusters appeared to play a decisive role in the CO oxidation catalysis.

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The geometric structure of metal doped silicon clusters

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A major issue in current atomic cluster science constitutes the possible existence of highly symmetric species which can be used as building blocks for nanotechnological applications. Several theoretical studies indicated the existence of metal-encapsulated silicon cages. In part, these predictions have been experimentally verified by reactivity experiments, photoelectron spectroscopy, photodissociation studies, and recently also X-ray spectroscopy.

Vibrational transitions provide a characteristic finger print of the geometric structure. Infrared spectra of gas-phase clusters can be measured by combining the messenger atom technique with infrared multiple photon dissociation (IRMPD). We report on IRMPD spectra of small vanadium, manganese, and copper doped silicon clusters ($\text{Si}_N\text{X}^{+,0}$, $X = \text{V}, \text{Mn}, \text{Cu}$, $N < 20$) using noble gas atoms (Ar and Xe) as a messenger. The experiments are carried out at the Free Electron Laser for Infrared eXperiments (FELIX) of the FOM – Institute Rijnhuizen in Nieuwegein, the Netherlands. Based on the combination of mass spectrometric observations and density functional theory, experimental evidence is provided for the transition between small exohedrally doped [1] to highly symmetric caged silicon structures.

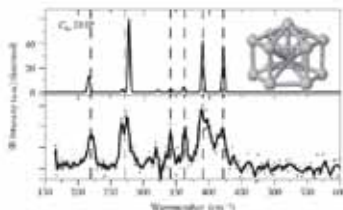


Figure 1: Lower trace: experimental IRMPD spectrum of $\text{Si}_{13}\text{V}^+\text{Xe}$. Upper trace: vibrational spectrum of the best fitting isomer calculated with DFT [2].

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Stability and structure of small mixed water ammonia clustersA. E. K. Sundén¹, K. Stöckel², P. Hvelplund², B. Dynefors³, K. Hansen¹¹ *Department of Physics, University of Gothenburg, Sweden*² *Department of Physics and Astronomy, Aarhus University, Denmark*³ *Department of Physics, Chalmers University of Technology, Sweden**erika.sunden@physics.gu.se*

Clusters containing water mixed with other molecules or atoms are of great interest because of their relevance to biological systems, in atmospheric processes, as well as model systems for studying intermolecular hydrogen bonding [1]. The solvation of ammonia in water is of particular interest because of its ability to form hydrogen bonds and its presence in the atmosphere. We have studied the spontaneous evaporation from small mixed water ammonia clusters with various ammonia concentration, $H^+(H_2O)_n(NH_3)_m$.

Experimentally, clusters are produced via high voltage corona discharge from a scanning tunneling microscopy needle in a gas containing a mixture of air, water and ammonia vapor. The clusters are drawn into vacuum through a capillary. After initial acceleration and focusing, the cluster ion beam is accelerated to 50 keV and thereafter mass selected in an electromagnet. After a free flight of 3.4 m, the clusters are analyzed according to kinetic energy using a hemispherical electrostatic analyzer and detected with a single particle detector [2]. Loss of molecules lead to a decrease in kinetic energy proportional to the mass lost, allowing identification of the evaporation channel.

The measurements on spontaneous evaporation from mixed water ammonia clusters show that in most combinations, the probability of losing a water molecule is much higher than the probability of losing an ammonia molecule, except when the clusters contain six or more ammonia molecules. In this case the probability of losing an ammonia molecule goes from basically unity for small sizes down to about one half when the total number of molecules in the cluster exceeds 11. Possible reasons for these observations will be discussed.

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Magic Stoichiometry of Ta-containing Tri-Metallic Small Clusters

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In a field of metallurgy, the Hume-Rothery rules suggest that the alloy is formed, if the metallic radius, electro-negativity and valency of the elements are similar and the crystal structure of the bulk metal is shared by the two elements. However, for sub-nano sized metal particles which are composed of several atoms, it is not known whether the different metal atoms coalesce or segregate in a cluster.

It is known that Ta_4^+ is one of the most stable cluster ions in Ta_n^+ . In previous study, bi-metallic cluster ions of Ta and other transition metal elements, M, was produced in the gas phase by a multiple laser ablation technique, and the abundance of $Ta_nM_m^+$ was measured [1]. It was found that Nb, Mo and W (group A) readily form stable $Ta_nM_m^+$ ($n+m=4$, $n \geq 1$), whereas Ag, Al, Au, Co, Cu, Fe, Hf, Ni, Pt, Ti, and V (group B) tend to form $Ta_nM_m^+$ ($m=0$, 1, 2, 3, ...). In this study, we examined if the rules proposed in the previous study hold for the tri-metallic clusters of different combinations, such as group A&A, A&B, and B&B.

Figure 1 shows the abundance distributions of $Ta_nNb_mW_k^+$, $Ta_nNb_mAl_k^+$ and $Ta_nV_mAl_k^+$ clusters. Magic stoichiometry of $Ta_nNb_mW_k^+$ with $n+m+k=4$ and $Ta_nNb_mAl_k^+$ with $n+m=4$ were found (diagonal dotted lines). Formation of stable magic stoichiometry suggests that a group A atom is able to replace the Ta atom in Ta_4^+ , holding its stability. In contrast, gradual decrease of the abundance suggests that a group B atom tends to sit outside of the stable Ta_4^+ structure. This difference between group A and B elements is likely to relate to the fact that the binding energy of the atoms of the group B elements is much lower than that of the group A (Nb, Ta, Mo and W; refractory metals).

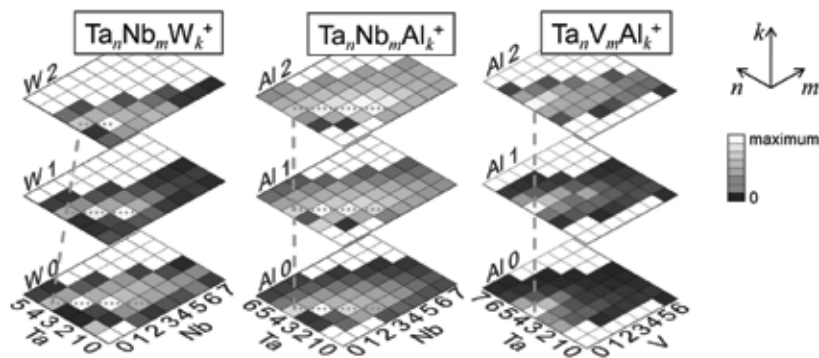


Figure 1: Maps of abundance distribution of $Ta_nNb_mW_k^+$, $Ta_nNb_mAl_k^+$ and $Ta_nV_mAl_k^+$ clusters. Cells for abundant clusters are shown in light color. Broken lines indicate the position of magic stoichiometry.

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The Nanostructure of Complex Pb Clusters Probed by X-Ray Photoemission Spectroscopy

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Understanding the role of metal clusters in complex nanophase systems is a key issue in the perspective of developing and optimizing functional nanostructured materials with technological relevance. The properties of isolated clusters are generally related to their size by scaling laws; yet, a multi-parametric approach involving, beyond the size, also morphology, composition stoichiometry, structural arrangement and spatial distribution of components is needed for a reliable description of systems grown with application-scale production technologies. XPS, due to its intrinsically local character, is a technique of choice for the investigation of electronic and geometric structure on a nanometer scale.

We present a XPS study of free lead clusters performed by coupling a pulsed vaporization cluster source to the I411 beamline at MAXLab. Pulsed character of the source produces clusters with variable size distribution and structural properties, according to different residence times in the source before supersonic expansion. The observed evolution with residence time of photoemission lines is discussed within the electrostatic shifts model for the binding energy in clusters [1]. The model is expanded relating the electrostatic radius to size distribution by means of a fractal dimension exponent parameter, so that the comparison with mass spectrometry data provides quantitative evaluation of the fractal character of the clusters.

Our results provide a generalization for a model previously provided for interpreting XPS spectra from free metal clusters [1], laying the ground for the establishment of an effective XPS-based approach to the characterization of complex nanoparticles.

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Exploring the energy landscape of Pd-Pt clusters

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In this work we present a thorough exploration of the potential energy surface (PES) of Pd-Pt bimetallic nanoparticles at the specific composition Pd₁₂Pt₁, using a combination of a Genetic Algorithm and the Threshold Method for global optimization and exploration of the barrier structure, employing the semi-empirical Gupta many-body potential for modeling the interatomic interactions. Structural and energetic analysis of Pd₁₂Pt₁ nanoparticles, including binding energies (E_b), symmetries and common-neighbor indices (CNI) allowed us to identify a set of nine structural *families* of local minima, with an icosahedral motif found to be the putative global minimum for Pd₁₂Pt₁. A detailed study of the icosahedral motif was carried out by calculating the corresponding transition probabilities between low energy isomers, in order to understand structural interconversion. 2-D tree (*disconnectivity*) graphs are plotted to map the structures of minima on the PES and the pathways connecting different isomers of Pd₁₂Pt₁.

Development and characterization of an experimental setup for cluster of alloy sample preparationA. Domingues¹, G. Di Domenicantonio¹, V. Rodrigues¹¹ *DFA, IFGW/UNICAMP, Brasil**adtds@ifi.unicamp.br*

Clusters, i.e. nano-particles formed by a few tens of atoms only, attract great interest because of their peculiar properties as enhanced magnetic moment and catalytic activity, size-specific fluorescence and non-bulky geometrical structures. The intriguing perspective is that those properties would be preserved in a solid state sample, in which clusters are used as building blocks, that could be employed for technological applications. However, in order to get a deeper understanding of the mechanisms taking place in these cluster-assembled samples, it is fundamental to have a good control of crucial parameters such as clusters size, composition, concentration and deposition energy. The experimental setup developed in our laboratory, allows the production of model samples in which the above mentioned parameters can be finely tuned over a wide range. A beam of cluster ions is produced, characterized and deposited under UHV conditions, using a magnetron sputtering cluster source. The source is based on the design of Haberland [1] with the innovative introduction of a cylindrical sputtering geometry intended to increase particle generation efficiency and to facilitate the production of clusters of alloy. A further advantage of the employed source is the low thermal dispersion of the particles that allows a great control of their energy, crucial during deposition. As a matter of fact, the energy of the beam can be defined applying an electrostatic potential to the aggregation region where particles are created. The beam can then be easily extracted, charge filtered and guided by an electrostatic lenses assembly that finally focuses the particles on the deposition surface. We present here the characterization of the attained beam with respect to the parameters, clusters mass distribution and energy dispersion, that are fundamental to the production of well characterized model samples. The first has been studied with a time of flight mass spectrometer, situated prior to the deposition chamber in orthogonal configuration, displaying in real time any change in mass distribution. The latter has been measured directly on the sample holder using retarding field analysis.

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Parameterized Control the Strong-Field Ionization Dynamics of Xenon Clusters embedded in Helium Nanodroplets

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The double-pulse technique [1] combined with femtosecond pulse shaping [2] are applied to resolve the ionization dynamics of xenon clusters exposed to strong-field femtosecond laser pulses (intensity $I_L \sim 10^{14} - 10^{16} \text{ Wcm}^{-2}$). Colored double-pulses [3] allow to separately sample both the optical delay and the relative intensity ratio, which have been proven to be the key parameters for an efficient charging of clusters [4]. The yields of highly charged Xe^{q+} (up to $q = 24$) are recorded as function of both parameters resulting in the so-called charge state-selective fitness landscapes. By studying the conditions leading to the maximum yield for each q we obtain the optimal temporal pulse structure. For $q \geq 15$, the corresponding pulses consist of a strong leading pulse and a weaker trailing pulse whereas the optimal intensity ratios modify with the applied input laser energy. The influence of the chirp is also revealed in the landscapes. So far, the experiments show that a negative chirp is more favorable to produce high- q ions. The results provide crucial information-toolkits towards understanding the complexity of optimal pulse structures obtained in free-optimization experiments on laser-cluster interactions.

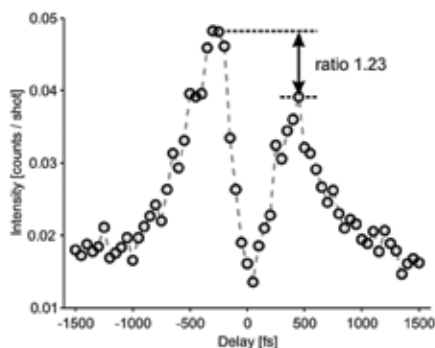


Figure 1: Typical yield of Xe^{17+} as function of the optical delay of colored double-pulses with an equal subpulse's intensity. A substantial enhancement of the ionic signal is observed for a negative optimal delay $\tau_{max} \simeq -300$ fs.

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Melting of a free cluster composed by 309 sodium atoms

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A theoretical study of the melting-like transition of the Na_{309} free cluster is presented. It is found that this cluster suffers a solid-solid transition before being melted; just as was deduced previously from calorimetry and photo-electronic experiments [1]. The cluster reaches the mechanical equilibrium not only at the perfect icosahedral configuration (ICO), but also at a ICO-HCP configuration: icosahedral core plus an incomplete shell of atoms in a hcp sequence. Although the binding energy of the cluster is bigger at its ICO than at its ICO-HCP configuration, there exist many ICO-HCP configurations for each ICO configuration. In this way, the energy increase transforms its perfect icosahedral structure to its ICO-HCP structure. The equilibrium configurations were determined by simulated annealing implemented with micro-canonical molecular dynamics modeling the atomic interaction with the Gupta potential model [2].

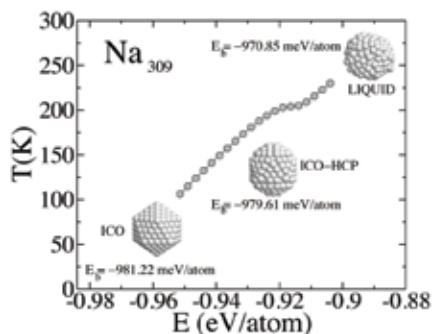


Figure 1: Caloric curve of the cluster Na_{309} . The melting is reached at the thermodynamic state with $E = -916$ meV/atom. Each thermodynamic state is determined from a constant energy dynamic trajectory of $0.1 \mu\text{s}$ using Molecular Dynamics with the Gupta potential model. In each structure, E_b is the corresponding binding energy.

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Structural, electronic and thermal properties of aluminium nanoclusters

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Recent measurements of the specific heat of anionic aluminum clusters with 45 and 47 atoms show characteristic shoulders around 200 K that have been tentatively interpreted as a signal of a superconducting transition. In order to get some insight into this matter, we performed a density functional study of the structural and electronic properties of neutral and charged Al₄₅, Al₄₆ and Al₄₇ clusters. The lowest-energy cluster structures were obtained by using the Gupta potential and a global optimization technique (genetic algorithms), and further relaxed within density functional theory in order to get the *ab initio* most stable structures. Their electronic densities of states were then calculated and compared with the corresponding experimental electron photoemission spectra, in order to select those theoretical structures where the best agreement is found. Finally, using these structures and the semiempirical Gupta potential, we performed a molecular dynamics simulation (up to the microseconds time regime) in order to determine if the jump observed in the specific heat, as a function of the temperature, of Al₄₅ and Al₄₇ has a structural or electronic origin.

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Structural and electronic properties of AuIr nanoclusters

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The lowest-energy structures of binary nanoclusters (AuIr)_n, n=1-20, modelled by the many-body Gupta potential, were obtained by using a genetic-symbiotic algorithm. The potential parameters used for the Au-Ir interaction were obtained by averaging the Au-Au and Ir-Ir ones. These structures together with the most compact ones were further optimized using density functional theory, in order to get the *ab initio* most stable structures for each composition. Segregation is observed in these clusters, with the Ir atoms in the core and the Au atoms on the cluster surface. Also the symmetry, chirality, compacticity, and electronic density of states of the lowest-energy clusters of each size were obtained. An important aspect emerging from the DFT-GGA calculations is the existence of cluster sizes particularly stable with respect to smaller or larger sizes.

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Theoretical study on self-assembly of TCNQ adsorbed on Cu(100) surface

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The interface between tetracyano-*p*-quinodimethane (TCNQ) and copper is considered a model system for the interfaces between the strong electron acceptors usually involved in organic light-emitting diodes or organic solar cells and the metallic contacts. Recent scanning tunnelling microscopy (STM) and low-energy electron diffraction (LEED) experiments have congruently observed self-organized patterns of TCNQ molecules adsorbed on Cu(100) surface [1]. Our DFT studies show that charge-transfer between the adsorbate and the substrate plays a key role in the self-assembly of TCNQ on Cu(100), which is consistent with X-ray photoelectron spectroscopy (XPS) and near-edge X-ray adsorption fine structure spectroscopy (NEXAFS) experiments [1]. The calculated adsorption energy is 2.23 eV for an isolated molecule on the surface, indicating a strong chemisorption. The binding energy for the complete monolayer is slightly larger, 2.35 eV per molecule, demonstrating further stabilization due to intermolecular interactions among the self-assembled molecules. The adsorbed TCNQ is no longer planar as in gas phase but has a bent conformation instead. The cyano groups are tilted towards the surface, confirmed by the experimentally measured bonding angle of 10.0–19.7° from NEXAFS analysis. The deformation of TCNQ at surface is enabled by the single-bond character of the Ph–CN bonds due to the charge-transfer of $\sim 1.5 e^-$ from the surface to each molecule, supported by both calculations and XPS experiments. At the same time, substantial rearrangement of surface is observed; the copper atoms underneath nitrogen atoms are lifted from the surface plane by $\sim 0.3 \text{ \AA}$. The rearrangement of copper atom creates a stress field in such a way that the energy cost to lift a second atom out of its unperturbed equilibrium position is significantly reduced for the immediate neighbors of the already reconstructed copper atom bonded to the cyano group. This stress field makes the reconstructed copper atoms tightly grouped and energetically allows the copper atoms attached to cyano groups of different molecules to be in close proximity, and thus has a profound effect on the self-ordering of TCNQ on Cu(100) which could not be predicted on the basis of the gas-phase conformation of TCNQ.

[1] T.-C. Tseng, C. Urban, Y. Wang, et al, *Nature Chem.*, in press.

**Evolution of metallic screening in small metal clusters probed by
PCI-Auger spectroscopy**

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Excitation-energy dependent Auger spectra of small copper clusters supported by a thin silica layer have been measured as function of cluster size. The Auger kinetic energy of the clusters clearly changes with the excess energy of the emitted photoelectron while not for the bulk. The kinetic energy shift is attributed to post-collision interaction (PCI) and exhibits a reduced metallic screening ability of small Cu-clusters. The spectroscopic data reveal an evolution from a long-range Coulomb-like interaction to a short-range “screened” electrostatic interaction within the sub-nm range. The data show that core electron spectroscopy such as PCI-Auger measurements can be used as a general tool to follow the metallic character of supported clusters.

**Electron confinement in cobalt atoms and clusters
on atomically flat NaCl layers on Au(111)**

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The study of the intrinsic properties of individual clusters with scanning tunneling spectroscopy (STS) currently is limited by the difficulty to create well characterized and atomically flat insulating layers, which decouple the clusters from the substrate. Alumina, magnesium oxide, silica, and sodium chloride (NaCl) are some of the proposed materials to support and electronically isolate clusters. Among these, crystalline NaCl is most promising because it can be grown as atomically flat layers on various substrates. In addition it can easily be deposited with the right stoichiometry, which makes it extremely suitable as support for the characterization of individual clusters.

We report on the successful growth of crystalline NaCl bilayers on Au(111) as revealed by atomically resolved scanning tunneling microscopy (STM). STS measurements focussing on the gold surface state demonstrate variations in the tunnel barrier on an atomic scale related to the NaCl cubic crystal and the gold herringbone reconstruction.

We will also discuss STM and STS results obtained on cobalt atoms and small cobalt clusters deposited on the NaCl layers. It will be shown that the layer strongly reduces the interaction of a supported nanoparticle with the underlying Au(111) substrate. The tunnel barrier leads to quantum-mechanical confinement phenomena and allows mapping the local density of states on single atoms.

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STM/STS investigation of stable TiO_x nanoparticles on Au(111)

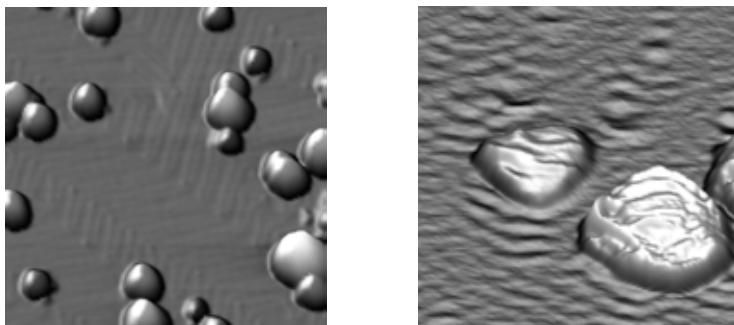
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Transition metal particles, and in particular TiO_x clusters are of high fundamental and technological interest due to their optical, catalytic, and photocatalytic properties. They are used in various applications, e.g., for UV absorption in sunscreen agents and the removal of various types of aqueous pollutants. Attempts to explore individual nanosized Ti particles, however, are scarce.

We have investigated preformed Ti clusters deposited on atomically flat Au(111) films with scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Measurements of both the morphology and electronic properties of these clusters are reported. Ti clusters with a size ranging from 1.5 nm to 4.5 nm are produced in the gas phase and are deposited onto a clean Au(111) surface ensuring low coverage under controlled UHV conditions. STM measurements performed before and after annealing up to very high temperatures (970 K) indicate a high thermal stability of the deposited clusters, which meanwhile are (partially) oxidized. The high thermal stability makes these clusters well-suited for catalysis. STS measurements reveal a n-type rectifying behavior, which is explained by partially oxidized n-type semiconducting TiO_x clusters forming a Schottky junction with the gold. Local influence of the clusters on the electronic surface state of the Au(111) substrate is observed.



Left: 100 × 100 nm² STM image of TiO_x nanoparticles on a Au(111) surface after annealing to 970 K ($V = -1.0$ V, $I = 0.1$ nA). Right: STS based image that reveals the scattering of Au(111) surface electrons at the gold - nanoparticle interface (25 × 25 nm², $V = 600$ mV, $I = 0.3$ nA).

Acknowledgments - This research is supported by the Research Foundation - Flanders (FWO) as well as by the Belgian Interuniversity Attraction Poles (IAP) and the Flemish Concerted Action (GOA) research programs. K. L. acknowledges the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen). K. S. is a postdoctoral researcher of the FWO.

Methyl bromide photodissociation on supported gold clusters: Size dependencies and perspectives for a laser-selective photochemistry

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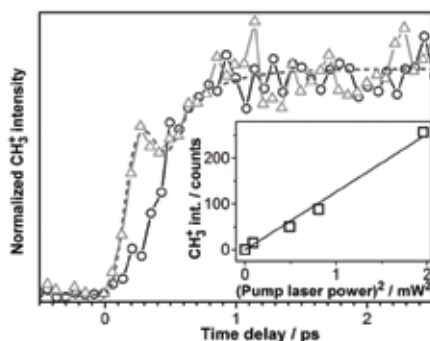
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Supported metal clusters are of utmost importance in chemical catalysis. Size-selected metal clusters on single crystal substrates and well-defined ultra-thin oxide films represent versatile model systems for the investigation of the physical and chemical properties of such nano-systems.

We employ femtosecond laser pump-probe mass spectrometry with resonance enhanced multi-photon ionization to reveal the time-dependent photodissociation dynamics of methyl bromide molecules adsorbed on supported noble metal clusters. This experiment reveals striking size-dependencies in the transient methyl desorption signal from gold clusters which are interpreted in terms of the cluster dimensionality on a magnesia substrate.[1-3]

In an effort to identify the fate of the photodissociation products on the surface, scanning tunneling microscopy is applied to analyze the supported clusters after the photoreaction. The combination of methyl product mass spectrometry and local surface analysis opens new possibilities to optimize laser pulse shapes for enhanced photoreaction and selective field localization on the surface.



Femtosecond time resolved pump-probe mass signal of methyl cations detected from a bare MgO/Mo(100) substrate (circles) and from the same surface covered by gold clusters (triangles). The inset shows the quadratic pump power dependence recorded for the excitation of CH_3Br on the bare MgO/Mo(100) substrate.[3]

- [1] M.E. Vaida, P.E. Hindelang, T.M. Bernhardt, *J. Chem. Phys.* 129 (2008) 011105.
- [2] M.E. Vaida, T.M. Bernhardt, *ChemPhysChem* 11 (2010) 804.
- [3] M.E. Vaida, T. Gleitsmann, R. Tchtnga, T.M. Bernhardt, *Phys. Status Solidi B* 247 (2010) 1001.

Size-selected Au cluster interactions with supporting graphite substrates: A DFT approach

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Computational modelling plays an important role in understanding the properties of nanometre-scale clusters, as it allows a prediction of the lowest energy isomer (i.e the global minimum, GM) structures [1]. However, most previous theoretical studies on clusters have been performed *in vacuo* and at 0 K, which is not experimentally representative. Furthermore, calculations of both cluster soft-landing and pinning processes (collisions) on graphite substrates has been limited to small sizes ($N < 10$) at high levels of theory [2].

In this work density functional theory (DFT) and tight-binding approximative (DFTB) calculations were used successfully on isolated Au₁₆ [3] and highly oriented pyrolytic graphite (HOPG) systems. The two systems were combined and again minimizations were successful, and in some cases on-going, with a view to finding the effect of defects to the cluster structure and orientation on the graphite surface. Pinning of the Au₁₆ cluster is also under investigation through molecular dynamics simulations.

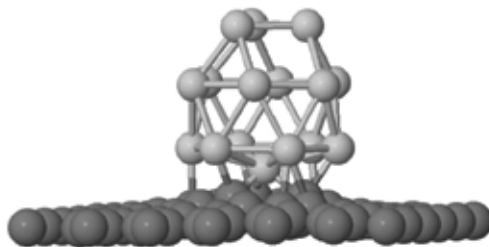


Figure 1: Au₁₆ soft-landed on HOPG with one surface defect.

- [1] R. L. Johnston. *Atomic and Molecular Clusters*. Taylor and Francis, London, 2002.
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Three-dimensional structure of size-selected Au and Cu clusters

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The activity and selectivity of nanocluster catalysts depend on their size, shape and atomic configuration, so the structural characterization of the nanoclusters is fundamentally important for understanding the catalytic performance. Aberration-corrected scanning transmission electron microscopy (STEM) has been successfully used in revealing the three-dimensional structures of size-selected Au₃₀₉ clusters [1]. In this paper, we report the morphological and structural determination of a further magic number cluster Au₉₂₃, as well as a series of Cu clusters, using the same technique.

The clusters were deposited with a radio frequency magnetron-sputtering, gas aggregation cluster beam source and lateral time-of-flight mass filter, with $M/\Delta M=20$ [2]. The high angle annular dark field (HAADF) STEM investigation was performed in a JEOL JEM2100F instrument with spherical aberration corrector (CEOS GmbH).

The HAADF-STEM investigation of the Cu clusters, relevant to methanol dehydrogenation [3], showed significant modifications in the particle sphericity when the size varied from 3000 – 10000 atoms. A high proportion of prolate clusters can be generated under appropriate cluster source conditions. On the atomic scale, the clusters exhibited a fcc structure, with the presence of single twins but no multiple twins.

Two kinds of structure were observed in Au₉₂₃ clusters, specifically, cuboctahedral and decahedral. Structural statistics from more than 40 clusters show that ~ 75% are cuboctahedral or FCC twin structures, consistent with previous theoretical calculations of the total potential energy [1]. In addition, the dynamical movement of surface atoms was observed through fast, serial-acquisition experiments on the same Au₉₂₃ particle. We found that the number and position of surface adatoms (both individual atoms and groups) displayed significant changes between consecutive images. It seems that some adatoms even move from one facet to another. Such weakly bound surface atoms may present interesting candidates as active site for catalytic reactions.

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[3] M. Tada, R. Bal, S. Namba and Y. Ywasawa, *Appl. Catal., A* **307** (2006) 78

Ageing of silver nanostructures

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Metal nanostructures have been proposed for many applications in nanomaterials, nanoelectronics etc, however there is a lack of information about the stability of those nanostructures against time. Since nanoparticles have a very high surface area to volume ratio, which provides a tremendous driving force for diffusion, morphological changes as sintering can take place at lower temperatures, over shorter time scales than for larger particles. In that respect it is of fundamental interest to know how does a nanostructure resist to corrosion.

To go further in the atmospheric corrosion at nanometerscale, which is still largely unexplored, we performed an experiment to test the stability of pure silver fractal nanostructures formed on graphite surface. These fractals are formed from physical methods that in contrast to chemical methods, avoid the polymer membrane covering the nanostructures. Moreover, the dendritic structure of fractal morphology has potential for efficient reactivity due to the surface geometry, porosity and large surface to volume ratio. The high surface area of the dendritic structures as well as the nanopores allows for rapid absorption of the reactant species. The stability of the synthesized silver nanofractals against atmospheric corrosion after exposure to air at ambient conditions was analysed by electron microscopy. We identify S and Cl as the two principle agents for the degradation of the fractal shapes and we show evidence of two fragmentation mechanisms, associated to two size distributions of fragments. Moreover when the silver fractals have been completely corroded, the largest fragment size distribution remained aligned in the fractal-like form, whereas the smallest one can be spread over the graphite surface.

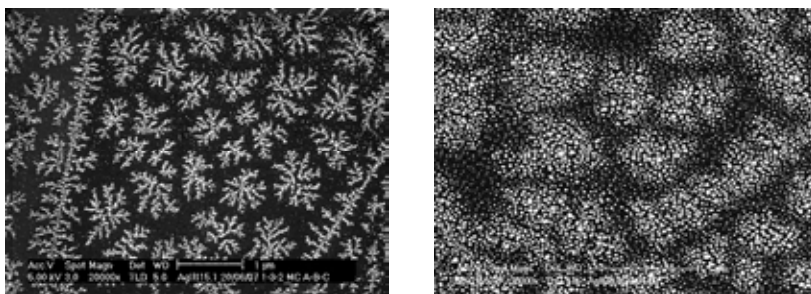


Figure: Silver nanostructures obtained by preformed silver clusters soft-landing deposition: just after deposition (left), and after several month of exposure to atmospheric corrosion.

**Ultrathin MgO films on Mo(100) as support for molecules and metal clusters:
Tuning the reactivity by thickness and composition**

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Ultrathin metal oxide films on metal single crystal substrates have become an extensively investigated research subject in recent years. Particularly, it has been proposed theoretically and confirmed experimentally that the electronic structure of adsorbates can be influenced by the layer thickness and the stoichiometry, i.e., the type and number of defects, of the oxide film. This has important consequences on the chemical reactivity of the oxide surface itself and of oxide supported molecules and metal clusters. It also opens new possibilities to influence and to control chemical reactions occurring at the surface of these systems [1].

In the present contribution, thermal desorption spectroscopy and surface femtosecond time-of-flight mass spectrometry are employed to investigate the absorption and the photoinduced reaction of methyl halide molecules on magnesia and magnesia supported gold clusters [2-5]. The influence and control of the reaction dynamics occurring on magnesia ultrathin films and on magnesia supported gold clusters through variation of film thickness and defect structure of the film will be presented.

- [1] M. E. Vaida, T. M. Bernhardt, C. Barth, F. Esch, U. Heiz, and U. Landman, *Phys. Status Solidi B* **247**, 1001 (2010).
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- [3] M. E. Vaida, P. E. Hindelang, and T. M. Bernhardt, *J. Chem. Phys.* **129**, 011105 (2008).
- [4] M. E. Vaida and T. M. Bernhardt, *ChemPhysChem* **11**, 804 (2010).
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Density Functional Theory of the adsorption of SF₆ on graphene

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Using the LDA approximation and molecular dynamics with the Born-Oppenheimer approximation, we show results for the study of the adsorption of SF₆ on a graphene layer at a temperature of 77K and atmospheric pressure. We performed our calculations using the Quantum-Espresso code [1]. We considered three different initial positions for the SF₆ molecule. In all three cases, the molecule is adsorbed, and it is not dissociated in the process. We obtained -0.89, -0.91, and -0.71 eV for the adsorption energies, for the initial positions a, b, and c, respectively. The adsorbed molecule desorbs when the temperature is increased to 470 K, 490 K, and 420 K for the cases a, b, and c, respectively.

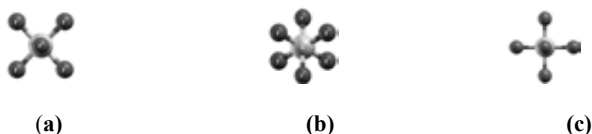


Figure 1: Different orientations of the SF₆ molecule with respect to the graphene layer.

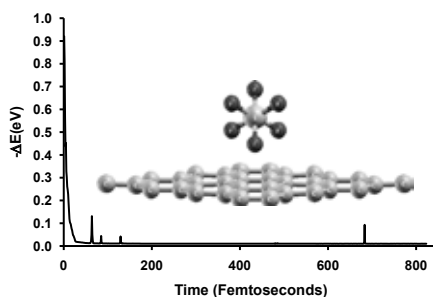


Figure 2: Time evolution of the interaction of the SF₆ molecule in orientation b with the graphene layer.

[1] S. Scandolo, P. Giannozzi, C. Cavazzoni, S. de Girono, A. Pasquarello, and S. Baroni, First-principles codes for computational crystallography in the Quantum-ESPRESSO package. *Z. Kristallogr.* 220, 574, 2005.

Density Functional Theory of the adsorption of H_2SO_4 on the [001] titanium surfaceIván Carrillo, L. F. Magaña*Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Código Postal 0100, México Distrito Federal, MÉXICO.**L. F. Magaña e-mail: fernando@fisica.unam.mx*

Using the LDA approximation and molecular dynamics with the Born-Oppenheimer approximation, we studied the adsorption of H_2SO_4 (trans) on the titanium [001] surface at a temperature of 300K and atmospheric pressure. We performed our calculations using the Quantum-Espresso code [1]. We found that the H_2SO_4 molecule is adsorbed and dissociated in the process. The four **O atoms** are transferred to the titanium surface to form titanium tri oxide. The remaining part H_2S , is physisorbed. When the temperature of the system is increased to 700 K, the H_2S molecule is desorbed. The adsorption energy of the H_2SO_4 molecule is -5.1eV. The nearest titanium atom is 2.31 Å away from the **sulphur** atom, after the adsorption occurs.

Previously, we calculated parameters for the equilibrium configuration of the H_2SO_4 molecule and the corresponding calculations for the titanium cell parameters. Our calculations agreed very well with the experimental results [2].

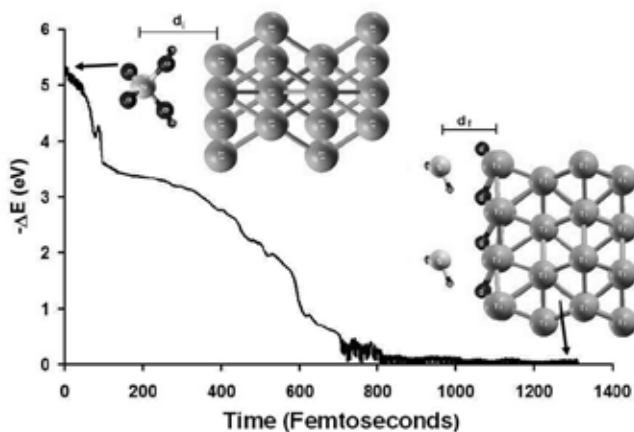


Figure1: Time evolution of the interaction of the H_2SO_4 molecule with the titanium [001] surface.

[1] S. Scandolo, P. Giannozzi, C. Cavazzoni, S. de Giron, A. Pasquarello, and S. Baroni, First-principles codes for computational crystallography in the Quantum-ESPRESSO package. *Z. Kristallogr.* 220, 574, 2005.

[2]. Lide DR, editor. *Handbook of chemistry and physics*. Boca Raton, FL: CRC; 2000. p. 9–16.

Cocatalytic effects studied with single-composition bimetal clusters on solid surface

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Catalytic activity can be promoted remarkably by introduction of trace amounts of other elements (cocatalysis). This occurs through electronic interaction such as charge polarization, electron transfer and promotion, etc, but details are still unknown. The fundamental mechanism of the cocatalytic effects can be elucidated with single-composition multi-element clusters as model cocatalysts. Furthermore, the size-effects of the multi-element clusters has a potential to be high-activity and new-functional materials due to specific electronic and geometric structures. For instance, we have shown in our STM studies [1-3] that platinum clusters with size > 20 have a monatomic layered geometry on a silicon surface [1,2] and the charge is polarized such as positive and negative at the center and periphery of the cluster, respectively [3]. Based on this finding, we are studying oxidation of CO proceeding on a bimetal cluster, Pt_NAg_M , where Ag is expected to increase the negative charge of the platinum clusters by electron donation.

The single-composition clusters were prepared on the silicon surface by low-energy impact of the mass-filtered cluster cations [4]. The reaction products were analyzed by high-sensitive temperature-programmed desorption mass-spectroscopy (TPD-MS). Figure 1 shows a TPD-MS result of CO oxidation catalyzed on the monatomic-layered Pt_{30} . In comparison with the same reaction on the Pt(111) surface, the sharp and the broad peaks are assigned to the oxidations by molecularly adsorbed O_2 and dissociatively adsorbed O, respectively. It is expected that lower-temperature oxidation is expected on Pt_NAg_M due to its larger negative charge than Pt_N .

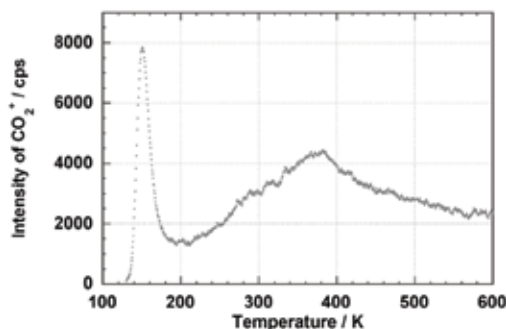


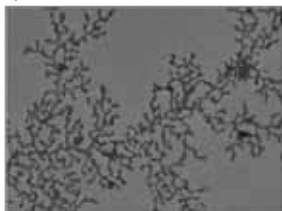
Figure 1: Temperature-programmed desorption mass spectrum observed in the oxidation of CO on monatomic-layered Pt_{30} prepared on a silicon(111) surface.

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- [2] H. Yasumatsu et al., *J. Chem. Phys.* **124**, 014701, 2006.
- [3] H. Yasumatsu et al., *Chem. Phys. Lett.* **487**, 279, 2010.
- [4] H. Yasumatsu et al., *J. Phys. Conf. Ser.* **185**, 012057, 2009.

Mass selected clusters deposited on surfaces: control of auto-organizationL. Bardotti¹, F. Tournus¹, P. Mélinon¹, M. Pellarin², M. Broyer²*Université de Lyon, F-69000, France and Université Lyon 1*¹*Laboratoire LPMC/N, CNRS, UMR 5586, F-69622 Villeurbanne Cedex, France*²*Laboratoire LASIM, CNRS, UMR 5579, F-69622 Villeurbanne Cedex, France*

The low energy deposition of clusters produced in the gas phase is an interesting route for synthesizing nanostructures with specific properties ^[1]. We have developed a new and versatile apparatus for the deposition of size selected clusters ^[2]. This allows us to explore the auto-organization of size selected metal clusters as a function of the kind of metal and of the surface reactivity. In case of gold clusters deposited on HOPG graphite, under ultra high vacuum, large ramified islands of fractal structures are observed (figure 1a). This is explained by the diffusion of clusters on the surface and by partial coalescence ^{[3][4]}.

a) Au



b) Pt

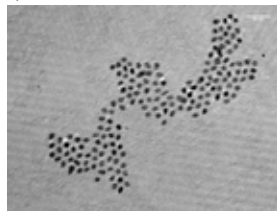


Figure 1. Size selected clusters ($d_m = 2.2$ nm) deposited on HOPG graphite.

a) Gold clusters

b) Platinum clusters

For platinum clusters deposited in the same conditions, completely different results are obtained. Pt clusters do not coalesce; the edge-to-edge distance is typically 1.2 nm and they are self-organized in a regular hexagonal pattern.

Experiments on gold clusters deposited in different vacuum conditions illustrate the sensitivity of the auto-organization to the possible adsorption of molecules at the cluster surface. Moreover, we have deposited mixed Pt/Au clusters of different relative compositions to study the transition between the two extreme situations in figure 1. For the same deposition conditions (substrate, incident cluster size and background vacuum) we observe intermediate behavior as a function of relative proportion of the two metals.

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[3] P. Jensen, Rev. Mod Phys. **71**, 5, (1999)

[4] D. Tainoff, L. Bardotti, F. Tournus, G. Guiraud, O. Boisson, P. Melinon JPCC. **112**, 6843, (2008)

**Soft-Landing of Organometallic Sandwich Clusters onto
Aliphatic Monolayers Coated on Metal-Oxide Surfaces**

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The functionalization of metal-oxide surfaces has been attracted intense interest due to the potential applications for optoelectronic devices and chemical biological sensors. Recently, surface modifications of a metal-oxide surface have been actively conducted to understand the nature of chemical interactions between the molecules and surface as well as to use as universal transparent electrodes for organic semiconductor devices. In this contribution, we newly propose the surface modifications of the metal-oxide surfaces with gas-phase synthesized novel chemical species. Aliphatic-monolayer coated on polycrystal tin-oxide layer and SnO₂ (110) single crystal surfaces were used for supporting substrate to isolate the gas-phase synthesized Cr(benzene)₂ sandwich clusters inside the monolayer matrices, and the adsorption properties of the landed clusters were characterized using surface science technical methods.

Chromium (Cr)–benzene complexes were synthesized in a molecular beam through laser vaporization, and mass-selected Cr(benzene)₂ cation beam was soft-landed onto an palmitic-acid monolayer (PM) assembled on the SnO₂ surfaces. Hyperthermal collision event (~20 eV) during the soft-landing penetrates the incoming Cr(benzene)₂ cations into the PM matrices. The structure and orientational preference of the landed clusters have been evaluated with infrared reflection absorption spectroscopy (IRAS), and Thermal desorption spectroscopy (TDS) was employed to investigate desorption kinetic of the clusters.

The IRAS measurements observed three IR absorption peaks at 972, 998, and 1427 cm⁻¹ after the landing of Cr(benzene)₂ cations onto SnO₂-based PMs. The observed vibrational frequencies reveal that the Cr(benzene)₂ clusters are keeping their native sandwich structure intact at the PM substrates as the neutral state. The TDS study disclosed that the desorption temperature and desorption activation energy of the landed Cr(benzene)₂ clusters from the polycrystal-based PM were significantly lower than those of single-crystal-based PM. The thermal desorption of the matrix-isolated clusters would be associated with phase transition process of the supporting monolayer matrices. The decrement of the desorption temperature and activation energy, therefore, reflects that the phase transition of PM on polycrystals takes place at lower temperatures than that on SnO₂ (110) surface. The decrement in the phase-transition temperature would be mostly due to physically heterogeneous character (large surface roughness) of the polycrystal layer.

A Crystallographic Analysis to Synthesize Stable Small Metallic Particles on Oxides

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When small metallic particles are supported on oxides to be used as catalysts, traditionally, little attention has been paid about the compatibility between the atom distribution of the oxides and the one of the support. Recently [1], it was shown that small particles can be supported on the surface of an oxide by first dissolving in it atoms of these particles. Then, this solid solution is heated to induce migration of the dissolved atoms, until they reach the surface of the solvent crystallites to form small particles. This method produces stable small particles, but requires the heating of the sample at large temperatures, which could transform the supporting oxide.

An alternative way to produce stable supported small metal particles on a specific oxide is to analyze those metals whose oxides have a crystallography compatible with it, or to find a support oxide that have a crystallography compatible with the oxide of the metal that will be supported.

Here, we present the application of the above analysis when rutile is the support and iridium the metal to be supported. Rutile has a tetragonal structure with a unit cell described by the space group $P4_2/mnm$ and lattice parameters $a = 0.4597$ nm and $c = 0.2959$ nm. Iridium oxide also has this crystalline structure with lattice parameters $a = 0.4536$ nm and $c = 0.3097$ nm. Therefore, when iridium was supported on rutile, the first iridium atoms arriving to the support interacted with the oxygen atoms and occupied sites that corresponded to titanium. This caused that any titanium atom position on support surface was a nucleation center for an iridium particle, generating high particle dispersion. The particle size, which was of the order of 1.0 nm, was determined by the difference of lattice parameters between iridium oxide and rutile.

The same procedure was used to support Sn, Rh, Ru and Pt particles on rutile with a high dispersion and particle sizes of the order of 1 nm. In the case of platinum oxide the symmetry of the unit cell is not tetragonal but orthorhombic; it, however, is related to the crystalline structure of rutile.

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Formation of silver and gold nanoclusters supported on thin silica films and mordenitesD. Kovalenko¹, V. Gurin², N. Bogdanchikova³, V. Petranovskii³, I. Tuzovskaya⁴, A. Pestryakov⁴¹ Gomel State University, Gomel 246699, Belarus² Physico-Chemical Research Institute, BSU, Minsk, Belarus³ Centro de Nanociencias y Nanotecnología - UNAM, Ensenada, B.C., 22800, México⁴ Tomsk Polytechnic University, Tomsk 634050, Russia

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Incorporation of small metal clusters and nanoparticles into different matrixes, such as silica glass films, zeolites, etc., attracted much attention due to easy practice for optical studies and importance for applied problems: nanoparticles can influence both linear and non-linear properties of composite materials. Refraction index of metal-dielectric media depends strongly on metal type, shape and size of clusters and metal-matrix interaction.

UV-visible spectra of silver supported on silica films obtained by sol-gel method displayed absorption bands in the range 350-490 nm. Calculations based on modified theory of light absorption by metal clusters determined that the observed peaks belong to Ag clusters with size from 5 to 30 nm (plasmon resonance band). Modeling showed that silica films containing such silver nanoparticles can be used for giant parametric light reflectance and non-linear optic effects.

UV-visible spectra of Ag/mordenite samples treated with H₂ exhibited intensive absorption bands in the range 270-330 nm attributed to Ag_n⁺ clusters. Using model of origin and growth of the clusters in the condensed medium we determined formation of Ag₂⁺, Ag₄²⁺, Ag₅⁰, Ag₈⁰, Ag₈ⁿ⁺ clusters in the zeolite channels. Forming Ag₂⁺ and Ag₄²⁺ states were observed at low concentrations of silver (1-2 wt.%) as a result of ion exchange process in zeolite. At higher Ag percentage (3-4 wt.%) complete substitution of H⁺ ions in the mordenite frame were observed with formation of Ag₈⁰ and Ag₈ⁿ⁺ clusters. Further rise of silver concentration led to appearance of silver nanoparticles with size up to 10 nm.

XRD and TEM analysis revealed that silver nanoparticles were formed on the external surface of zeolite while clusters Ag_n (n≤8) were localized inside mordenite channels without changes of its crystal structure. Type of silver clusters and their portion depends strongly on SiO₂/Al₂O₃ molar ratio of mordenites. It is caused mainly by differences in Brønsted acidity of zeolite surface. Proton acid sites favored formation and stabilization of the metal clusters inside mordenite channels.

Comparison of the obtained results with Au/mordenite samples prepared from [Au(NH₃)₄](NO₃)₃ complexes revealed that in zeolite channels silver clusters were formed easier than gold ones. It is explained by larger size of Au(NH₃)₄³⁺ ions (as compared with Ag⁺ ions) that complicated ion exchange process because of steric factor. Moreover, presence of ammonia ligand favored partial reduction of gold ions during ion exchange.

Simulation of the dissociative adsorption of hydrogen on the edges of graphene nanoribbons

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Hydrogen powered electric cars are a promising and appealing alternative to present gasoline cars. However, the on-board storage of hydrogen remains as a challenging technological problem. It has been shown that nanoporous carbon materials, eg. carbide derived carbons (CDC) [1], activated carbons (AC) [2], etc. exhibit storage capacities of up to 6 wt% hydrogen at low temperatures (77 K). However, at room temperatures the capacities drop (to about 1 wt% hydrogen) well below the value of 6 wt% hydrogen required for their technological application. The reason is mainly due to the small (about 100 meV) binding (physisorption) energy of hydrogen to the pore walls. The optimal size and shape of the pores for hydrogen storage has been also investigated [3]. The pore walls can be viewed as interconnected curved nanoribbons or nanographenes with exposed edges. Our aim is to investigate the adsorption of hydrogen to the graphene edges and its contribution to the storage capacity of nanoporous carbons. These questions had not been addressed so far. As a model for the exposed edges of the pore walls we have considered carbon nanoribbons with armchair and zigzag terminations. We have performed Density Functional calculations (DFT) to elucidate the competition between two adsorption mechanisms: i) the molecular physisorption and ii) the dissociative chemisorption of hydrogen. Our results indicate that hydrogen dissociates and chemisorbs with no activation barrier on both edge terminations (see Fig. 1). The chemisorption energies range from 2.7 - 5.0 eV per hydrogen molecule with respect to the free molecule. Clearly, the exposed carbon edges of the nanoribbons are very active chemically and therefore, "adsorb" hydrogen very easily. However, this chemisorbed hydrogen does not contribute to an increase in the reversible storage capacity of the material, since it cannot be released at room temperature. However, metal nanoparticles dispersed in the nanoporous carbons, could act as catalysts for hydrogen desorption at room temperature. The contribution of saturated edges to the storage capacity will be also discussed.

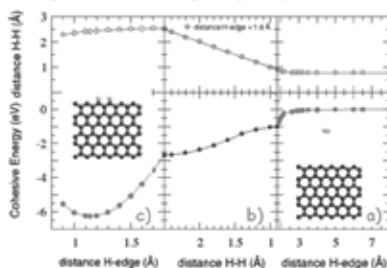


Figure 1: Dissociative chemisorption of H_2 on a graphene zigzag edge: a) molecular hydrogen approaches the graphene edge, b) the H_2 molecule dissociates in the proximity of the edge, and c) the two hydrogen atoms chemisorb in two adjacent non saturated carbon atoms of the edge.

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Optical activity in single-wall carbon nanotubes

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Tremendous progress has been made toward the synthesis of monodisperse carbon single-walled nanotubes (SWNTs). However, most of these methods result in SWNTs mixtures that have a broad range of diameters, chiralities, and electronic properties, which are generally unsuitable for applications because their physical properties are not uniform. The separation and selection of SWNTs with desired properties is still a challenging task. Recently, scientists have turned their attention to sorting left-handed and right-handed SWNTs. In an effort to separate racemic mixtures, many mechanisms have been devised to obtain SWNTs with small diameters and well-defined helicities. Nowadays, the most successful approach that yields enantiomeric excess, involves the wrapping of SWNTs with chiral molecules. The success of the enantiomeric separation and/or enrichment was confirmed by measuring the electronic circular dichroism (CD) of the samples. In spite of CD measurements have been successful, the origin of the optical activity in SWNTs and its interpretation remain as a challenge. In this work, the optical activity in metallic and semiconductor single-wall carbon nanotubes is investigated by performing first-principles calculations of CD [1]. The origin of optical activity is explained in terms of the structural, optical, and electronic properties, such as the nanotube's diameter, chiral index, density of states, and optical absorption. The calculated CD is in excellent agreement with experiments, providing the nanotubes absolute configuration. These results determine which nanotubes are present or not in CD measurements and their chiral indices, providing a framework to understand the enantioselectivity process in recent experiments. Additionally, these results offer a strong theoretical support to understand chirality at the nanoscale, which is fundamental in problems that involve the synthesis, characterization, and functionalization of SWNTs, which are important in electronics, biology, medicine, and pharmacology, among other disciplines.

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Formation mechanism of polyynes and cyanopolyynes by laser ablation in liquids

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Polyynes, $\text{H}(-\text{C}\equiv\text{C}-)_n\text{H}$ ($n \geq 2$), are simple model compounds for sp-carbon chain molecules with alternating single- and triple-bonds. The doubly degenerate π -electron system is intriguing in view of optical properties and electric conductivities. Cyanopolyynes, $\text{H}(-\text{C}\equiv\text{C}-)_n-\text{C}\equiv\text{N}$ ($n \geq 2$), are known to be abundant in space and applied to the study for molecular evolution in dark clouds. Recently, polyynes were formed by laser ablation in organic solvents and identified by their UV absorption spectra. Size-separated polyynes were characterized by normal Raman and SERS [1], resonance Raman [2], and optical emission spectroscopy [3]. The reactive molecules were stabilized inside single wall carbon nanotubes forming $\text{C}_{2n}\text{H}_2@\text{SWNTs}$ and studied by Raman spectroscopy [4-6]. Very recently, we found that polyynes were readily formed by intense femtosecond laser pulses filamenting in liquid hydrocarbons [7].

We produced polyynes, $\text{H}(-\text{C}\equiv\text{C}-)_n\text{H}$ ($n=4-8$), and cyanopolyynes, $\text{H}(-\text{C}\equiv\text{C}-)_n-\text{C}\equiv\text{N}$ ($n=3-6$), by laser ablation of carbon particles in hexane or acetonitrile. These molecules were size-selected by high performance liquid chromatography, HPLC, and characterized by UV absorption, resonance Raman, and NMR spectroscopy. Using ^{13}C -isotope-enriched carbon particles, mixing of carbon atoms in the formation of linear sp-carbon chains was investigated in more detail. Figure 1 shows ^1H -NMR spectra of cyanopolyne, HC_9N , as an example. Starting from $\sim 96\%$ ^{13}C particles, the isotopic abundance in the product molecule, HC_9N , was much reduced to less than 75% - 50% ^{13}C in average. This observation indicates that carbon atoms from solvent molecules are contributing as building blocks for the sp-carbon chain in HC_9N . Detailed analysis for the isotopomer distribution will be discussed.

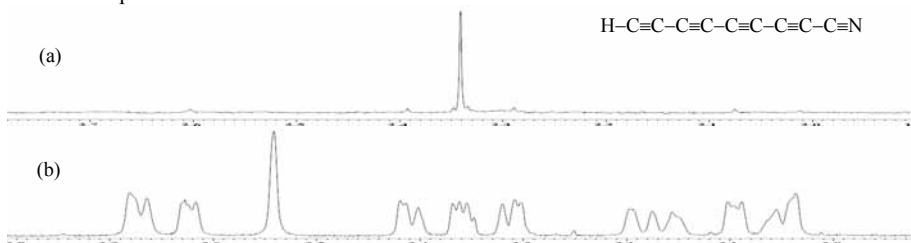


Figure 1: ^1H -NMR spectra of HC_9N produced from carbon particles of (a) 10% or (b) $\sim 96\%$ ^{13}C in acetonitrile.

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Preparation of high-purity nitrogen-doped endohedral fullerene N@C₆₀

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Nitrogen-doped fullerene, N@C₆₀ [1], have attracted broad interests in many aspects including quantum information processing by its electron-nuclear spin system [2]. For detailed characterization of physical and chemical properties, we have developed experimental procedures for preparation of high-purity samples of N@C₆₀ [3].

Nitrogen gas was discharged by an induction coil applied with high frequency. Cationic species produced in the plasma were extracted by a static field of -80 V. Fullerene C₆₀ was heated in a crucible and sublimed to be deposited on a surface of an electrode, where the C₆₀ molecules were bombarded with the cations. After the ion bombardment, the material deposited on the electrode was dispersed in a small amount of carbon disulfide and examined by electron spin resonance (ESR) spectroscopy. We estimated a typical number of target molecules, N@C₆₀, obtainable by 5-hours bombardment to be $\sim 10^{14}$. The material after the ion bombardment contained a four-orders-of-magnitude larger amount of empty C₆₀.

In order to concentrate N@C₆₀, we employed a recycling system for high performance liquid chromatography (HPLC). The retention time of N@C₆₀ was $\sim 3\%$ longer than that of C₆₀. With this difference, the target molecules were separated from the bunch of C₆₀. By repeating these procedures, i.e., bombardment, separation, and concentration, we could detect N@C₆₀ by its UV absorption. The purified N@C₆₀ was used for characterization of the spin dynamics in solutions.

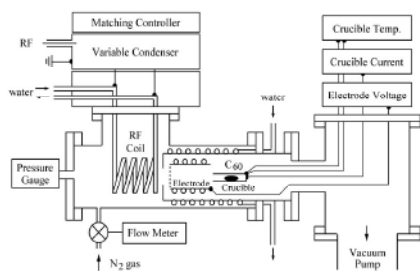


Figure 1: Apparatus for ion bombardment [3].

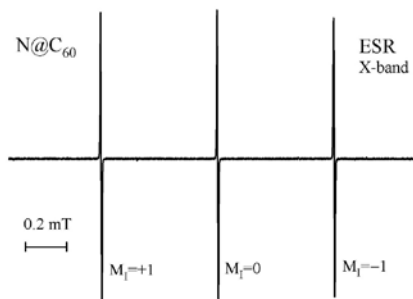


Figure 2: ESR spectrum of purified N@C₆₀ in toluene.

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**HYDROGEN STORAGE INSIDE AND ON A CARBON NANOTOROUS.
INFLUENCE OF SCANDIUM AND BERYLLIUM ATOMS.**

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Ab initio DFT (density functional theory) calculations were performed to study the hydrogen molecule adsorption inside a toroidal carbon C₁₂₀ nanostructure, a nanotorous. Hydrogen molecules were added inside this structure, one by one until 15 molecules and for each one of these systems a geometry optimization was obtained. The cohesive energy values show that these structures are energetically stable. The same nanotorous was coated outside its surface with only one Be or Sc atom to study the hydrogen adsorption.

In this work we present a comparative study not only of the different hydrogen quantities that each system can adsorb, but also we explain this taking into account the differences of the electronic structures of the coating atoms, beryllium and scandium.

All these calculations were done under the GGA (generalized gradient approximation) of Perdew and Wang (PW91), making use of the Materials Studio v. 4.3 code. Total energy, HOMO-LUMO, Mulliken population analysis and charge density will be compared for the above systems. It is discussed if the difference between the electronic configuration for the beryllium and scandium atom can increase the hydrogen storage capability for Sc coated nanotorous compared to the Be coated system.

FIRST PRINCIPLES STUDY OF ADSORPTION OF HYDROGEN SULFIDE (H₂S)
ON GRAPHENE

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Density Functional Theory, as implemented in the quantum ESPRESSO package [1], has been used to analyze the interaction between hydrogen sulfide and graphene. The electron-ion interaction is modeled using ultrasoft pseudopotentials, the Exchange-correlation energy is approximated by the method of local density approximation (LDA) and the generalized gradient approximation (GGA) within the parameterization PZ (PerdewZunger) [2] and PBE (PerdewBurkeErnzerhof) [3], respectively. Four different coverages (one H₂S molecule per 8, 16, 18 and 32 C atoms) have been studied; geometries, binding energies and Density of states (DOS) are calculated. We studied several preferential sites (top, bridge, center) where the molecule may be adsorbed. Our results show that the molecule H₂S suffers a physisorption process; the DOS of grapheneH₂S system shows a metallic behavior which coincides with the behavior of isolated graphene. Finally, the stability of the hydrogen sulfide remains when is adsorbed by the graphene.

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Modeling of the functionalization of single-wall carbon nanotubes towards its use in drug-delivery systems

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A density functional theory (DFT) study of some functionalized single-walled carbon nanotubes (SWCNT) is presented. Our pristine SWCNT computational model consists of a finite, open tube with (5,5) chirality. All dangling bonds at the tips are capped with hydrogen. The structural and electronic properties of the pristine tube, with formula, C₈₀H₂₀, are compared to the SWCNT with a simulated vacancy defect at the sidewall, providing insight at the reactivity induced by the presence of these defects. Functionalized nanotubes (f-SWCNT) were formed with the following covalent-binding organic molecules: (a) **formic acid**, as a model carboxylic acid, (b) **aminotriethylene glycol**, as a model amide, (c) **ethyleneglycol** as a model of the corresponding polymer. These molecules have been used in recent experiments for its capability to bind CNTs to certain drugs [1]. We model the effects of functionalization on both the pristine SWCNT and the defect-SWCNT. Furthermore, we study the binding of some of these f-SWCNTs with methotrexate, a drug of common use in cancer therapy. Binding energies are computed as well as structural and electronic parameters such as dipole moments, ionization potentials, electron affinities, the HOMO-LUMO gaps and the free Gibbs energies of solvation. The level of DFT theory is the non-empirical DFT functional PBE [2], employed with two computational methods: (a) The DACAPO code that employs pseudo potentials and super cells with a plane-wave basis set and (b) The molecular-orbital code with localized basis set 6-31G(d,p), as implemented in the GAUSSIAN 03 code. Our results show that formation of these f-SWCNT and the drug nanovectors is in general thermodynamically favorable and that they are soluble in water, thus improving its biocompatibility and decreasing its toxicity.

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Aptamer-modified gold nanoshells

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Gold nanoshells possess optical tunability from the visible to the near infrared region controlling the particle size as well as the ratio of core radius to shell thickness. Gold nanoshells are attractive to be used in the treatment and detection of breast cancer owing to their absorbing and scattering properties in the near infrared region [1], a region where light penetrates tissues deeply. To succeed in using nanoshells to treat cancer, the nanostructures must be bound to tumor cells, to achieve this; bioconjugated nanostructures must be highly selective and sensitive to cancer cells. As a result, bioconjugation of gold nanoparticles with aptamers was made in order to acquire ability and control of all the parameters to bioconjugate gold nanoshells synthesized by bench chemistry. The aptamers offer many advantages over the antibodies [2]. The bioconjugation of gold nanoparticles and gold nanoshells were confirmed through specific binding of the aptamers toward platelet-derived growth factor (PDGF). PDGF is over-expressed in cells with malignancies and developmental abnormalities as in breast cancer cells. Results from UV-Vis spectroscopy, TEM and photographs which demonstrated the color change of the colloid are presented to sustain the bioconjugation.

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Synthesis and characterization of metal oxide nanomaterials by thermal decomposition of carboxylate precursors

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The synthesis and characterization of metal oxide nanomaterials [M=Co (II), Zn(II), Cu(II) and Fe(III)] by thermal decomposition of carboxylate complexes for potential biomedical applications was realized. The synthesis of carboxylate complexes of Co(II), Zn(II), Cu(II) and Fe(III) with tartaric acid, salicylic acid and acetic acid was realized by metathesis reactions of metallic salts with the organic ligands in aqueous solution [1] and they were characterized by infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Subsequently, all the materials were calcinated in a blast furnace at 500°C during 1, 3 and 5 hours and 700°C during 4 hours for allowing the full elimination of the organic ligand. The metal oxides obtained were characterized by FTIR spectroscopy, elemental analysis by X-ray dispersion (EDS) and scanning transmission electron microscopy (STEM) and we observed the elimination of the organic ligands in the calcinations during the first hours in almost all the cases. The elemental analysis in all the samples corresponded to the formula ZnO, Fe₂O₃, CoO and CuO, and in the analysis by STEM almost all the materials were aggregated but the size range of the nanoparticles obtained was in a range between 20-80 nm, and in the case of CoO it was observed the presence of cubic nanostructures in the micrography. To avoid the aggregation and to start with the surface modification for biomedical applications, 300 mg of all the powders were resuspended in water, an stoichiometric quantity of 3-aminopropyltrimethoxysilane (TMS) was added to the suspension and all the suspensions were maintained with stirring at 60°C during 4 hours [2]. The materials were washed, dried and recovered for characterization by the techniques previously mentioned. All the results obtained will be presented in the talk.

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Nano-structured materials from imidazolines and oxazolidinone

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Nanoparticles have attracted considerable attention because of their unique physical and chemical properties, which depend on size, shape and morphologies that are extremely different from other particles. The nanoparticles properties may find excellent applications in materials science, biomedical engineering and drug delivery among other fields.¹

Our research interest is focused on the synthesis of organic compounds and within this context we have designed and synthesized some low weight molecules, Figure 1, that were used in the building of nanocolloids and gels.

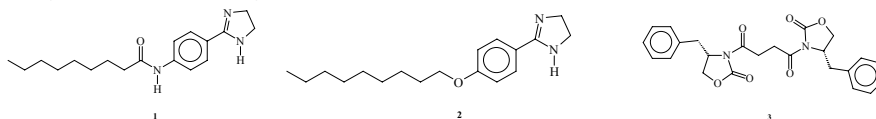


Figure 1. Compounds used in the preparation of nanocolloids and molecular gels.

Imidazolines 1 and 2 either alone or combined with ricinoleic acid, were used to prepare colloids, which were characterized by DSC, fluorescence spectroscopy, SEM and TEM. Figure 2.

Oxazolidinone 3 and Cr(III) afforded a gel, that was characterized by TGA, DSC, fluorescence spectroscopy SEM and TEM, Figure 3. The properties analyzed until now indicate that indeed a molecular gel structure is present.² The important feature is the fact that DMF and water formed a gelified system. A discussion is presented on the synthetic method for the new nanoparticles, their properties and potential utility.

This is the first report of the formation of nanoparticles systems using these compounds.

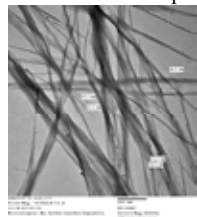


Figure 2.
Nanocolloid
TEM of 1 and
ricinoleic acid.

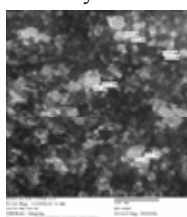


Figure 3. Gel TEM of 3.

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Thermal Characterization of SiO₂ nanofluids for photodynamic applications

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Thermal lens spectrometry (TLS) was used to measure the thermal diffusivity of nanofluids, prepared by dispersion of SiO₂ nanoparticles in water. Complementary techniques as SEM and EDS were also used to characterize the SiO₂ nanoparticles which have spherical shape with diameters varying from 100 to 500 nm average size. In the TLS technique was used the two mismatched mode experimental configuration, with a He-Ne laser as a probe beam and an Ar⁺ ion laser as the excitation one. Experimental determination of the characteristic time constant of the transient thermal lens signal was obtained by fitting the theoretical equation of TLS to the experimental data. From the obtained characteristic time constant it is possible to calculate the sample thermal diffusivities, which were calibrated with water, and the obtained results show an increment in the thermal diffusivity.

Thermal characterization of L-Cysteine nanofluids by using two photothermal techniques

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Thermal diffusivity (D) and effusivity (e) measurements were carried out in L-cysteine nanofluids by using thermal lens spectrometry (TLS) and photopyroelectric (PPE) techniques respectively. In TLS technique was used the two mismatched mode experimental configuration, with an Ar⁺ laser, 514 nm wavelength, used as the heating source and an intensity stabilized He-Ne laser as the probe beam. Experimental determination of the characteristic time constant of transient TL signal is verified theoretically. The PPE technique was used to obtain the sample thermal effusivity (e), in this technique the temperature variation of a sample, exposed to a modulated radiation, is measured with a pyroelectric sensor. Measured thermal diffusivity and effusivity values are in agreement with literature values. The results of the present study could be applied to the detection of tumors by using the L-Cysteine nanofluids.

Synthesis and stability of gold nanoparticles and their functionalization with Cysteine and Cysteine-Glycine

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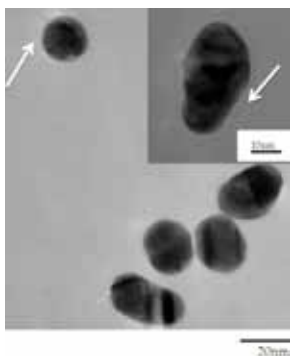


Figure 1. Gold nanoparticles functionalized with Cys-Gly

Recently gold nanoparticles (AuNPs) are intensively applied as vehicles in drug delivery. The present work is dedicated to synthesis, stabilization and functionalization of AuNPs for their further application in drug delivery. AuNPs were prepared using sodium citrate as reduction and stabilizing agent [1], and their interaction with L-cysteine (Cys) and Cysteine-Glycine (Cys-Gly) was investigated varying their molar concentration from 0.5 to 50mM. The formation and functionalization of AuNPs with diameter around 10-20 nm was confirmed by TEM (Figure 1). Characterization of this material was carried out with UV-Vis spectroscopy and Z-potential analysis. UV-Vis measurements revealed the interaction of the AuNPs with Cys and Cys-Gly even for diluted concentrations. Increase of Cys and Cys-Gly concentrations leads to a rapid assembly of gold nanoparticles [2]. A red-shifted peak appeared along with plasmon resonance peak for AuNPs functionalized with Cys that is characteristic of AuNPs aggregation, due to the electric dipole-dipole interaction and a coupling between the plasmons of neighboring particles [2, 3]. AuNPs functionalized with Cys and Cys-Gly were stable after 1 month of storage in air. Zeta potential analysis gave a value -52 mV for the gold colloidal samples after reduction with citrate, while for the functionalized-AuNPs it increased to -33 and -39 mV for AuNPs-Cys and AuNPs-Cys-Gly, respectively. Therefore, the addition of Cys and Cys-Gly reduces the negative surface charge of the gold nanoparticles, thus increasing their tendency for aggregation.

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UV-Vis and FT-IR characterization of gadolinium oxide nanoparticles and singlet oxygen photosensitizer for photodynamic therapy

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Photodynamic therapy (PDT) has emerged as a promising alternative to cancer treatment. However, conventional photosensitizers (PS) have numerous limitations due to their unsuitable pharmaceutical formulations and lack of selectivity. There is an increasing interest in developing ceramic-based nanoparticles (NPs) as carriers for drug delivery [1]. Ceramic-based NPs have several advantages over organic carriers: particle size, shape, porosity, and mono-dispersibility, there is no swelling or porosity change occurring in these particles with change of pH. In this work, 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) adsorption onto the Gd₂O₃ NPs surface was examined. The NPs were obtained by polyol mediated synthesis in a low-temperature process (~180°C) by polyol mediated synthesis and structurally characterized by X-ray diffraction and transmission electron microscopy. The structure of ceramic NPs was a cubic phase with particle size between 50-100 nm. The preparation of Gd₂O₃-attached TCPP in a wide pH range was characterized by spectroscopic techniques (UV-Vis and FT-IR) and ζ potential. The stability of Gd₂O₃ nanoparticles is pH-dependent and was measured by ζ potential. The hybrid Gd₂O₃-attached TCPP was obtained after to define the optimal pH. Absorption spectra were conducted in different samples containing TCPP, NP and NP-attached TCPP at different pH. At pH 2 NP-attached TCPP remains as a homogeneous colloid but a heterogeneous aggregate at pH 3-6 exists. Gd₂O₃-attached TCPP was precipitated when pH \geq 7. This precipitated can be re-dispersed in aqueous solution at pH 7 indicating stability of NP-attached TCPP. Finally we correlated the results for proposing a formation mechanism of stable hybrid.

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Formation and Growth of Gold Nanoparticles by Bio-reduction Inside Epithelial Cells: in vivo

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One of the most exciting challenges of nanotechnology is the interaction between man-made nanostructures with biological structures. Magnetic nanoparticles are of great interest in biomedical applications, are well-known and has been studied its various applications: drug delivery, cell dying, cancer cells diagnostic, hyperthermia, etc.

In the present work we report the synthesis of gold nanoparticles inside live epithelial cells (Au-NPs/LEC), in vivo, upon bio-reduction of aqueous tetrachloroauric ions. Neither a reducing agent nor a protecting chemical were added during this biosynthesis method. Gold nanoparticles in epithelial cells were characterized by UV/VIS spectroscopy and transmission electron microscopy (TEM), samples were prepared by ultramicrotome. The UV/VIS spectrum of epithelial cells treated with an aqueous solution of tetrachloroauric acid shows an absorption band at 553 nm. This is the same wavelength region where aqueous colloidal gold exhibits a surface plasmon resonance (SPR) band. Transmission electron micrographs show that gold nanoparticles are mainly spherical with an average diameter between 20 to 70 nm depending on the relative position of the cell. The electron diffraction pattern of these nanoparticles reveals a crystalline structure whose interplanar distances correspond to fcc metallic gold. It is even possible to observe particles of 2 nm after a cell lysis treatment, despite the cellular material. The present method of gold nanoparticle synthesis using epithelial cells as bioreactors may be used for introducing these nanoparticles into cancer cells thus providing a more efficient treatment with hyperthermia therapy. Compared with conventional procedures of introducing gold nanoparticles intravenously into biological tissue, in situ synthesis may improve both the low cell targeting efficiency and eliminates the contamination of the cells with cytotoxic chemical species used in the preparation of gold nanoparticles ex situ.

Time-resolved photoelectron Spectroscopy: Photoexcitation, Photodesorption and PhotoisomerizationCh. Braun¹, K. Koyasu², S. Proch¹, G. Gantefoer¹¹ *Department of Physics, University of Konstanz, D-78457 Konstanz, Germany*² *Department of Chemistry, Tohoku University Aramaki, Sendai 980-8578, Japan**Christian.Braun@uni-konstanz.de*

Clusters have unique properties and these properties change with each additional atom. But not only the geometrical and electronic structure of the ground states are fascinating, clusters also exhibit unique dynamical properties. They show new and unexpected excited state dynamics and, even more interesting their photochemical properties are very different from the ones of the corresponding bulk surfaces. E.g., electronically excited states may have lifetimes, which are orders of magnitude longer than in the corresponding bulk phases. Photodesorption efficiencies of metal clusters can be close to one, while bulk efficiencies are close to zero. We present results on the dynamical behaviour of size-selected clusters using time-resolved photoelectron spectroscopy. Our work focuses on bare and reacted clusters of simple metals such as Cu, Ag, Au and Al with sizes up to 20 atoms. With our time-resolution of about 100fs we can watch an O₂ molecule desorbing from a metal cluster while it travels along the excited state potential surface. In the future, we aim at time-resolved studies of the photochemical splitting of water molecules adsorbed to small metal clusters.

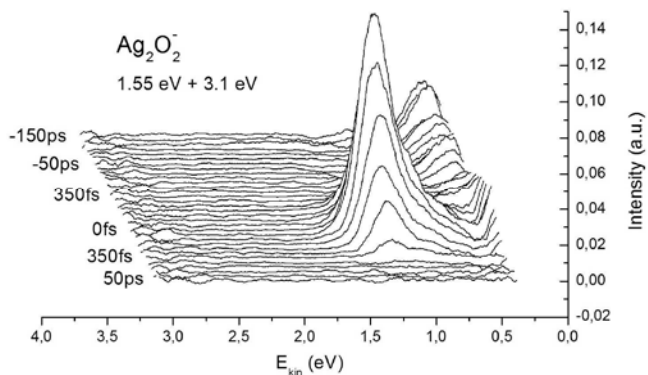


Figure 1: Pump-Probe Photoelectron spectra of Ag₂O₂⁻. With increasing negative delay (corresponding to an excitation with 3.1eV and probe with 1.55eV) the O₂ desorbs and the Ag₂⁻ spectrum appears (peak at 0,5 eV).

Tunable Plasmonic Nanospheres Studied by Femtosecond Pump-Surface Plasmon Probe Spectroscopy

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Electronic relaxation and interparticle electromagnetic coupling processes were examined in thin-shell (<10 nm) hollow gold nanospheres (HGNs) and HGN aggregates. The development of sensitive ultrashort laser-based spectroscopic probes, including femtosecond pump-surface plasmon probe spectroscopy, to investigate dynamics of high surface-to-volume metal and alloy nanostructures will also be discussed. As one example, we found that plasmon-tunable HGNs exhibited an unexpected, but systematic, blue shift of the spectral position of the surface plasmon resonance upon nanoparticle aggregation. Femtosecond time-resolved measurements, high-resolution TEM, and Finite-Difference Time-Domain calculations demonstrated that this blue shift resulted from interparticle coupling, representing a unique effect that is not observed for solid nanospheres. The efficiency of the interparticle coupling can be tailored by controlling HGN aspect ratio over a vast range of particle sizes (20 nm to 80 nm outer diameter). Ultrafast electron-phonon coupling rates were also measured for the thin-shelled HGNs, which decreased upon aggregation, indicating significant delocalization of the Fermi-gas over multiple particles. For example, a 48-nm HGN with 7-nm shell thickness exhibited ultrafast electron-phonon coupling with a lifetime of 300 ± 100 fs. Upon aggregation, this lifetime increased to 730 ± 100 fs. The femtosecond time-resolved surface plasmon data strongly suggested that confinement effects in HGNs allowed for enhanced energy transport over nanometer distances. This effect can be applied to developing more efficient optical and electronic devices, including photovoltaics.

Towards quantum interferometry with metal clusters

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The wave behavior of matter is one of the most essential evidence of quantum physics. Within the last decades research has tried to explore and to benefit of this property in plenty of experiments on studying fundamental phenomena and precision metrology related to the quantum delocalization of cold atoms[1]. But the extension to the coherent manipulation of large clusters and hot complex molecules need special experimental requirements.

A most promising instrument, at present, is an all-optical time domain Talbot-Lau interferometer. It promises to shift matter wave interferometry to masses even beyond the limit of a million atomic mass units [2].

We discuss the advantages of interferometry in the time domain: How such an interferometer can become important for exploring fundamental decoherence and dephasing phenomenon, and how the time domain should improve precision metrology of electromagnetic or structural properties of nanoparticles [3,4].

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Raman scattering in nanostructured semiconductors: an application to Si and Ge

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During the last decade great research efforts have been focused on the nanostructured semiconductors, such as nanowires and porous materials. In particular, Si and Ge are semiconductors with indirect electronic band gaps, i.e., optical transitions require the assistance of phonons. This disadvantage seems to be overcome in their nanostructured counterpart. In this work, a microscopic theory of the Raman scattering based on the local bond-polarizability model is presented and applied to the analysis of phonon confinement in porous silicon and porous germanium, as well as their nanowire structures. Within the linear response theory, the Raman shift is calculated by means of the displacement-displacement Green's function and the Born potential, including central and non-central interatomic forces. For the porous case, the supercell method is used and ordered pores are produced by removing columns of Si or Ge atoms from their crystalline structures [1]. This microscopic theory predicts a remarkable shift of the highest-frequency of Raman peaks towards lower energies, in relation to the crystalline case. This shift is quantitatively analyzed within the quantum confinement framework and compared with the experimental results obtained from porous silicon samples, which were produced by anodizing p-type (001)-oriented crystalline Si wafers in a hydrofluoric acid bath [2].

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Ionization dynamics of embedded Xenon clusters in strong laser fieldsC. Peltz¹, T. Fennel¹ K.-H. Meiwes-Broer¹¹ *Institute of Physics, University of Rostock, Germany**meiwes@uni-rostock.de*

Efficient energy absorption and the emission of highly charged atomic ions are well known effects emerging from the interaction of ultrashort and intense optical laser pulses with clusters. Besides the many corresponding experiments on free clusters, where the dynamics of heating and ionization is relatively well understood, studies on embedded clusters show comparable or even higher charge states at moderate laser intensities^[1]. For a theoretical study of matrix effects on the absorption and ionization processes, such as an early plasmon resonance^[2] or ionization threshold lowering in the cluster medium^[3], we use a semiclassical molecular dynamics approach^[3]. Results on the spatially resolved energy absorption as well as on final ion charge spectra for dual-pulse excitation of $Xe_N@He_M$ as function of laser intensity and size of the matrix will be presented.

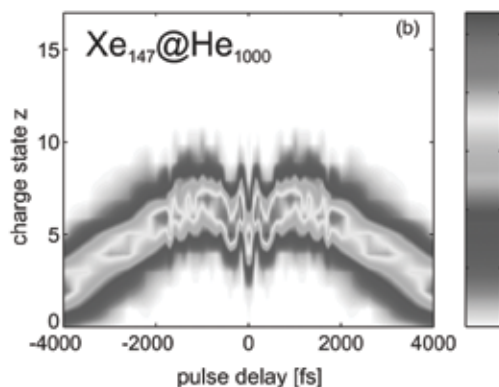


Figure 1: Final ion charge spectra z of xenon ions emerging from the double pulse excitation (each with 50 fs duration at 800 nm and 1×10^{14} W/cm²) of $Xe_{147}@He_{1000}$ for different pulse delays.

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MD-TOF Imaging: A new tool for analyzing energetic ions emitted from clusters exposed to strong laser fieldsC. Schaal¹, R. Irsig¹, J. Tiggesbäumker¹, K.-H. Meiwes-Broer¹¹ *Institut für Physik, Universität Rostock, Germany**meiwes@uni-rostock.de*

The behaviour of metal clusters in intense laser pulses exhibit strong ionisation dynamics, leading to highly charged ion emission. The impact of the pulse structure on the charge state distribution has been studied in detail, see Fennel et al. for a recent review [1]. However less attention has been attributed to the interplay between ionisation and recoil energy. In previous studies, for instance by Ditmire et al. [2], energy distributions have been obtained by time-of-flight measurements combined with a retarding field analysis. Lezius et al. [3] applied magnetic deflection to determine the charge state specific energy distribution. We have extended this method by using a position sensitive delay-line detector (Magnetic Deflection Time-of-Flight Imaging, MD-TOFI), which allows for the analysis of single laser-cluster interactions. As an example, Fig. 1 shows the results of an experiment where nanometer-sized silver particles have been exposed to 2.9 ps laser pulses of 5×10^{13} W/cm². Under these conditions highly charged silver ions are obtained with narrow energy distributions.

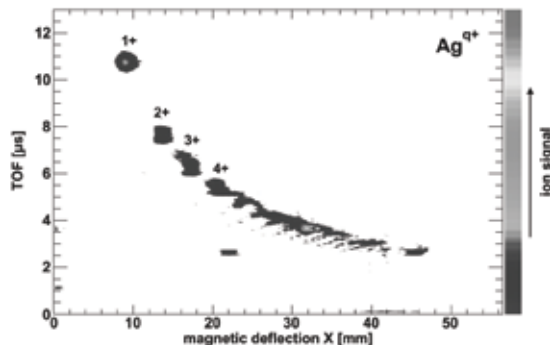


Figure 1: MD-TOF image spectrum of silver ions from large clusters ($N \approx 3000$) irradiated with single laser pulses of 2.9 ps and 5×10^{13} W/cm². Using this method it becomes possible to simultaneously study the ion charge state and energy with high resolution.

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Nanometer-scale optical imaging of collagen fibers using gold nanoparticlesL. C. Estrada¹ and E. Gratton¹¹Laboratory for Fluorescence Dynamics, University of California, Irvine, United States.
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The interaction of fluorophores with metal nanoparticles (NPs) has been extensively studied in recent years [1]. Due to plasmonic effects, metallic NPs can highly modify the emission of fluorescent molecules [2]. We describe a method to move along a collagen fiber, in a controlled manner, in 3D, and with nanometer resolution, gold NPs. As the NPs moves along the fiber, it spectroscopically interacts with the intrinsic fluorophores present in the fiber enhancing the weak fluorescence of the collagen and mapping their 3D structure with high spatial and temporal resolution. We distinguish between conventional 3D Orbital Tracking (OT) [3], and the nano-imaging tracking technique introduced in this work (Gold Enhancement Nano-Imaging, GENI) [4]. In 3D OT, the laser performs an orbit which follows the moving NP by continuously changing its position according to the NP movement. On the contrary, using the GENI technique we move the NP by slowly moving the orbit. In other words, the NP follows the movement of the orbit. Figure 1 shows the trajectories of a conventional 3D OT and of a GENI experiment.

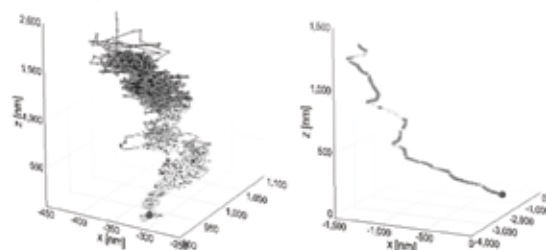


Figure 1: 3D trajectory reconstruction for a conventional orbital particle tracking experiment (left) and for a Gold Enhancement Nano-Imaging experiment (right). The Figure shows the differences between an experiment where we follow the movement of the particle and an experiment where we move in a controlled manner the NP along a collagen fiber.

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Heat diffusion in layered systems excited by a periodic and laser pulse

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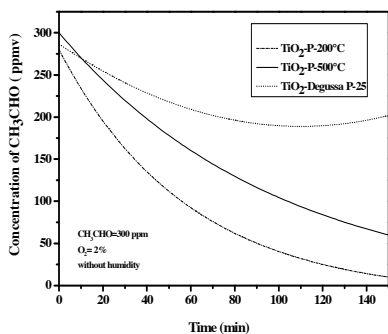
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Periodic and pulsed photothermal techniques provide useful methods based on linear relations between measurable quantities to obtain the thermal diffusivity and thermal conductivity of homogeneous materials. In this work, the effective thermal parameters of two-layered films are defined starting from an homogeneous layer which at the surfaces, produces the same temperature fluctuations and the same photothermal signal that the composite heated by a fast pulse or periodic-laser. Our theoretical model predicts that the effective thermal parameters of the layered system can only be calculated in the limit when the laser pulse duration is smaller than the characteristic time of each layer respectively meanwhile the effective thermal parameters are well defined using a chopped incident laser radiation. The temperature distribution is calculated in each layer by using the Fourier integral and the time-dependent one-dimensional heat diffusion equation with appropriate boundary conditions according to the experimental conditions. Within this approximation, we found an analytical expression for both, the effective thermal diffusivity and thermal conductivity which depend significantly on the thickness and the thermal parameters of each film.

Photodecomposition of acetaldehyde by sol-gel TiO₂ nanoparticlesR Carrera¹, A. L. Vázquez², S. Castillo³¹ *Estudios de Posgrado e Investigación, Instituto Politécnico Nacional, México*² *Departamento de Ingeniería Metalúrgica, Instituto Politécnico Nacional, México*³ *Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, México*

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A variety of environmental problems now affect our world, among which air pollution is one of the largest problems [1]. Nowadays, TiO₂ nanoparticles is an interesting material since, one of the most important targets in the VOC's control is the decomposition of low concentrations of formaldehyde and acetaldehyde in indoor environments through photoassisted reactions. The aim of the present research work was to synthesize by means of the sol-gel method and acid hydrolysis sol-gel TiO₂ nanoparticles with interesting physicochemical properties. The obtained nanoparticles were characterized by the XRD-Rietveld refinement, BET and FTIR techniques and tested in the photodecomposition of acetaldehyde. The acetaldehyde decomposition degree reached by the TiO₂ sol-gel nanoparticles was directly proportional to the brookite mass fraction, but inversely proportional to both the anatase mass fraction and the crystal size.

Fig. 4 Acetaldehyde decomposition as a function of time for the TiO₂ nanoparticles

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Thermal Properties of TiO₂ Nanoparticles doped Solutions

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Thermal properties of nanofluids were studied by photothermal techniques. Thermal lens spectrometry (TLS), photopyroelectric (PPE), Scanning electron microscopy (SEM), and X-ray diffraction (XRD) techniques were employed to investigate the concentration effect of TiO₂ nanoparticles, with spherical shape and 81 nm of average size, dispersed in water. Thermal diffusivity, effusivity and conductivity versus the nanoparticle concentration (gr/ml) were obtained. An increment of the thermal conductivity with the concentration of nanoparticles was obtained, indicating that the high concentration of TiO₂ nanoparticles in fluids could be an efficient means to obtain more efficient nanofluids for some applications as in laser media.

GREEN CHEMISTRY APPLIED TO THE SYNTHESIS OF SILVER AND GOLD NANOSTRUCTURES

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An important aspect of nanotechnology concerns the development of experimental processes for the synthesis of nanoparticles of different sizes, shapes and controlled dispersity. In general, chemical reduction is the mainly method to prepare metal nanoparticles. Recently, the use of eco-friendly synthesis methods is becoming more important. [1] The synthesis of silver and gold nanostructures by a simple procedure, involving the reduction of aqueous Ag^{+1} and Au^{+3} by the extract of *Camellia sinensis* and *Opuntia ficus indica* is described in this work. The procedure offers control over size, shape and optical properties, particularly the position of the surface plasmon resonance. The morphology and optical properties of nanoparticles were characterized by means of transmission electron microscopy (TEM) and UV-Vis spectroscopy, respectively. The effect of reducing agent concentration in the reaction yield, shape and size of nanoparticles, was studied using UV-Vis and monitoring the formation of silver and gold nanoparticles as a function of time by means of TEM. Our results indicate that the reduction agent concentration plays the main role in the formation rate and size of the nanoparticles. The characteristic plasmon for silver nanostructures varies from 405 to 430 nm and for gold nanoparticles from 530 to 550 nm. It is important to mention that the plasmon signal changes as a consequence of the extract concentration. However, the metal ions concentration and the reaction time also play a crucial role in their optical properties and size. We thank F. Ruiz for technical help.

[1] A.R. Vilchis-Nestor, M. Avalos-Borja, S.A. Gómez, José A. Hernández, A. Olivas, T.A. Zepeda. Applied Catalysis B: Environmental 90 (2009) 64–73

Electric field effect in amorphous semiconductor films assembled from transition-metal-encapsulating Si clusters

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We have developed amorphous semiconductor films assembled from transition-metal-encapsulating Si clusters $M@Si_n$ ($M = \text{Mo, Nb and W}$), where $n=7-16$ [1]. While the $M@Si_n$ film has Si networks like hydrogenated amorphous Si (a-Si:H), we observed superior properties owing to a reduction in electronic disorder in Si networks as a result of the $M@Si_n$ clusters being used as the building blocks for the films. For example, the $\text{Mo}@Si_n$ ($n=8$ and 12) films have higher hole mobility of 13 and $32 \text{ cm}^2/\text{Vsec}$ than those in a-Si:H films. While the a-Si:H is a useful material to fabricate thin film transistors (TFT), the carrier mobility is limited up to $0.1 \text{ cm}^2/\text{Vsec}$ because of the presence of electronic disorders. Therefore, the $M@Si_n$ cluster film is an attractive material for TFT applications. We present the electric field effect in the $M@Si_n$ films by demonstrating the I_d - V_d characteristics of our TFT.

Figure 1 shows device structure and drain current (I_d)-drain voltage (V_d) characteristics for the $\text{Mo}@Si_{10}$ film TFT at room temperature. The $\text{Mo}@Si_{10}$ film ($t \sim 15 \text{ nm}$) was synthesized by deposition of hydrogenated $\text{Mo}@Si_{10}H_x$ clusters onto a thermally oxidized Si substrate ($\text{SiO}_2 = 200 \text{ nm}$, N-type, $0.01 \Omega\text{cm}$) at RT, followed by annealing at $\sim 500^\circ\text{C}$ for 10 minutes in an ultra high vacuum for dehydrogenation. The hydrogenated $\text{Mo}@Si_nH_x$ clusters were formed through the gas phase reaction of laser-ablated Mo atoms in a SiH_4 ambient. Al electrodes were formed by vacuum deposition for Source/Drain ($L \sim 100 \text{ nm}$, $W \sim 300 \text{ nm}$) and back gate contact. We observed the electric field effect characteristic of p-channel enhancement mode. The threshold voltage (V_{th}) determined from (I_d)-gate voltage (V_g) characteristics (at $V_d = 0.2 \text{ V}$) was $\sim -3.0 \text{ V}$, and the field effect mobility (at $V_g = -5 \text{ V}$ and $V_d = -1.0 \text{ V}$) roughly estimated from the linear I_d region was $\sim 3 \times 10^3 \text{ cm}^2/\text{Vsec}$. These facts suggest that the $\text{Mo}@Si_{10}$ film is a semiconductor with low density of midgap states. However, the field effect mobility was much lower than that of Hall measurements ($\sim 1.3 \text{ cm}^2/\text{Vsec}$). This is caused by carrier trapping by defect states within the film or at the interfaces.

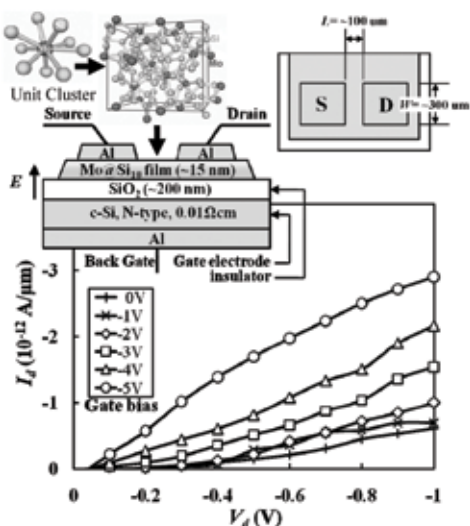


Figure 1: Device structure and I_d - V_d characteristic for the $\text{Mo}@Si_{10}$ film channel TFT.

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Experimental and theoretical study of the superconducting temperature variation with the Barium content of the $Ru(Sr_{2-x}Ba_x)GdCu_2O_{8\pm z}$ system

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The samples of the $Ru(Sr_{2-x}Ba_x)GdCu_2O_{8\pm z}$ system, with $0 \leq x \leq 0.50$ were synthesized by solid state reaction at ambient pressure, where the temperature and time of the synthesis in air were: $T = 1010-1015$ °C and 100-120 hrs., respectively, following by annealed in oxygen flux at 960°C for 6-12 hrs. X-ray diffraction results indicate the formation of the solid solution up to $x = 0.20$. In addition, the Rietveld analysis results, demonstrate that a and c cell parameters of the samples increase with the Barium content and all samples show a tetragonal unit cell with a space group $P4/mmm$. The results of the temperature dependence of the electrical resistivity show a superconductor behavior where the superconducting transition temperature (T_c) depends with the Ba concentration and the annealing time in oxygen flux. In the other hand to explain this behavior, an appropriate association between the content of Ba with the hole doping (p) was proposed, and a good approximation between experiment and theory was obtained applying the Generalized Hubbard Model with charge-density interaction hoppings [1]. We conclude that increase of second neighbor hopping t' could to explain the enhance of T_c and the location of the optimal hole doping.

[1] Luis A. Pérez, J. Samuel Millán, Chumin Wang, *Physica B* **359**, 569-571 (2005).

POSTER SESSION B

B-01 *Protected clusters, nanocrystals, and self assembly*

B-02 *Electronic structure and quantum effects in nanostructures*

B-03 *Cluster reactivity and nanocatalysis*

B-04 *Nanomagnetism*

B-05 *Optical properties*

B-06 *Technological applications*

Counting the Atoms in Supported, Monolayer-Protected Gold Clusters

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It was recently demonstrated that size-selected atomic clusters can be used as novel mass standards [1] to “weigh” other nanoparticles, via quantitative high angle annular dark field imaging in the scanning transmission electron microscope (HAADF-STEM). We have applied this “atom counting” method to the problem of monolayer-protected Au₃₈ (MP-Au₃₈) clusters – do they really contain 38 Au atoms? We co-deposit size-selected Au clusters and MP-Au₃₈ nanoparticles on the same TEM grid. Quantitative analysis shows that the integrated HAADF intensity for the nominally MP-Au₃₈ clusters corresponds to 47 Au atoms equivalently. However, once the contribution due to the ligands is calibrated, the MP-Au₃₈ clusters are found to contain 38 ± 2 Au atoms [2].

The detailed atomic structure of the MP-Au₃₈ clusters was investigated using aberration-corrected STEM. Optimized experimental conditions were developed to minimize the instability of these small clusters under the electron beam. We obtained serial-acquisition images at a high speed (0.2 s/frame). By comparing these serial images, we found many clusters have an elongated projected shape, with an aspect ratio up to ~ 1.4 . Thus, the theoretically predicted preference for a prolate low-energy structure was confirmed in the experiment, but not the predicted dumbbell shape.

[1] N. P. Young, Z. Y. Li, Y. Chen, S. Palomba, M. Di Vece, R. E. Palmer, Phys. Rev. Lett. 101 (2008) 246103. Also see Research Highlights Extract, Nature Nanotech. 4(2009)76

[2] Z. W. Wang, O. Toikkanen, F. Yin, Z. Y. Li, B. M. Quinn, R. E. Palmer, J. Am. Chem. Soc. 132 (2010) 2854

Structural properties of bare Au₄₉, Au₇₉, and Au₈₉ clusters, and their relation with the metallic core of the ligand-protected Au₁₀₂(SR)₄₄ cluster

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After crystallization, x-ray structure determination, and previous density functional calculations of the p-mercaptobenzoic acid (p-MBA)-protected Au₁₀₂(p-MBA)₄₄ cluster [1], it had been shown that this system is best described as consisting of an approximately D_{5h}-symmetric Au₇₉ metallic core with a protective gold-thiolate layer of composition Au₂₃(p-MBA)₄₄.

Here, we study the lowest-energy (most stable) structures of the unprotected Au₄₉^Z, Au₇₉^Z, and Au₈₉^Z (Z=-1,0,1) clusters, combining a global optimization technique (genetic algorithms) and a many-body Gupta potential, plus a further local minimization, using density functional theory (DFT) within the generalized-gradient approximation (GGA) [2]. The objective is to compare the known structures of the different core metallic layers forming the Au₁₀₂(p-MBA)₄₄ protected cluster with the most stable structures of the bare gold clusters containing the same number of atoms. Our results show that the Marks decahedral-Au₄₉, D_{5h}-Au₇₉, and C₅-Au₈₉ cluster structures, characterizing the metallic cores of the Au₁₀₂(p-MBA)₄₄ protected cluster, correspond to high energy isomers of the potential energy surface of bare 49-, 79-, 89-atom gold clusters, respectively. On the other hand, the lowest-energy (most stable) isomers obtained in this study for bare Au₄₉^Z, Au₇₉^Z, and Au₈₉^Z (Z=-1,0,1) clusters have structures with low or null symmetry. These results suggest that the physicochemical properties of the internal metallic core of ligand-protected gold clusters, with the present size, would not be related to the intrinsic properties of the most stable bare Au clusters composed by an equivalent number of atoms.

[1] Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D.; *Science* **2007**, *318*, 430; Whetten, R.L.; Price, R. C.; *Science* **2007**, *318*, 407.

[2] Santizo, I. E.; Hidalgo, F.; Pérez L. A.; Noguez, C.; Garzón I. L.; *J. Phys. Chem. C* **2008**, *112*, 17533, and references therein

**Assembling new materials from Ta@Si₁₆F super molecular units:
first principles calculation of aggregates, wires, and bulk phases properties**

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Motivated by recent experiments suggesting that Ta@Si₁₆⁺ is a very stable cation with a high Homo-Lumo gap [K. Koyasu et al, J. Phys. Chem. A **111**, 42 (2007)], we have studied, by means of first principles calculations, the structural and electronic properties of the following systems: i) Ta@Si_n⁺ clusters in the range n = 14-18; ii) (Ta@Si₁₆F)_m aggregates with sizes m = 1-8 formed by Ta@Si₁₆F molecules; iii) infinite wires formed by stacking triangular (Ta@Si₁₆F)₃ aggregates along the vertical axis; and iv) bulk fcc and NaCl phases of Ta@Si₁₆F. The projected density of states of these systems show that the Homo-Lumo gap of the superatom unit is reduced by a factor of ~ 4. Many near degenerate isomers were obtained corresponding to different F bond sites, but with very different dipole moments.

In Figure 1 is represented the lowest energy configuration (or an equilibrium local minimum) of some of these systems: a) for n = 16 cations we have found two nearly degenerate isomers with C_{3v} and D_{4d} symmetry, respectively; b) the molecule Ta@Si₁₆F, which is formed preferably with the D_{4d} isomer of Ta@Si₁₆ super-atom; c) (Ta@Si₁₆F)₆ formed by two triangular aggregates stacked along the vertical axis and twisted 60° each other; d) part of the optimized infinite wire which has the previous aggregate as the unit cell; e) Ta@Si₁₆F bulk within fcc phase. The systems in c), d) and e) are local minima, and we have estimated their stability by means of short runs (10 picosecond) of first principles molecular dynamics at 300 K.

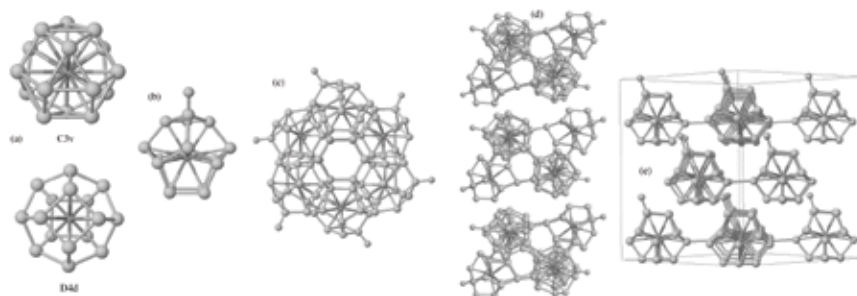


Figure 1: Equilibrium configuration of several systems (see text) assembled from Ta@Si₁₆F.

We acknowledge the financial support of Spanish Ministry of Education and Science (Mat2005-03415) and Junta de Castilla y León (GR120). H. C-L. acknowledges support from DFG of Germany.

On the Origin of the Optical Activity Displayed by Chiral-Ligand-Protected
Metallic Nanoclusters.

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Different mechanisms, such as the inherently chiral metallic cluster core, the dissymmetric field effect, and the chiral footprint model, have been proposed to explain the nonzero circular dichroism (CD) spectra in ligand-protected metallic clusters since it was observed that this kind of materials at nanometric scale exhibit optical activity when chiral molecules are used as protecting units. Even though these theories are useful to explain the optical activity in chiral ligand-protected gold nanoclusters, they have limitations that do not allow for a complete explanation about these phenomena. In this work [1], the CD of the ligand-protected $[\text{Au}_{25}(\text{SR})_{18}]$ cluster is studied using an efficient first principle formalism to gain insight into the physicochemical origin of the optical activity measured for the glutathione-protected $[\text{Au}_{25}(\text{SG})_{18}]^-$ cluster. Two types of ligands, the achiral methylthiolated and the chiral L-cysteine were considered for the calculations. The obtained CD spectrum of the cysteine-protected cluster, with $\text{R}_{\text{cys}} = \text{C}_\beta\text{H}_2\text{-C}_\alpha\text{H}(\text{NH}_2)\text{COOH}$, shows good agreement with the experimental data obtained for the glutathione-protected cluster. Analysis of the calculated CD spectra of the peculiar two-shell metallic core and the two distinct thiolate-Au binding modes existing in the $[\text{Au}_{25}(\text{SR}_{\text{cys}})_{18}]^-$ cluster showed that the weak CD signal due to the slight distortion of the cluster core is enhanced by the dissymmetric location of the ligands. This result shows that the inherently chiral metallic cluster core mechanism and the dissymmetric field effect proposed to explain the optical activity of chiral-ligand-protected metallic clusters cannot be differentiated but they are acting concurrently. It is also predicted that the CD line shape should be highly sensitive to the orientation of the thiolate ligands forming the protecting layer and to the stability of the thiolate-Au binding modes. In the other hand, it was found that methylthiolated-protected cluster shows a non-zero (CD) spectrum. This fact suggests that ligand-protected metallic clusters protected with achiral molecules can exhibit optical activity as well as the clusters protected with chiral molecules.

[1] A. Sanchez-Castillo, C. Noguez, and I.L. Garzon, *J. Am. Chem. Soc. (Comm.)* **132**, 1504 (2010).

Metalloid Clusters as Superatoms

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Metalloid clusters, aggregates of metal atoms stabilized by a surface ligand shell, are an interesting intermediate state of matter between molecular complexes (that contain individual metal atoms M in various oxidation states) and the reduced M^0 atoms in the bulk metal. The bonding in these systems is dominated by metal-metal bonds versus metal-ligand bonds. Various metalloid clusters of Group III ($M = \text{Al, Ga}$) elements have been isolated and characterized using experimental and theoretical techniques [1]. Previous studies have presented a case against the “jellium model” as the source of the stable behavior found for metalloid clusters composed of aluminum [1]. Here we illustrate that the stability of experimentally isolated aluminum clusters with a variety of ligands can be explained using the delocalized electron shell model with a proper counting of electrons taking into account the ligand chemistry. Thus, metalloid clusters with Al core may be considered “superatoms” similar to the ligand-stabilized gold clusters [2].

[1] H. Schnöckel, Dalton Transactions **33**, 4344 (2008).

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Synthesis and electrical properties of nanocrystalline silicon/silicide composite films

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Silicon nanocrystals (nc-Si's) show fascinating properties, which have never been observed in a bulk Si, due to quantum size effects. For example, luminescence energy of nc-Si's is tunable from a bulk band gap value of 1.12 eV to a visible region at room temperature by changing the size of the nc-Si's [1]. Recently, the nanostructured Si, which consists of the cascade connection of nc-Si's, attracts attention as thermoelectric materials because grains of the nc-Si's attribute to the scattering of phonons at interfaces, leading to large reductions in lattice thermal conductivity [2]. Thus, the size of nc-Si's is a key parameter to control the thermal conductivity of the nanostructured Si.

To control the size of nc-Si's in the nanostructured material, we developed the synthesis method of nc-Si's/nanocrystalline transition metal (M) silicide composite films using a phase separation of Si and silicide regions from amorphous M-Si alloys. The M-Si silicides, such as MSi₂, have mainly metallic properties. For the application of the thermoelectric material, nanostructured materials should be a semiconductor. Here, we selected Mo-Si alloys with composition of Si/Mo= 10-12, because the hexagonal-MoSi₂ is a semiconductor. Amorphous Mo-Si alloy films with thicknesses up to 1 μm were deposited on silica substrates by the dc magnetron sputtering in

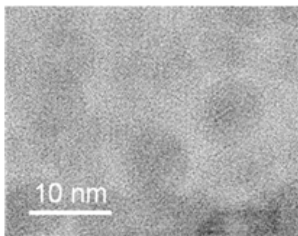


Fig. 1. Typical TEM image for nanocrystalline silicon/Mo silicide composite films.

Ar of 3.3×10^{-3} Torr. After the deposition, to synthesize nc-Si's, thermal annealing was performed at 800 °C for 30 minutes in Ar presence. Raman scattering spectra indicate synthesis of nc-Si's and the hexagonal MoSi₂. Figure 1 shows transmission electron microscopy (TEM) image of the annealed Si/Mo=12 film. We observed spherical the nc-Si's and nanocrystalline hexagonal MoSi₂ (nc-h-MoSi₂) composite films. The dark contrast areas correspond to the nc-h-MoSi₂. The averaged diameter was estimated to be ~8 nm for both of

nanocrystals. Electron beam diffraction patterns indicate that the nc-Si's and nc-h-MoSi₂'s consist of single crystal Si and hexagonal MoSi₂, while Mo₃Si₅ pattern is observed as a minor case.

We synthesized the nanostructured Si material consisted of nc-Si's and nc-h-MoSi₂'s as the result of the phase separation from amorphous Mo-Si alloys. The relationship between electrical properties and nanocrystal size will be discussed.

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Electric Deflection Measurements of Sodium Clusters in a Molecular Beam

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Rotationally averaged polarizabilities and intrinsic electric dipole moments of sodium clusters are measured and reported. The experimental method is a molecular beam deflection. Our precision is the highest (<5%) and the range of the cluster sizes is the broadest to date ($\text{Na}_{10} \sim \text{Na}_{300}$). Compared to the earlier measurements, our data covers all sizes with no gaps up to the largest cluster. The fine structure in the polarizability curve is previously unobserved. We have carefully ruled out several possible explanations. And we find an earlier existing theory could explain the facts but will lead to magic numbers which were not seen in some previous experiments. A detailed theory is needed to understand the behaviors we see.

Intrinsic electric dipole moments (EDM) of sodium clusters are probed to answer the intriguing question: Do metal clusters develop electric dipole moments like molecules? Some theories have predicted the existence of EDM in ground state sodium clusters and gave their magnitudes. We put upper bounds on the EDM of sodium clusters and find that they are orders of magnitude smaller than the predictions. This provokes an interesting question: how can one define metallicity in metal clusters?

Our measurements are performed at cryogenic temperature 20 Kelvin. Temperature dependences are investigated (20 ~ 80 Kelvin). In this temperature range the clusters are believed to be in their vibronic ground states.

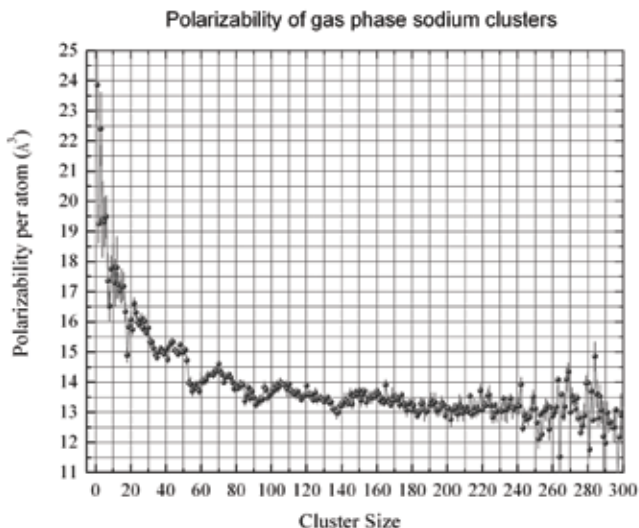


Fig1. Average static dipole polarizability of free sodium clusters at 20 Kelvin.

Protectant-free production of gold nanoparticles with less than 2 nm diameter using carbon nanotubes

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Metal nanoparticles with the diameter of less than 2 nm have attracted much attention because of their prominent quantum size effects. These small nanoparticles were usually produced using protectants such as PVP and SDS molecules in order to stabilize their reactive surface, although these protectants themselves tended to make their prominent properties lower. In this study, we examined protectant-free production of gold nanoparticles using carbon nanotubes.

A droplet of HAuCl_4 ethanol solution was deposited on a Cu grid coated with carbon nanotubes, and was irradiated by a high-pressure type Hg lamp for 3 min. The obtained grid was observed using a field-emission type scanning electron microscopy.

Figure 1 shows a bright-field STEM image of the grid thus prepared. Small gold nanoparticles are found to be formed on carbon nanotubes. The diameter of these nanoparticles is typically observed at 2.0 nm while some of them are observed as small as 1.5 nm in diameter. In addition, the observed nanoparticles seem to be well isolated each other. Taking into consideration of the present recipe without using any protectant molecules, the produced small gold nanoparticles were considered to be bound to carbon nanotubes and to be prevented from aggregation.

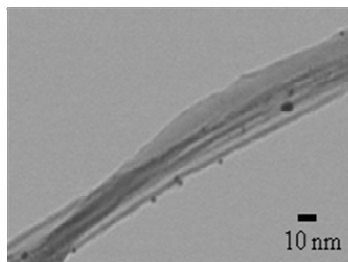


Figure 1: Bright-field STEM image of the nanoparticles formed on carbon nanotubes.

Pb nanoparticles produced by ion implantation in Si and Al

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Pb nanoparticles are synthesized by high fluence ion implantation in Si(100) wafers and in single crystalline epitaxial Al films and subsequent annealing. Their size (5-20 nm) and size distribution was tuned by varying the implantation fluence and temperature, as well as the annealing temperature and time. The size and structural properties were characterized by Rutherford backscattering spectrometry, x-ray diffraction, small angle x-ray scattering and transmission electron microscopy. Different growth regimes could be distinguished and identified by the different scaling behaviors of the average particle radius with the implantation parameters. The crystal structure of the Pb nanoparticles and their epitaxial orientation and strain in the Si and Al matrix are studied in detail.

The superconducting properties of the Al films with implanted Pb nanoparticles are investigated by electrical transport measurements for different volume ratio's of Pb nanoparticles in the Al matrix. The superconducting critical temperature of this hybrid system was found to increase with growing volume ratio of the Pb nanoparticles in a way consistent with superconducting proximity effect models for bilayer systems.

This research has been supported by the Fund for Scientific Research - Flanders (FWO) as well as by the Belgian Interuniversity Attraction Poles (IAP) and the Flemish Concerted Action (GOA) research programs.

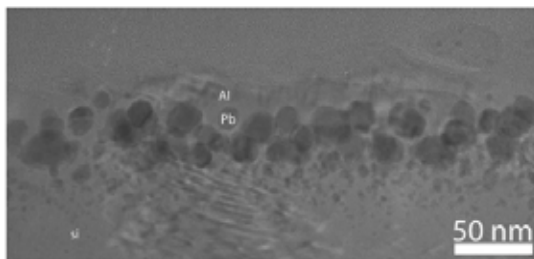


Fig. 1: Cross-sectional TEM picture of Pb nanoparticles (10-25 nm) embedded in an Al-film.

Synthesis of highly reactive copper nanoparticles by photo irradiation

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Copper nanoparticles have attracted much attention because of their optical, catalytic, mechanical and electrical properties. However, copper nanoparticles have been synthesized under hard condition such as high temperature. In this study, we investigated synthesis of copper nanoparticles by photo irradiation under room temperature. The obtained products were examined by using scanning transmission electron microscopy (STEM) and UV-vis absorption spectroscopy.

Copper (II) acetate monohydrate and polyvinylpyrrolidone were dissolved into ethanol. This solution was mixed with an aqueous solution of sodium sulfite. The mixed solution was irradiated by a high-pressure type Hg lamp at room temperature for 5 hours. UV-vis absorption spectrum for the obtained solution was measured. STEM images were also observed using a collodion-coated Cu grid with the obtained solution.

Figure 1 shows UV-vis absorption spectrum of the obtained solution. The absorption peak was observed at 570 nm. This peak can be assigned to the surface plasmon resonance absorption of copper nanoparticles. While this peak disappeared when the obtained solution was exposed to the fresh air, the peak reappeared when the solution was irradiated by the lamp again. These results suggest that synthesized copper nanoparticles have a high reactivity.

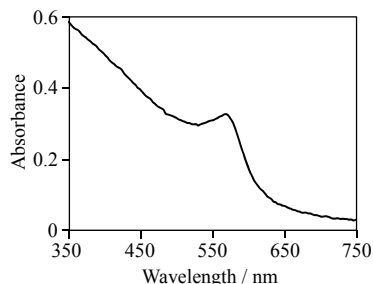


Figure 1 : UV-vis absorption spectrum of produced copper nanoparticles.

Production of gold nanoparticles with carbon nanotubes by laser ablation in solutionT. Endo¹, F. Mafune², T. Takahashi¹, N. Nishida¹, H. Tanaka¹¹ *Department of Applied Chemistry, Institute of Science and Engineering, Chuo University, Japan*² *School of Arts and Sciences, The University of Tokyo, Japan**crotakahiro@yahoo.co.jp*

Carbon nanotubes are regarded as one of the most prospective nanomaterials for building blocks. Especially, nanocomposites of the carbon nanotubes and metal nanoparticles are desired to be produced because they are expected to realize nanocircuits. In this purpose, it is essentially important to establish a technique to attach metal nanoparticles onto carbon nanotubes. In this study, we examined to produce gold nanoparticles by laser ablation in solution suspending carbon nanotubes. The obtained products were analyzed by field-emission type scanning electron microscopy (FESEM), UV-vis absorption spectroscopy and energy dispersive X-ray spectroscopy (EDX).

A gold plate was placed in the bottom of a glass vessel filled with 10 mL of carbon nanotube suspension in pure water, and was ablated by Nd:YAG laser with fundamental oscillation operated at 10Hz. Afterwards, the solution containing suspended carbon nanotubes was deposited on a Cu grid, and was dried. The grid specimen thus prepared was observed using an FESEM. In addition, a solution without mixing carbon nanotubes was also prepared with similar procedure and observed in comparison.

In the STEM images of the specimen prepared with carbon nanotubes, most of the gold nanoparticles were observed on carbon nanotubes, and they seemed to be isolated each other. Figure 1 shows a histogram of number of the observed nanoparticles plotted as a function of particle diameter. The diameter distribution is composed of two peaks positioned at 4 and 15 nm. On the other hand, diameter of gold nanoparticles prepared without carbon nanotubes was observed dominantly at 15 nm.

The coincidence of the diameter at 15 nm indicates that the 15-nm nanoparticles were firstly formed in the solution and were subsequently deposited onto carbon nanotubes. Meanwhile, efficient production of the smaller nanoparticles prepared with carbon nanotubes indicates that these nanoparticles were directly formed on carbon nanotubes. This picture is also plausible considering prevention of aggregation induced by migration because the nanoparticles probably stuck to carbon nanotubes.

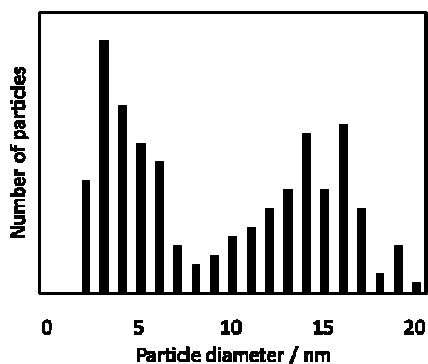


Figure 1: Diameter distribution of gold nanoparticles observed on carbon nanotubes.

Control of the crystalline structure of 3D silver nanocrystal assemblies

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5 nm Silver nanocrystals are synthesized in mixed functionalized reverse micelles and coated by either decanethiol (C10) or dodecanethiol (C12). The main parameters, which dictate the supracrystalline structure of the silver nanocrystals self-assembled at the micrometer scale, are evidenced. They are the alkyl-chain length, the deposition temperature, the concentration of the colloidal solution and the nature of the substrate. By varying the deposition temperature (from 15° to 50°C), from the same batch of nanocrystals (same size, same coating agent), dense (fcc, hcp) and loose (bcc) supracrystals or disordered arrangements (rcp) are produced [1]. By tuning the nature of the substrate (HOPG or amorphous carbon) and its temperature, the final size of the supracrystals is controlled. A solvent with a high boiling point (Toluene, decane, dodecane, toluene) is optimum to produce thermodynamically stable arrangements. Whatever the substrate temperature is, a too fast evaporation rate leads to metastable 3D arrangements.

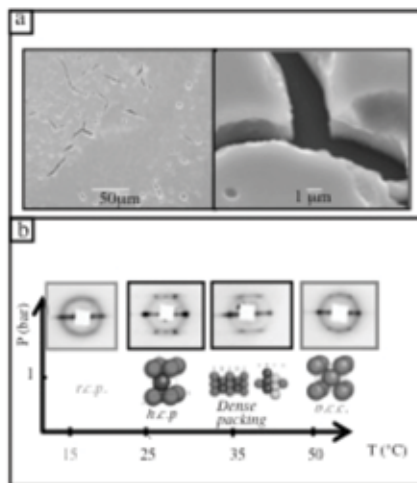


Figure 1: a) Typical SEM image of a 3D film made of silver nanocrystals deposited on a HOPG substrate called supracrystal and the corresponding tilted image, b) Crystalline phase diagram of 3D assemblies of silver nanocrystals coated by dodecanethiols.

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Photochemical Synthesis of Noble Metal Nanoparticles Arrays Based on Block Copolymer Templates

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The assembling of nanocrystals into ordered two and three-dimensional array is highly required because of its potential application in various fields such as electronics, photonics, sensors, and catalysis. Such strategy has become a hot topic in recent years. Among various methods for the assembling of nanocrystals, block copolymer templates have drawn much attention owing to their great capability to self-assemble into well-ordered nanostructures[1]. Such nanostructures can also be used to manipulate the patterning of inorganic materials, among which noble metal nanoparticle arrays have been studied intensively because of their unusual properties[2-4].

Here we present a method to synthesize ordered noble metal (Ag, Au, Pt) nanoparticle arrays by UV-assisted reduction of noble metal ion from polystyrene-block-poly (4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer[5]. The phase-segregated PS-*b*-P4VP templates with ordered patterns are prepared by spin-coating of PS-*b*-P4VP chloroform solution on silica substrate and subsequent solvent-annealing. Noble metal ion solutions are dropped onto the PS-*b*-P4VP film and metal ions are selectively adsorbed on poly (4-vinylpyridine) (P4VP) domains. With UV irradiation, these metal ions are reduced and aggregated to form hierarchical self-assembling metal nanostructures which decorate the P4VP domains. A dependence of the surface plasmon resonance (SPR) of the metal nanoparticle arrays on UV exposure time is demonstrated.

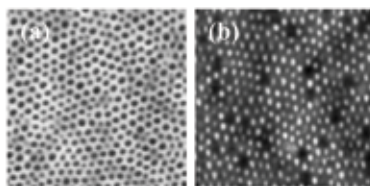


Figure 1 AFM height image($1\mu\text{m}\times 1\mu\text{m}$) of (a) PS-P4VP template, (b) Ag^+ -loaded PS-P4VP template with UV-irradiation of 2h., respectively.

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[3] Z. T. Shi, M. Han, F. Q. Song, J. F. Zhou, J. G. Wan, G. H. Wang, *J. Phys. Chem. B* **110**, 18154 (2006)

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Self-assembly Film of Cholesterol Molecules on the Au (111): An STM Study

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Abstract

The study is based on development of new methodology for preparation and the STM visualization of monomolecular thick films of cholesterol consisted of individual molecules or cholesterol supramolecular aggregates. Films were prepared on the Au (111) as a substrate, using different solvents: water, methanol and ethylene glycol, at different concentration range. Imaging was carried out by STM (ex-situ, in air) in order to characterize the topographic properties of the cholesterol films, at the nano-scale level.

we observed that surface morphology of the cholesterol film depends on the used solvent, in all cases, large vacancies (defects) in the film were detected. Beside identification and visualization of the individual cholesterol molecule in the adsorbed film, we also successfully prepared and visualized molecular films of the cholesterol self-assemblies. A self-assembly unit consists of two cholesterol molecules, organized into very specific, quasi-quadratic boxes (0.68 nm x 0.68 nm). Images and models, developed in our study, clearly revealed that supramolecular boxes of the cholesterol dimers are organized into monolayer thick film and connected via interactions between the electron rich cyclic hydrocarbons. In the center of each supramolecular box a quadratic cavity with atomic space dimensions: 0.278 nm x 0.278 nm, and depth of 0.173 nm, was found. Boxes are separated by insulating (electron poor) aliphatic chains.

Formation and characterization of the cholesterol supramolecular assemblies (boxes) at the Au (111) substrate are very promising issue from the point of the surface functionalization and design of the nano-scale devices.

LDA APPROXIMATION BASED ANALYSIS OF THE ADSORPTION OF THE O₃ BY BORON NITRIDE CLUSTER

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Through first principles calculations based on Quantum Mechanics according to the Theory of Density Functional (DFT) at the LDA (PWC) investigates the adsorption of the molecule of ozone (O₃) by boron nitride sheet (represented by C_nH_n-like a cluster) [1]. 4 geometries are investigated, parallel to the N-B-N bond, perpendicular to B, the N and central hexagon. The results indicate that the molecule is adsorbed with an energy of 0.41 eV in a planar geometry for optimal geometry of boron nitride, also reacts with epoxide group to form a sheet with hexagonal lattice and an oxygen molecule into an unstable configuration, analogous to that reported in the literature for adsorption of the molecule of O₃ by the graphene.

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E. Chigo Anota, H. Hernández Coccoletzi, M. Salazar Villanueva, accepted in *Phys. Status Solidi C* (2010);

E. Chigo Anota, H. Hernández Coccoletzi, M. Salazar Villanueva, accepted in *Phys. Status Solidi C* (2010);

E. Chigo Anota, H. Hernández Coccoletzi, M. Salazar Villanueva, accepted in *J. Nanosci. Nanotechnol.* (2010)

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Short range interactions and aurophilic attraction in $[\text{ClAuL}]_2$ model dimers and the role of the neutral ligand L

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A systematic investigation of the effect of the ligand *L* on the aurophilic $\text{Au(I)} \cdots \text{Au(I)}$ closed shell interaction in perpendicular $[\text{ClAuL}]_2$ model systems (see Fig. 1) is carried out. An analogous study of the effect of the halide *X* (here Cl) exists [1], and showed a correlation with the softness of the ligand *X*. In this work, we study the correlation with *L* = N-heterocyclic carbenes (NHC), cyclic diphosphinocarbenes (PHC), NF_3 , CO , CN-Me , PF_3 , SH_2 , NH_3 , CP_2 , H_2O , pyridine, CPH_3 , C_3H_2 , and a model system CN_2 . A novel mathematical expression on short range interaction (van der Waals-type equation) to explain the attraction observed in the series of complexes, is derived. The NHC's yield stronger interactions than PH_3 . The spatial orientation of certain ligands in a 'paddle' configuration can also play an important role on the strength of the interaction. All are examples on aurophilicity.

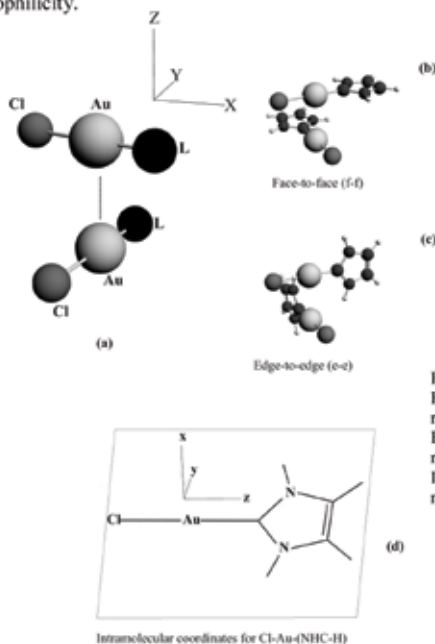


Fig.1 (a) $[\text{ClAuL}]_2$ model dimer. (b) Face-to-face orientation for a representative of the series. (c) Edge-to-edge orientation for a representative of the series. (d) Intermolecular coordinates for monomer system.

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Study the electronic responses of individual nanoparticles by electron energy loss spectroscopy in a transmission electron microscope

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Electron energy loss (EEL) spectroscopy (EELS) in a transmission electron microscope equipped with a cold field emission gun exhibits the spatial resolution of 1nm and the energy resolution of 0.25eV, which allows the study of the features of the electronic responses of individual nanoparticles.

Here we show two examples. (1) Plasmon coupling of dimers of Ag nanoparticles is studied by the EELS as shown in Fig 1a [1]. The spectroscopic images in the above are extracted from 2.8eV, 3.4eV and 3.6eV respectively, where one can see the preferable exciting points of the features around the Ag nanoparticles. With the aid of DDA calculation, the three features are identified as the in-phase plasmon coupling, non-coupling and anti-phase coupling modes. The in-phase mode is able to conduct the light transportation, which redshifts from the 3.4eV at large spacings to 2.7eV near touching. (2) We employ both the core-loss EELS and the valence EELS on the same Co-doped ZnO nanoparticles by spatially mapping the dopant concentration distribution via the core-loss EELS and simultaneously by identifying the dopant features in the accumulated valence EELS via the measured dopant richness. Three Co dopant states related to the local DOS are successfully determined (see the above in Fig. 1b). The experimental inputs feed the first-principles calculation, which generates the full electronic structure of the doped ZnO nanoparticles [2].

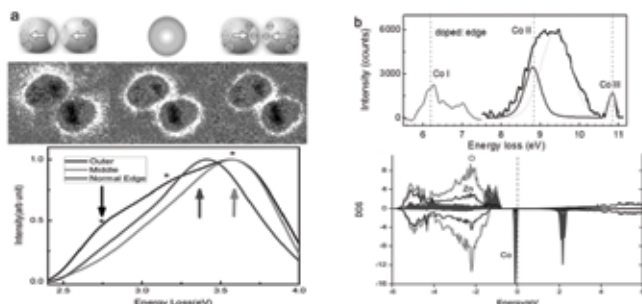


Figure 1: a shows the spectroscopic images of a dimer of Ag nanoparticles and the EEL spectra extracted from the selected points. b shows the extracted EEL features of the Co dopant in an individual ZnO nanoparticle in the above inset and the simulation of its electronic structure below.

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The new ClusterTrap setup

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ClusterTrap [1] has been designed to investigate properties of atomic clusters in the gas phase with particular emphasis on the dependence on the cluster size and charge state. The combination of cluster source, Penning trap and time-of-flight mass spectrometry (ToF-MS) allows a variety of experimental schemes including collision-induced dissociation, photo-dissociation, further ionization by electron impact, and electron attachment. Due to the storage capability of the trap extended-delay reaction experiments can be performed [1].

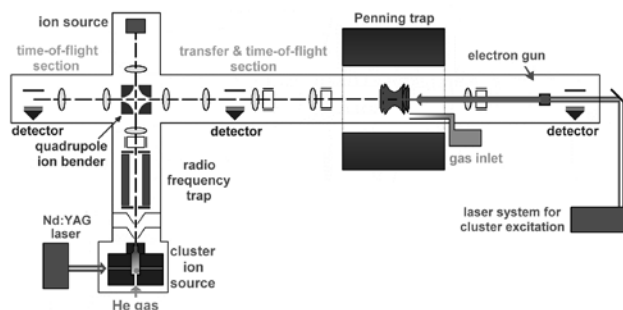


Figure 1: The modified ClusterTrap setup.

Several modifications of the older design [2] have resulted in a new setup (Fig. 1). In particular, an electrostatic quadrupole deflector allows the coupling of several sources or detectors to the Penning trap. By source attachment perpendicular to the main axis of the apparatus neutrals are separated from the beam of charged clusters to be captured in the trap. In addition, ToF-MS for product-ion analysis can now be performed into the direction of the deflector and sources, which results in better access to the trap region from the other side of the superconducting magnet. Furthermore, a linear radio-frequency quadrupole trap has been added for accumulation and ion bunching and by use of a drift tube the kinetic energy of the cluster ions can be adjusted on their way towards or from the Penning trap. Recently, experiments on multiply negatively charged clusters [3] have been resumed which will be described as well as the details and performance of the new ClusterTrap features.

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Precise ab initio calculation and the nature of binding in the 3d transition-metal dimer Sc₂

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The problem of calculation of the electronic structure of transition-metal clusters still presents a challenge for computational chemistry. The reason is that the expansion of the ground state wave function on electronic configurations does not contain a principal configuration and a large number of reference configurations must be treated equally. Thus the multi-reference (MR) approaches are, in general, mandatory.

Although the Sc atom has only one 3d electron, its dimer presents an extremely complex system, since in the dimer there are 270 low lying almost degenerate molecular states. The calculation at the MR CISD(+Q)/cc-pV5Z level showed that the Sc₂ has its minimum at 5.20 Å and corresponds to a quintet, $^5\Sigma_u^-$, which is in an agreement with ESR experiment and previous precise calculations. The triplet $^3\Sigma_u^-$ state is located about 1.1 kcal/mol above.¹ Spin S = 2 can be realized only if one of Sc atoms dissociates in an excited state. It is proved that in the asymptotic dissociation limit one of Sc is created in the second quartet excited state Sc (3d¹4s¹4p¹; 4F_u).² Studies at the complete basis set (CBS) limit give the binding energy of Sc₂ D_e = 50.25 kcal/mol (with respect to the dissociation limit: Sc (3d¹4s²; 2D) + Sc (3d¹4s¹4p¹; 4F_u)) and D_e = 9.15 kcal/mol (in respect to the experimentally measured dissociation limit Sc (3d¹4s² 2D_g) + Sc (3d¹4s²; 2D_g)). In contrast with the Mn₂ dimer, which is bonded by the weak van der Waals (dispersion) forces with D_e = 0.62 kcal/mol,³ the Sc₂ dimer is valence-bonded molecule due to a strong attractive interaction between Sc in the ground state and Sc in an excited state. The main contribution in bonding has a 4sσ type as a result of interaction of the two atomic 4s orbitals.

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Photoluminescence dynamics of organic molecule-passivated Si nanoclusters

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Si nanoclusters have attracted much attention due to their highly-efficient photoluminescence (PL). The factors that dominate the PL of Si nanoclusters are considered to be quantum size effects, surface states, defects and so on, but details are still unclear. In this work, we have carried out the PL and time-resolved PL measurements of organic molecule-passivated Si nanoclusters in order to elucidate the intrinsic relationship between quantum size effects and PL in Si nanoclusters without the effects of defects and surface states. We synthesized phenyl-passivated Si nanoclusters with the diameters of 1.5 and 1.3 nm which are oxygen contamination-free. The PL energy and the corresponding PL excitation (PLE) energy measured in the 1.5 nm-sized nanoclusters are 3.2 and 3.6 eV, respectively. In the 1.3 nm-sized nanoclusters, the PL and PLE energies are 3.4 and 4.2 eV, respectively. Figure 1 shows the size dependence of the PL decay curves measured at room temperature in the 1.5 and 1.3 nm-sized Si nanoclusters. The PL decay becomes shorter with decreasing nanocluster size. The decay curve consists of two kinds of decay components. In 1.5 nm-sized nanoclusters, the two kinds of PL lifetimes are 1.4 and 4.5 nsec. The PL lifetimes in the 1.3 nm-sized nanoclusters are 0.8 and 4.5 nsec. The fast decay components (~1 nsec) depend on the cluster size, but the slow decay components are constant. These facts indicate that the fast and slow decay components are responsible for the core and surface states in nanoclusters, respectively. In the core of nanoclusters, the k-conservation rule will be broken by the spatial confinements of the electrons and holes. It is suggested that the size-dependent decreasing of the PL lifetimes is due to the increasing of zero-phonon transition probability originating from quantum confinement effects.

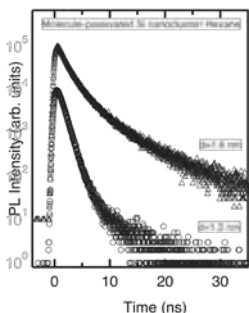


Figure 1: Time-resolved PL spectra of phenyl-passivated Si nanoclusters with the diameter of 1.5 and 1.3 nm

Synthesis, Electrospray Mass Spectrometry and Photoelectron Spectroscopy of semiconducting Cluster Anions: ligand-stabilized Cadmium Selenide and Cadmium Sulfide

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We report on an extensive photoelectron spectroscopic study of ligand-stabilized semiconductor cluster dianions which were synthesized and structurally characterized by single-crystal X-ray diffraction [1]. Clusters anions studied comprise the core sizes corresponding to $\text{Cd}_8\text{Se}_{17}$, $\text{Cd}_{17}\text{Se}_{32}$ and $\text{Cd}_{32}\text{Se}_{50}$. Gas-phase spectroscopy is made feasible by electrospray ionization of these multiply charged negative ions – in part by using appropriate ligand exchange agents. [2]

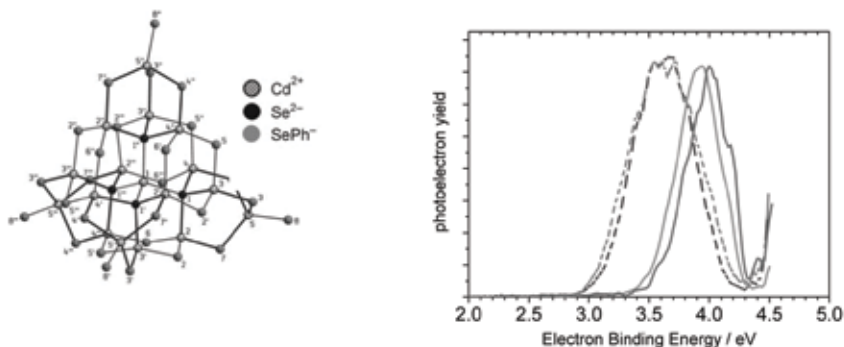


Figure 1. Left: X-ray structure of cluster core anion $[\text{Cd}_{17}\text{Se}_4(\text{SePh})_{28}]^{2-}$ [2]. Right: photoelectron spectra of $[\text{Cd}_8\text{Se}(\text{SePh})_{16}]^{2-}$ and $[\text{Cd}_8\text{Se}(\text{SePh})_{12}\text{Cl}_4]^{2-}$ (dashed curves) and $[\text{Cd}_{17}\text{Se}_4(\text{SePh})_{28}]^{2-}$ and $[\text{Cd}_{17}\text{Se}_4(\text{SPh})_{28}]^{2-}$ (solid curves), respectively, all taken at a detachment wavelength of 266 nm.

From the photoelectron spectra taken at several detachment wavelengths electron affinities and repulsive Coulomb barriers for the outgoing electron are derived. The Stark shift in EAs is interpreted on the basis of localized surface charges and a concomitant cluster size effect. A detailed computational study - based on density functional theory - is supporting this interpretation showing that the excess electrons are essentially occupying Se 4p or S 3p states on the outermost corner position of these tetrahedral clusters.

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Effect of the dopant atom and the charge state on the stability, geometry, and electronic structure of doped six-atom coinage metal clusters

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Transition metal doped six-atom coinage metal clusters of different charge states were studied with density functional theory. The effect of the dopant on the geometric and electronic structure was quantified considering the density of states distribution (DOS), the total and partial electron localizability indicator (ELI and pELI), and aromaticity criteria. The results were interpreted in terms of the phenomenological shell model for metal clusters (PSM).

Au_6Y^- is a planar, σ -aromatic, D_{6h} six-atom ring with a central Y atom. The 10 itinerant electrons in this circular compound arrange, in accordance with the PSM, in a closed shell $1S^2 1P_x^2 1P_y^2 1D_{xy}^2 1D_{x^2-y^2}^2$ structure. Its neutral counterpart, Au_6Y , has an open shell structure resulting in a Jahn-Teller distorted, ellipsoid structure with a fluxional behavior [1]. Cu_6Sc^+ and Au_6Y^+ are experimentally detected as stable species. They have 3D structures with 8 delocalized electrons in $1S^2 1P^6$ closed electronic structures, again in accordance with the PSM [2]. The ELI shows that the bonding in these clusters is determined by the itinerant electrons. Interestingly, Cu_6Sc^+ has a tri-capped tetrahedron shape, while Au_6Y^+ has an eclipsed geometry. These isomeric differences are studied in more detail by considering the $\text{Cu}_x\text{Au}_{6-x}\text{Sc}^+$ ($x=1-6$) series. The relative energy of the eclipsed structure decreases compared to the staggered form with decreasing x .

The electronic structure of the planar D_{6h} Au_6Mn ring was also interpreted using an extension of PSM, where the shell orbitals hybridize with the atomic $3d$ orbitals of Mn. The conclusions of the model are in line with the shape, multiplicity and the stability of this cluster [3].

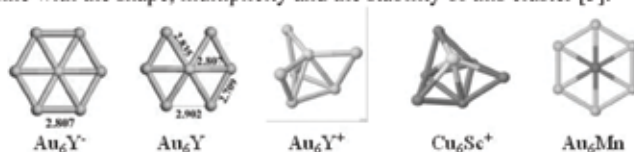


Figure 1: Ground states structures of Au_6Y^- , Au_6Y , Au_6Y^+ , Cu_6Sc^+ , and Au_6Mn

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XPS STUDY OF NANOPARTICLES OF Zn_xCd_yS GROWN ON MORDENITE BY DIRECT SYNTHESIS AND ION EXCHANGE

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This work is dedicated to a compositional and structural analysis of semiconductor nanoparticles of the Zn_xCd_yS compound grown on mordenite-type zeolite. The nanoparticles were grown using two techniques: Zn and Cd ion exchange from Na-Mordenite, and by direct synthesis of $[Zn,Cd]$ -Mordenite through a variant of Sol-Gel technique, followed by sulfidation treatment with H_2S . Morphological, compositional, and structural characterization of the samples was realized using the x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Inductively coupled plasma spectroscopy (ICP-AES) techniques. Using the x-ray photoelectron spectroscopy (XPS) a study of the semiconductor nanoparticles structure has been possible. Except for small differences in the oxidation state of Cd ions depending of the growth method, from XPS analysis it could be concluded that the structure of nanoparticles can be described essentially as a ZnS core covered by sulfided and oxidized Cd ions. This model confirms the assumptions made by Raymond *et al* [1, 2] to explain the size and confinement quantum effects observed from optical properties measurements.

Acknowledgments.

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Surface passivation and anisotropic effects in β -SiC nanostructures from first principlesJ.L. Cuevas, A. Trejo, M. Calvino, and M. Cruz-Irisson*ESIME- Culhuacan, Instituto Politécnico Nacional, México**alejandrb13@gmail.com*

Nanostructured semiconductors have received considerable attention due to their excellent properties and widely potential applications. In particular, silicon carbide nanowires (SiC NWs) have been attracting extensive interest due to their excellent electronic, physical and chemical properties and wide application in semiconductor, microelectronics optoelectronics and industry, operating in harsh environment like high temperature, high power and high frequency. The anisotropic and surface passivation effects on the electronic and optical properties of silicon carbide nanowires with zinc blende (3C) structure are investigated using first-principles calculations within density functional theory and generalized gradient approximation. In particular we have used a modified version of Perdew, Burke, and Enzerhof (RPBE) exchange and correlation functional, based on the pseudopotential plane-wave approach with the supercell technique [1]. The dangling bonds of the surface atoms in the quantum wires are passivated using hydrogen and hydroxyl atoms. The supercell model emphasizes the interconnection between 3C-SiC nanocrystals, delocalizing the electronic states [2]. However, the results show a clear quantum confinement signature, which is contrasted with that of nanowire systems. The calculation shows a significant response to changes in surface passivation. This chemical tuning of the band gap opens the possibility plenty applications in nanotechnology.

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Effects of the Molecular Doping and Quantum Confinement on the Electronic Properties of Silicon Nanowires

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We report *ab-initio* calculations on SiNWs oriented along the [110] and [111] directions based on density functional theory (DFT). The influences of the molecular doping and quantum confinement on the electronic properties onto SiNWs are studied [1]. We present results for SiNWs with diameters of 1.0 and 1.5 nm oriented along the [111] doped with NH₃, whose band structure are shown in Figs. 1(a) and 1(c), respectively. It can be seen for SiNW of 1.5 nm that the adsorbed molecule contributes with a localized state close to the conduction band edge, where it pins the Fermi level. Therefore the adsorbed molecule is found to be a good donor, as carriers can be thermally excited into the conduction band. However for SiNW of 1.0 nm the localized state is too deep states to be an active electron donor. The molecular natures of these states are further supported by the total electronic density of states (DOS) and the projected DOS, where projections are made on every element [Fig. 1(b), (d)]. There it can be seen that the localized states is almost exclusively made up of N and H contribution, thus it is localized at the molecule adsorption site. In larger SiNW, where the band gap is smaller due to a reduced quantum confinement, this state is expected to be shallow enough to be an active electron donor.

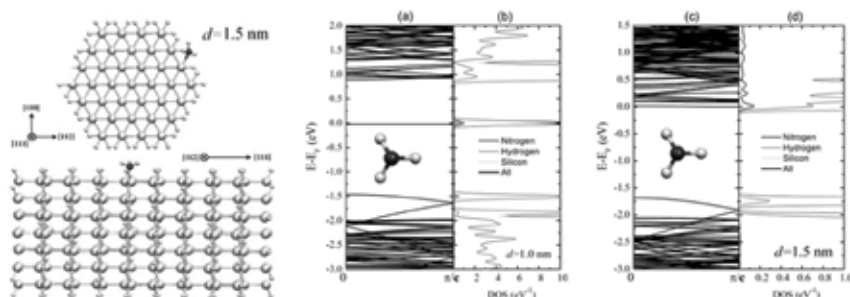


Figure 1: SiNW doped with NH₃, and the electronic bands structure and the total and projected DOS.

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Size evolution study of *ab-initio* Bader atomic polarizabilities in gold nanoclustersJ. I. Rodriguez¹, F. L. Castillo-Alvarado¹, J. Autschbach²¹*Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, México*²*Department of Chemistry, State University of New York at Buffalo, USA*juan@esfm.ipn.mx

In this work we present the main results of our study on Bader atomic polarizabilities for a family of gold clusters, Au_n (n= 6,12,20,34,54), at their most stable geometry [1]. For each cluster, after geometry optimization, a *n-body* DFT perturbation theory calculation was performed for computing cluster polarizability and the polarizability of each atom in the cluster using Bader's "Quantum Theory of Atoms in Molecules" (QTAIM) [2]. We determine quantitatively the contribution of surface and core atoms to the cluster isotropic and non-isotropic polarizabilities. Among other facts, we found a strong quadratic correlation (R=0.98 in average) of the isotropic polarizability of atoms in the cluster and their distance to the cluster center of mass. Based on the analysis of this correlation with cluster size, we show how to predict both cluster and atomic polarizabilities of larger cluster without performing expensive DFT calculations.

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Temperature effect on theoretical polarizabilities of copper clusters: a Born-Oppenheimer Molecular Dynamics Study

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In this work we cast light on the mismatch between experimental [1] and theoretical [2-3] polarizabilities of copper clusters, Cu_n (n=9,10,11,12). Polarizabilities and dipole moments were computed as average over DFT Born-Oppenheimer Molecular Dynamics (BOMD) trajectories at several temperatures, T= 68K, 500K, 800K, 1100K and 1700K. We found that a one order of magnitude mismatch between experimental polarizabilities and our theoretical ones still remains even at high temperatures. Our simulations also show that each cluster has an inherent dipole moment. Based on our findings, we try to explain the source of the controversial mismatch [4].

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Theoretical Study for the Interactions of Small Transition Metal Clusters with Benzene: $\text{TM}_n\text{-(Benzene)}_m$, $\text{TM} = \text{Fe and Ni}$, $n \leq 7$, $m \leq 4$

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The ground state, GS, geometries of $\text{TM}_n\text{-benzene}_m$ clusters were determined by means of all-electron calculations done with the BPW91/6311++G(2d,2p) method. The stability of $\text{TM-(C}_6\text{H}_6)_{1,2}$ is due by the formation of $\text{TM-C } \eta^6$ coordinations in the half-sandwich and sandwich GS structures, which are of lower total spin, S , than the free TM atoms. Departures from η^6 occur on $[\text{Fe-(C}_6\text{H}_6)_2]$, as the GS of this anion, of less symmetric sandwich geometry, presents η^6 and η^2 coordinations, which is mainly due to the enhanced repulsion of the adsorbed benzene units. On $\text{TM}_2\text{-(C}_6\text{H}_6)_{1,2}$ the stronger Fe_2 or Ni_2 bond, produce rice-ball (RB) geometries, where the TM_2 dimer is preserved [1]. Multiple decker sandwich (MDS) GS was found for $\text{Fe}_2\text{-(C}_6\text{H}_6)_3$, as Fe_2 is broken, which is unexpected, as the experiment suggest MDS for $\text{TM}_n\text{-(C}_6\text{H}_6)_m$ of earlier transition metals (TM); and clusters covered with benzene (RB structures) for late $3d$ atoms; however, a RB state was found to be degenerate with the GS [2]. The adiabatic electronic affinities are in agreement with the experimental results, yielding confidence on the assigned MDS or RB GSs for $\text{TM}_n\text{-(C}_6\text{H}_6)_m$. RB structures were found for $\text{Fe}_{6,7}\text{-(C}_6\text{H}_6)_m$. The adiabatic ionization energies (IE) of $\text{TM}_n\text{-(C}_6\text{H}_6)_m$ are smaller than those of TM_n and C_6H_6 , but nearer to the former, implying that the electron is mainly deleted from TM_n [3,4]; the IEs are even smaller than those of the alkaline atoms, which are the ones with the smallest IEs. Adsorption of benzenes quenches strongly the magnetic moments of TM_n , implying that the magnetic effects play an important role in the adsorption process.

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Hydrodesulfuration of Organosulfur Compounds: A Study of Molecular Dynamics

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The organosulfur compounds present in fossil fuels vary widely in their reactivities in catalytic hydrodesulfurization process^[1]. It is known that the alkyl and di-alkyl dibenzothiophene derivatives exhibit low reactivity, they are considered refractory compounds. The positions of the alkyl groups on derivatives of dibenzothiophene play an important role in the control of the reactivity of these compounds. Studies on deep hydrodesulfuration, suggest that the primary reason for the poor reactivity of 4,6-dimethyldibenzothiophene is the steric hindrance of the methyl groups, which make the sulfur atom inaccessible to the active sites of the catalyst^[2]. On the other hand, due the hydrodesulfuration of refractory compounds, such as, the DBT and 4,6-DMDBT is a complex problem; for it, we have carried out studies of molecular dynamics using density functional theory (DFT), through the interaction of 4,6-DMDBT and a cluster model of MoS₂ and a excess of H₂ to constant volume. In this case the excess of H₂ simulates the pressure of the system experimentally. The results show that the Mo of the surface dissociates to hydrogen molecular forming protons which react itself to regenerate the H₂ in the surface. Due the protons formation is feasible, it is necessary to promote a sufficient amount of protons that can be activate so much to the surface of MoS₂ like to DBT and 4,6-DMDBT. We think that these is role player the Ni or Co atoms to promote the protons formation and in this way favored to hydrogenation mechanism in the hydrodesulfurization of DBT and 4,6-DMDBT.

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Prediction on new small clusters of BaTiO₃ from DFT calculations

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In this study, total energy and electron property calculations were performed by using DFT, as implemented in the Dmol3 software. Many initial structures are constructed in this work to identify the true global minima. Geometry optimizations were performed for a large range of initial geometries without symmetry constrains. For n=3 and 5 were found the structures with most stability for these clusters.

CO adsorption on AuIr nanoalloys

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The lowest-energy and more compact structures of binary $(\text{AuIr})_{10}$, $\text{Au}_5\text{Ir}_{15}$, and $\text{Au}_{15}\text{Ir}_5$ nanoclusters, modeled by the many-body Gupta potential, were obtained by using a genetic-symbiotic algorithm. These structures were further relaxed within the DFT-GGA framework in order to obtain the most stable structures for each composition. Segregation is observed in the $(\text{AuIr})_{10}$ clusters, where the Ir atoms occupy the cluster core and the Au atoms are situated on the cluster surface. On the other hand, since there is experimental evidence that the addition of Ir to Au/TiO₂ catalysts has a synergistic effect on the CO oxidation, we also performed first-principles density functional calculations of the CO adsorption on bimetallic Au-Ir nanoclusters with the three compositions mentioned.

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Modelling ligand-induced structural rearrangement of bimetallic nanoparticles.P. West¹, R. L. Johnston¹, G. Barcaro², A. Fortunelli¹¹*School of Chemistry, University of Birmingham, UK*²*IPCF, CNR, Italy**r.l.johnston@bham.ac.uk*

Bimetallic nanoparticles have been shown to be useful for applications varying from catalysis to optics [1]. It has recently been shown that various molecules bound to the surface of nanoparticles can result in the nanoparticles changing structure [2]. We have modelled three bimetallic systems, AuPd, PdPt and CuPt, using 38 atom Truncated Octahedral (TO) structures, with a composition of A_6B_{32} and its inverse (B_6A_{32}) [3]. Three structures were studied, including the perfect core-shell structure (shown in figure 1). CO and H atoms were bound in the atop position on the center of a (111) face. The energy gaps between the different homotops were found to change as a single CO or H was added to a cluster. In addition, binding to different sites on a cluster also affected binding energy which resulted in a splitting between different sites. This was especially seen in the “hex” structures. This rearrangement could be useful for producing “smart catalysts”, where different reactions can take place on the same nanoparticles, depending on chemical conditions [2].

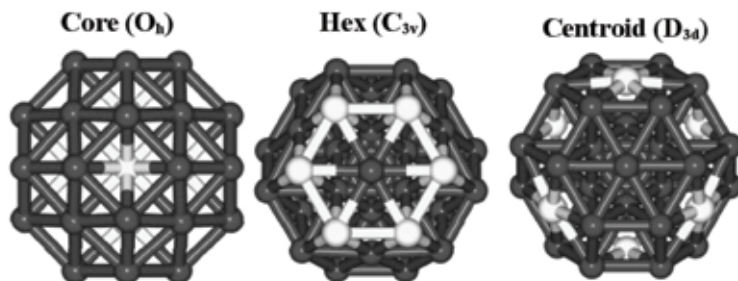


Figure 1: The different homotops used in this study. CO and H are bound to the center of every non-symmetrically equivalent site in the center of the (111) surface.

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Infrared-induced reactions on rhodium cluster surfaces

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Transition metal clusters lie in the intriguing but poorly-understood regime between isolated atoms and bulk metal. Recently, far-infrared spectroscopic characterisation of these clusters has been used to determine their structure.[1] We have extended this technique by using infrared absorption to heat rhodium clusters and induce reactions of small molecules on the cluster surfaces.

Molecularly adsorbed nitrous oxide has been observed on the surface of small cationic rhodium clusters by infrared multiple photon dissociation (IR-MPD) spectroscopy. Infrared excitation of the N₂O vibrational modes heats the clusters and induces a reaction on the cluster surface producing partially oxidised rhodium clusters Rh_nO⁺. [2] Infrared excitation of the Rh-O stretch of a coadsorbed O atom induces the corresponding reaction in Rh_nO(N₂O)⁺ clusters, providing further evidence that this reaction is thermally-induced.

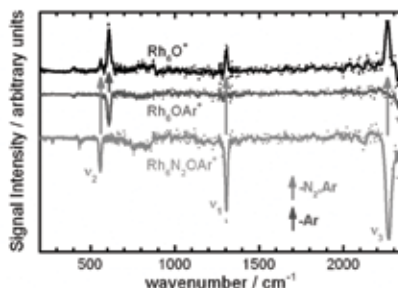


Figure 1: IR-MPD depletion spectra of Rh₆N₂OAr⁺ and the resulting enhancement in the Rh₆N₂O⁺ and Rh₆O⁺ signal. The spectrum in the Rh₆O⁺ channel shows clear enhancement at wavenumbers corresponding to excitation of Rh₆N₂O⁺ modes, indicating infrared-driven cluster surface chemistry.

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Donor Acceptor Map for metal clusters: Are metal clusters able to modulate oxidative stress?

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One of the mechanisms used for scavenging free radicals and therefore reduce the oxidative stress is that of the electron transfer reaction, which can be analyzed in terms of the electron donor-acceptor properties of the systems. The scavenging activity of metal clusters is analyzed in this work considering the electron transfer mechanism. Such processes have been modeled using Density Functional Theory for a wide variety of metal clusters and free radicals. Vertical ionization energy (I) and electron affinity (A) are used to obtain the electrodonating power (ω^-) and the electroaccepting power (ω^+). A plot of ω^+ vs ω^- provides an electron Donor Acceptor Map (DAM) useful to classify any substance regarding its electron donating-accepting capability. Using this DAM, a qualitative comparison amongst all the studied compounds is presented. Our results indicate that the size of the metal cluster has a significant effect on the free radical scavenger capacity when reacting through the electron transfer mechanism. The electron transfer reaction mechanism depends on the characteristics of the free radical and on the nature of the metal clusters.

Methane activation and partial oxidation on free gold and palladium clusters: Cooperative and highly selective cluster catalysis

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Practical interest in the catalytic activation and conversion of methane into valuable products, such as methanol, formaldehyde, or light olefins, and in particular ethylene, is driven by industrial and economical considerations, and has motivated extensive research aimed at the identification and development of heterogeneous catalyst materials for these processes. However, the required high reaction temperatures and/or the use of highly active reactants to activate the stable C-H bond of methane (bond dissociation energy 440 kJmol^{-1}) renders a selective synthesis of the desired products difficult. Consequently, the selective catalytic functionalization of methane poses a longstanding central problem in organometallic chemistry.

Employing ion trap mass spectrometry [1], our experiments aim to discover new selective catalytic methane activation reactions employing small mass-selected clusters of gold and palladium. In addition, even more importantly, a molecular understanding of the involved size-dependent catalytic reaction mechanism is aspired. Toward this goal the combination of our gas phase reaction kinetics measurements with first principle calculations performed by U. Landman and coworkers are an essential prerequisite [2-5].

Following this approach it was possible to demonstrate the selective activation of methane on free Au_2^+ . Most interestingly, coadsorption effects proved to be crucial in the reaction mechanism because one methane molecule alone would not be dehydrogenated, but the cooperative interaction of two methane ligands initiated a complete thermal catalytic ethylene formation cycle. The cycle was closed by the subsequent adsorption of a third methane molecule that cooperatively activated the release of ethylene [4].

Further investigated reactions on Au_n^+ and Pd_n^+ include the size-dependent adsorption of multiple CH_4 [5], the hydrogen promoted O_2 activation [3, 6], as well as the coadsorption of CH_4 and O_2 eventually leading to oxygen containing partial oxidation products of methane.

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High catalytic activity in a strong metal-support interaction system: CO oxidation on TiO₂(110)-supported Pt nanoclusters

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We report on the catalytic activity of small Pt clusters ($1 < n < 200$) on TiO₂(110)-(1x1) as a function of size, surface preparation and surface temperature. Pt as a group VIII noble metal is known to have "strong metal-support interaction" (SMSI) on titanium oxide (TiO₂), when reduced at high temperatures ($T_s > 700\text{K}$). The SMSI effect has been intensively studied over the three last decades and found to occur in the case of diverse metal clusters on diverse reduced oxide surfaces [1-5]. It manifests by encapsulation of the metal clusters by a reduced thin layer of the support oxide [2-5].

The unique combination of an in situ low temperature STM and a UHV chemical reactor allows determining the correlation between morphology and reactivity. Fig.1a shows STM pictures ($T_s = 80\text{K}$) of Pt clusters on TiO₂(110)-(1x1), prepared in ultrahigh vacuum. The corresponding CO₂ production rate as a function of surface temperature is shown in Fig.1b. O₂(36) and CO(29) are pulsed on the catalyst at a well defined delay and the CO₂ signal is monitored, synchronized either with O₂ or CO. The preparation conditions of the Pt clusters shown in Fig.1a (deposition, annealing, sputtering, annealing) make them highly active for CO oxidation. Pt clusters grown by deposition and annealing show an almost identical morphology as in Fig.1a but very low catalytic activity. We conclude that the cluster support interaction plays a crucial role in the activation of metal clusters for this particular catalytic reaction.

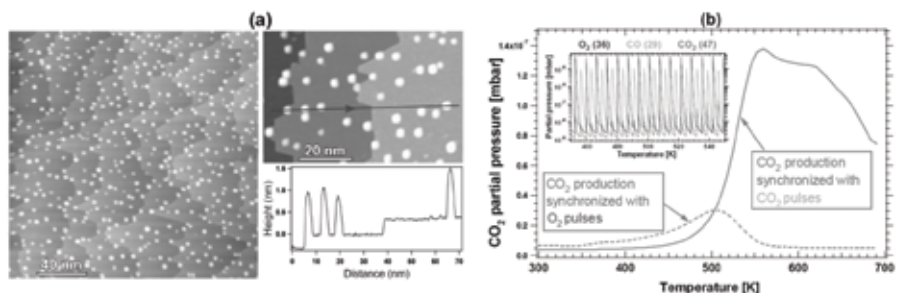


Figure 1: (a) STM characterization of Pt clusters on TiO₂(110)-(1x1). (b) CO₂ production (red) obtained on the model catalyst shown in (a) by pulsing CO (green) and O₂ (blue).

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Reduction of Dinitrogen at Room Temperature by Tungsten Clusters Supported on Graphite

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Metal clusters catalyze unique chemical reactions that are not feasible on bulk metal surfaces. This is well illustrated by gold clusters: they catalyze various chemical reactions while the bulk gold is almost inert. In nature, clusters, which usually contain a few atoms of transition-metal elements, can be found at the reaction centers of metalloenzymes. The enzymes catalyze difficult chemical reactions under mild conditions, for which the clusters are known to play key roles. A well-known example of such clusters is the FeMo cluster sitting at the reaction center of enzyme nitrogenases that reduces almost inert dinitrogen (N₂) to ammonia at room temperature. Although detailed mechanism is unknown, it is believed N₂ is activated in molecular form on the cluster and reduced.

Another example that shows capability of clusters for peculiar nanocatalysis is a tungsten cluster. We recently reported N₂ is adsorbed on W₅ at 140 K with a W-N-N-W geometry in which the N-N bond is highly activated, and that the activated N₂ reacts with H₂O to form N₂O [1]. This leads us to expect if such an activated N₂ is also available at room temperature, it may be reduced to form ammonia under mild conditions as is done by the FeMo cluster.

To check the possibility, we have studied activation and reduction of N₂ at room temperature on the supported tungsten clusters (W_n). In the experiment, size-selected tungsten cluster ions W_n⁺ (n=2~6) were soft-landed on an HOPG (highly-oriented pyrolytic graphite) surface. The deposited clusters were exposed to N₂ and/or H₂O and chemical reactions among them were investigated by X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS).

In the study we found N₂ is adsorbed on W₅ in the activated form also at room temperature without dissociation. It was also found when N₂ and H₂O are simultaneously fed to the cluster, an N1s XPS spectrum with a peak at ~ 400.8 eV shows up. It turned out the spectrum has a strong resemblance to that for hydrazine (N₂H₄) adsorbed on the cluster. The result suggests that the activated N₂ reacted with the hydrogen from H₂O, leading to the formation of hydrazine-like species. Factor analysis of the spectra revealed N₂ is reduced to N₂H_x and also ammonia. The formation of ammonia was confirmed by TDS measurements. The result shows the room temperature reduction of N₂ to ammonia, which is done in nature by the FeMo cluster, is also feasible on the supported tungsten cluster. Detailed results of the experiments will be reported at the conference.

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Carbon monoxide adsorption on neutral doped gold clusters

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Gold is a noble metal, but when its size is reduced to the nanometer range, it loses its nobleness and becomes highly reactive or even catalytically active. For example small anionic gold clusters can combust carbon monoxide [1]. The unexpected size and also composition dependence of the chemical and catalytic properties of bare and doped gold clusters turned it into an active research topic [2]. Although the charge state is a crucial parameter for the reactivity, experimental studies on neutral gold and doped gold clusters are still scarce.

We report on experiments probing the reactivity of neutral doped gold clusters (Au_nM_m , $M = V$, Y , and Ag) towards CO gas and compare the results with earlier experiments on the reactivity of bare neutral gold clusters [3].

The clusters are produced by laser vaporization at different source temperatures and subsequently pass through a low-pressure collision cell containing CO gas. Cluster abundances of reacted and non-reacted species are measured with time-of-flight mass spectrometry as function of the pressure in the cell. Fitting the kinetic traces provides insight in the reaction mechanism and leads to the corresponding rate constants for the association and dissociation reaction steps. Application of the statistical RKKM allowed extracting cluster-CO binding energies from the temperature dependence of the dissociation rate constants.

The main results can be summarized as follows: (i) the reactivity of the doped gold clusters increases with lower cluster temperatures; (ii) the dissociation reaction rate strongly depends on the cluster size and on the kind of dopant, and reveals a correlation between reactivity and cluster electronic shell closings; (iii) there is an overall decrease of cluster-CO binding energy with increasing cluster size.

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Enantiospecific adsorption of cysteine on chiral Au_{34} clusters.J.J. Pelayo Cárdenas¹, I.E. Santizo¹, L.A. Pérez¹, and I.L. Garzón¹.¹ *Instituto de Física**Universidad Nacional Autónoma de México
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Since the discovery of chirality, a lot of interest to investigate its effects was born. After the enantiospecific adsorption of chiral molecules in metallic nanoparticles was theoretically demonstrated for the case of amino acids in Au_{55} [1], and after the existence of intrinsically chiral Au_{34} clusters with C_3 was supported by experimental and theoretical evidence [2], it was just natural to analyze the adsorption of chiral amino acids on chiral Au_{34} clusters.

In this work, we use the SIESTA code [3] to perform a DFT study of the enantiospecific adsorption of cysteine on a chiral Au_{34} cluster with C_3 symmetry. Previous results on the adsorption sites of cysteine on Au_{55} clusters were considered as initial conditions [1,4].

In the first stage of this work it is found the most favorable adsorption site for the cysteine's thiol group on the cluster, and then to use that site to generate suitable enantiomers for both the cluster and the cysteine, and study the enantiospecific adsorption for the thiol-adsorption mode. The second stage of the work was dedicated to obtain the most stable adsorption sites of the cysteine's thiol and amino groups interacting simultaneously on the gold clusters [4], optimizing several configurations obtained from the thiol's most stable one, and studying the enantiospecific adsorption for both groups.

Obtained results indicate that the maximum adsorption energy is reached when the cysteine's functional thiol group is adsorbed on "bridge" sites (between two gold atoms) and when the amino group is adsorbed on a "top" site (on top of a gold atom).

It is also found that the adsorption energy depends on the chirality of the system.

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CO Oxidation Processes on Neutral and Single Ionized Au₈ Clusters: A Theoretical Study

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Experiments on the reactivity of Au nanoclusters have shown a local maximum for the CO adsorption of the first molecule for Au₈ and its cation, whereas O₂ adsorption has been mainly observed on Au₁₈⁻¹. In this work we determine the Fukui coefficients from the Mülliken population analysis for the Au₁₈^{0,±1} clusters with C_{2v} symmetry (the most stable Au₁₈ isomer symmetry) to calculate the electrophilicity and evaluate the response of the non-equivalent sites to the attack of the nucleophilic CO or the electrophilic O₂ molecules. We report the results of the calculation of the binding energies of the CO and O₂ for the most electrophilic and nucleophilic sites respectively, and study the CO oxidation process by the subsequent adsorption of the CO on the O₂ molecule, which was previously adsorbed on the corresponding gold cluster site. The study is based on a DFT-GGA calculation with the PW91 functional.

Bimetallic 18-atoms gold-silver clusters: a theoretical proposal for an efficient catalyst for the NO_x (x =1,2) dissociationJ.R. Soto^a, B. Molina^a, and J. J. Castro^b^aDepartamento de Física, Facultad de Ciencias, UNAM, Apdo. Post. 70-646, 04510 México, D.F.^bDepartamento de Física, CINVESTAV del IPN, Apdo. Post. 14-740, 07000 México, D.F.

The selective catalytic reduction (SCR) of NO_x is an alternative solution proposed to control the emission of these pollutants produced by the lean-burn engines. Theoretical studies based on DFT calculations of the adsorption processes of NO_x (x=1-3) on Ag_n (n=1,8) [1] and α-alumina [2] have shown a marked odd/even alternation of the adsorption energies and suggests a possible poisoning of the systems during the SCR process. In this work we present DFT calculations, within the framework of the relativistic zeroth-order regular approximation (ZORA), of the adsorption energies of the NO_x (x=1,2) on the more reactive sites of different homotops of the 18-atoms gold-silver clusters Au_mAg_n in two alloy compositions (m/n = 2,1). We also discuss the possibility of the dissociation of the NO_x in an atmosphere rich in H₂, with the subsequent formation of some adducts on the cluster surface. This kind of bimetallic cluster have a lower poison probability than single metallic ones, therefore we propose them as a more efficient catalytic systems for NO_x dissociation.

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Gas Phase Synthesis of Au clusters deposited on defect-controlled titania and their chemical reactivity

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It is known that Au clusters deposited on titanium oxides show catalytic activity for CO oxidation. Here, interaction between the Au clusters and the titanium oxide surface is likely to play critically important roles, as the reaction occurs at the boundary region of the cluster and the surface. Chemical reactivity of isolated Au clusters has been examined in the gas phase. However, Au clusters deposited on titania have never been synthesized in the gas phase, as far as we know. We found that we are able to synthesize a variety of titanium oxides that have different stoichiometries, and the chemical reactivity of Au clusters deposited on titania shows prominent chemical reactivity to CO depending on the stoichiometry of titania.

We produced titanium oxide clusters in the gas phase by the laser ablation of a Ti rod in the He and O₂ molecular beam. Titanium oxide clusters, Ti_nO_{2n+k}⁺ (k=-1, 0, 1 and 3) were dominantly formed: Clusters with *n* titanium atoms and 2*n* oxygen atoms are formed in addition to the oxygen-rich and oxygen-poor clusters. Au clusters were then deposited on the titanium clusters downstream of the molecular beam. We examined chemical reactivity of the clusters with CO in the gas phase.

Figure 1 shows reactivity of Au₂-Titania clusters for the different stoichiometry of Ti and O. Color codes exhibit reactivity of the clusters: The higher value corresponds to the higher reactivity. From this plot, the reactivity of Ti_nO_{2n+k}⁺ for *k*=1 are higher than that for *k*=0. This finding indicates that interaction of Au with oxygen atom induces chemical reactivity of the cluster with CO.

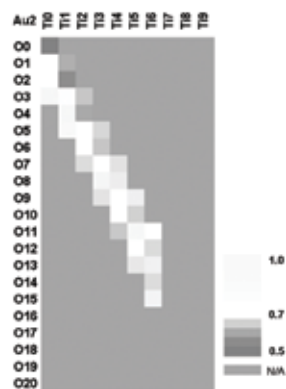


Fig. 1. Reactivity of Au₂-titania clusters with CO.

Interplay between formation of carbon nanotubes and catalytic activity of Ni/Mordenite catalysts in dependence on zeolite SiO₂/Al₂O₃ molar ratio

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The aim of present work was to study the influence of mordenite SiO₂/Al₂O₃ molar ratio (MR) on formation of catalytic centers and activity of the samples in the selective catalytic reduction (SCR) of NO by propene and CO. It was shown that MR is one of the important parameters managing acidity, ion-exchangeability, and metal coordination as well as the size of metal nanoparticles prepared on zeolite support [1].

Mordenites with MR of 13, 20 and 90 were supplied by Zeolist International. Ni exchange was done from excess of 0.1 N aqueous solution of Ni(NO₃)₂ at 60 °C, under stirring, during 24 h. Samples were characterized by XRD, EDS, UV-Vis diffuse reflectance spectroscopy (DRS) and HRTEM. Catalytic activity was measured in a continuous flow reactor containing 0.1 g of catalyst using mixture of NO, oxygen and propene and CO as reducing agents. The activity was determined as NO conversion within temperature interval 25 - 550 °C with a heating ramp of 1 °C/min.

EDS data had shown the Ni loading equal to 1.8, 0.9 and 0.44 wt. % for mordenites with MR of 13, 20 and 90, respectively. As expected, rise of MR decreased the amount of exchanged Ni. XRD analysis confirmed stability of zeolite structure after all treatments applied. In the UV-Vis spectra of all Ni-exchanged samples a band at 390-400 nm and a doublet with a maxima at 650 and 720 nm were observed, which is typical for an Ni(H₂O)₆²⁺ ions octahedrally coordinated by water molecules. Also, spectra of the samples with MR of 20 and 90 showed absorption around 250-300 nm that can be due to partial dehydration on Ni²⁺ ions and their coordination with O²⁻ of zeolite framework, and electronic transition in a charge-transfer complex. In contrast, the sample with MR equal to 13 showed no absorbance in region of high energy ($\lambda \sim 200$ -350 nm) unlike the other two samples.

Catalytic activity of the samples was decreased in line with increasing of MR. Only for sample with MR=13 complete conversion of NO was observed, while for samples with MR of 20 and 90 conversion at maximum reached 8.3 and 2.4 %, respectively.

In the TEM micrographs of only sample with MR equal to 13 carbon nanostructures are observed as fibers, containing nickel carbide particles, some of them located on the tips of the fibers and other encapsulated, all surrounded by sheets of rhombohedral graphite. The particles location is very important for the catalyst stability because when the particle is at the top of the filament, it is accessible to the reactant gases, and, hence, it keeps the catalytic activity; on the contrary, upon encapsulation the metal particles lost their activity because they are not accessible to reactants.

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Synthesis and characterization of catalysts based on nanostructured chalcogenides of Ru-WS₂/C Y Ru-WS₂/NTC

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The fuel cell proton exchange (PEM) represent an alternative energy that contributes to the reduction of pollution, are devices that directly convert chemical energy of reactants into electricity [1-3].

One of the essential elements for the proper operation of PEM fuel cells is the electrocatalyst, usually a precious material such as platinum and therefore expensive [4]. Today, the research for platinum alternative materials, which is the most efficient electrocatalyst for PEM cells, represents one of the major challenges in the field of electrocatalysis. Until now, it has not found a satisfying electrocatalyst in acid medium, that can be used as cathode or anode electrode and less expensive.

The interest of this work is based on the development of nanoelectroprecursors of ruthenium chalcogenides with a metal loading of 20% by weight of Ru_xW_yS_z to generate: Ru_xW_yS_z/C, Ru_xW_yS_z/C and Ru_xW_yS_z/NTC as electrocatalysts.

The characterization techniques showed that the synthesized materials can be applied as cathodes in acid for the RRO, being more selective Ru_xW_yS_z electrocatalyst for the cathode reaction.

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Dissosiative Chemisorption of CO on Ti_n ($n=2-7$) clusters: Theoretician prediction from DFT calculations.

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In this work the structural and electronic properties of Ti_n clusters when C–O is adsorbed on them will be discussed. Spin-unrestricted density functional theory (DFT) calculations were employed to explore the trends of CO adsorption energy on these clusters. The effects of the transition metal electronic structure onto the adsorption energy of C–O and the vibrational stretching frequency of C–O, and how these chemical parameters can be correlated to the catalytic activity of transition supported metal catalysts that involve the adsorption, surface diffusion, and C–O bond dissociation elementary steps in heterogeneous catalytic surface reactions, are discussed. Thus for $n=3$ and 6 are the isomers most preferred to adsorbed C–O within range 2-7 atoms.

DFT study of the enantiospecific adsorption on Au₅₅ clustersX. López-Lozano¹, Luis A. Perez², I. L. Garzon²¹ *Department of Physics & Astronomy, The University of Texas at San Antonio, United States.*² *Instituto de Física, Universidad Nacional Autónoma de México, Mexico.**Xochitl.LopezLozano@utsa.edu*

The exploration of the adsorption of organic molecules on Au nanostructures started to be investigated mainly due to the potential applications, e.g., in heterogeneous enantioselectivity catalysis and the pharmaceutical industry [1]. However, in order to fully exploit the enantioselective property of Au clusters one has to investigate the different mechanisms of reactions of organic functional groups on the cluster facets. Therefore, a detailed study of the atomic structure of the isolated Au clusters and with the attached molecule(s) is essential to the understanding of its electronic properties for the future design of a particular application. In this work, we present a theoretical density functional study of the adsorption of a chiral organic molecule (cysteine) on Au₅₅ clusters. We investigated the adsorption of this molecule on an achiral and chiral clusters in order to study the property of enantioselectivity of these nanostructures. The highest adsorption energies were found when the amino and thiolate functional groups of cysteine are bonded to the lowest coordinated edges of the chiral cluster facets with largest area. Enantiospecific adsorption is primarily obtained from the different bond location and strength, at the cluster edge, of the carboxil groups forming the left and right-handed enantiomers. Our results provide important insights about the energetic, structural and electronic properties to be considered, e.g., in the designing of gold nanoclusters-based organic sensors and novel nanocatalysts.

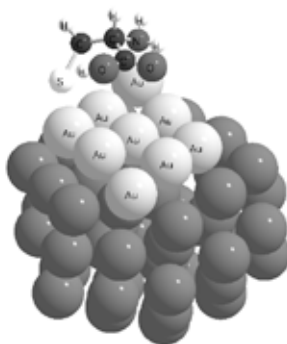


Figure: Perspective view of the lowest energy structure of cysteine adsorbed on the chiral Au₅₅ cluster facet of largest area.

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**Citral Hydrogenation on Ir/TiO₂ and IrAu/TiO₂ catalysts.
Effect of the preparation method and gold addition.**

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Catalytic hydrogenation of α,β unsaturated aldehydes to unsaturated alcohols is an important step in the preparation of various fine chemicals [1], particularly if the catalysts may produce a preferential hydrogenation of the C=O group leading to unsaturated alcohols. Interesting results have been obtained by using supports that present the SMSI effect, such as TiO₂ [2]. Ir/TiO₂ catalysts reduced at high temperature are very active catalysts for liquid phase citral hydrogenation [3-4]. On the other hand, over gold catalysts, reaction mechanisms involved in these reactions are more complicated than assuming a simple geometric model (gold particle size) or a perimeter-interface model, as is suggested to be the active site in CO oxidation. In this work, Ir/TiO₂ were prepared by DPU and IrAu/TiO₂ prepared by sequential incorporation of the metal precursors on the support using a combined DPU-incipient wetness impregnation approach. Catalysts were reduced at 573K (LT) and 775K (HT). The main objective was to study, on one side the effect of the preparation method when compared to Ir/TiO₂ prepared by classical wet impregnation and, on the other, the effect of gold addition. Metal loading was 1 wt.% for Ir/TiO₂ and 2 wt.% for Ir-Au/TiO₂ (Ir/Au=1). A reference Ir/TiO₂ catalyst was prepared by classical wet impregnation. Ir/TiO₂ DPU and IrAu/TiO₂-S, reduced at high temperature were more active than the reference Ir/TiO₂ prepared by wet impregnation. In addition, 100% selectivity towards unsaturated alcohols (nerol and geraniol) was observed. These properties were explained in terms of the metallic precursor and the preparation method. IrAu/TiO₂-S catalyst, reduced at high temperature (773 K) was the most active sample. However, the effect of addition of gold to iridium catalysts is more evident in the case of the LT samples when compared to Ir/TiO₂ DPU and Ir/TiO₂ w reference catalysts.

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Size effect on aerobic oxidation catalysis of PVP-stabilized Au clusters studied by mass spectrometry

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Small (<2 nm) Au clusters stabilized by poly(vinylpyrrolidone) (Au:PVP) can catalyze various types of aerobic oxidation reactions.[1] We recently proposed that activation of molecular oxygen by negatively-charged Au cores in PVP is responsible for the size-specific catalysis.[2] This mechanism is in parallel with reactivity of free Au clusters against O₂[3] even-numbered Au_n clusters with $n \leq 20$ have high-lying LUMO level and can activate O₂ by partial electron transfer when they are negatively charged. In order to test whether this simple guiding principle can be applied to the real catalysts, Au:PVP, we studied herein correlation between catalytic activity and Au core size distributions of Au:PVP which are probed by non-destructive MALDI-MS spectrometry.[4]

Four samples of Au:PVP were prepared by microfluidic and conventional batch mixing of aqueous solutions of HAuCl₄ and NaBH₄ in the presence of PVP at 313 K (**1**, **2**) and 273 K (**1'**, **2'**), respectively.[4] The Au core size was evaluated by MALDI mass spectrometry utilizing DCTB as a matrix. Figure 1 shows typical MALDI mass spectra of Au:PVP in the negative ion mode recorded at the minimum laser fluence to suppress fragmentation. A series of naked Au cluster anions, Au_n⁻, were observed in all the spectra, indicating that only the Au cores embedded in PVP were detected. From a static analysis of mass spectra of **1** and **2**, we determined the magic numbers of the Au cores to be 35±1, 43±1, 58±1, 70±3, 107±4, 130±1, and 150±2. The smaller magic numbers can be explained in terms of electronic shell model based on Woods-Saxon potential (fig. 1). In contrast, the magic numbers were less prominent for **1'** and **2'** prepared at the low temperature.

Then, catalytic activities of the four Au:PVP samples were compared for the oxidation of *p*-hydroxybenzyl alcohol in water under ambient conditions (fig. 2). Figure 2 shows that the activity decreases in the order of **1** ~ **1'** > **2'** > **2**. Interestingly, **1** and **1'** exhibit comparable activities, although the population of magic clusters in **1** is higher than in **1'**. This result suggests that *the Au_n cores with $n < 70$ exhibit a similar activity regardless of the core sizes*. We found that the rate constants for Au:PVP are proportional to the population of Au_n cores with $n < 70$ (fig. 1). On the assumption that Au_n cores with $n < 70$ show identical activity, this finding suggests that *70-mer is a critical size for the Au cores in PVP to be catalytically active for oxidation*, which is significantly larger than that (~20-mer) for free Au cluster anions.[3]

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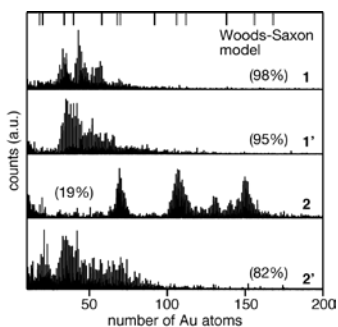


Figure 1 Negative ion MALDI mass spectra of Au:PVP samples. Values in parentheses represent populations of the clusters smaller than 70-mer.

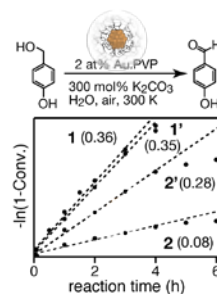


Figure 2 Time course of oxidation of *p*-hydroxybenzyl alcohol catalyzed by Au:PVP (**1-4**). Values in parentheses represent rate constants.

Synthesis and catalytic characterization of Au, Pd, Pd_{core}Au_{shell} and Au_{core}Pd_{shell} nanoparticles embedded in SiO₂

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ABSTRACT

Monatomic and heteroatomic Au, Pd, Pd_{core}Au_{shell} and Au_{core}Pd_{shell} nanoparticles were synthesized utilizing ascorbic acid in aqueous solution from their respective metal salts (HAuCl₄ and PdCl₂), which were placed in SiO₂ (monoliths and granular material). Sol-Gel methods were used to, firstly, obtain SiO₂ monoliths with embedded metallic nanoparticulas (MNP-SiO₂) and secondly, to produce granular SiO₂ in order to impregnate the nanoparticles on the surface (MNP/SiO₂). The synthesis process of nanoparticles is highly dependent on ascorbic acid concentration and was characterized in order to obtain nanoparticles with low poly-dispersity as well as to control the size, shape and chemical ordering. Structural details were obtained by TEM and optical absorption measurements. Nanocomposites were used to study catalytic activity, which was examined in all cases through specific reactions for several thermodynamic states. It was found that nanocomposites exhibit an outstanding catalytic activity and relative stability in the oxidation reaction of CO into CO₂.

Nanocatalysis on Graphene

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Graphene has attracted great interest both for a fundamental understanding of its unique structural and electronic properties and for important potential applications in nanoelectronics and devices. The combination of highest mobility, thermal, chemical and mechanical stability with the high surface area offers many interesting applications in a wide range of fields including heterogeneous catalysis where metallic and bimetallic nanoparticle catalysts can be efficiently dispersed on the graphene sheets.

We have developed a facile and scalable chemical reduction method assisted by microwave irradiation for the synthesis of chemically converted graphene sheets and metal nanoparticles dispersed on the graphene sheets [1,2]. In this talk we will present another novel method for the synthesis of graphene from graphite oxide by a fast laser irradiation process that does not involve the use of chemical reducing agents and allows the production of high quality graphene for many applications in electronics, devices and catalyst support.

We will also present new results on nanocatalysis involving metallic and bimetallic nanoparticle catalysts supported on graphene for the synthesis of complex organic molecules using the Suzuki, Heck and Sonogashira coupling reactions. These reactions have typically been performed under homogeneous conditions to enhance the catalytic activity and selectivity for specific reactions. However, the issues associated with homogeneous catalysis remain a challenge to the broader application of these synthetic tools due to the lack of recyclability and potential contamination from residual metal in the reaction product.

Our results demonstrate, for the first time, that palladium-graphene (Pd/G) nanocatalyst is a highly active catalyst for the Suzuki, Heck and Sonogashira C-C coupling reactions. This highly catalytic activity is accompanied by an unusual recyclability of the catalyst over seven times with essentially no drop of activity and a reaction that achieves 100% yield. Reasons for the exceptional activity and stability of the Pd/G catalyst will be discussed.

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Do Some Non-stoichiometric Boron Nitride Clusters Possess Magnetism?

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Boron nitride (BN) have wide bandgap, high melting point, high mechanical strength, hardness, corrosion and oxidation resistance as well as outstanding thermal and electrical properties, indicating that BN nanostructures may have potential applications to nanosized electronic devices, high heat-resistance semiconductors and insulator lubricants. However, most of work have been concentrated on stoichiometric large BN clusters so far. In the present study we used the first-principle calculation to investigate the stability, electronic and magnetic properties of non-stoichiometric clusters B_nN_{20-n} ($n = 6, 7, 10, 11, 13, 14$) by means of the density functional theory with the generalized gradient approximation for correlation potential. It is found that their structures belong to six families: single-ring(R), two-ring(2R), three-ring(3R), graphite-like sheet(G), fullerence(F) and other configuration(O). Among them $B_{10}N_{10}^R$ is the most stable one with C_1 symmetry, the highest binding energy of 6.1897eV and HOMO-LUMO gap of 4.069eV. $B_7N_{13}^G$, $B_{11}N_9^R$ and $B_{13}N_7^{3R}$ show nonzero magnetic moments of 1.998, 2.000 and 1.999 μ_B respectively. Detailed analysis indicates that these magnetic moments are mainly located on boron atoms, such as 1.182 μ_B for $B_7N_{13}^G$, 1.831 μ_B for $B_{11}N_9^R$ and 1.855 μ_B for $B_{13}N_7^{3R}$. It is also demonstrated that the $2p$ electrons in boron atoms play a dominant role in the determination of magnetism of B atoms in these BN clusters and their magnetism may come from local symmetry breaking, change of coordination number, charge transfer from boron atoms to nitrogen atoms and spd hybridization.

Structural and magnetic properties of Fe_xM_y (with $x + y = 7$, $\text{M} = \text{Ru, Rh, Pd and Pt}$) nanoalloys

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We have performed an extensive *ab initio* density-functional calculations to investigate the structures and magnetic moments of the small binary clusters Fe_xM_y (with $x + y = 7$, $\text{M} = \text{Ru, Rh, Pd, Pt}$). We use the fully unconstrained version of the density-functional method as implemented in the SIESTA code within the generalized gradient approximation to exchange and correlation. We compute the geometries, electronic structure, the structural transition observed as a function of the cluster composition and related properties of free-standing binary alloys. We have considered all those possible structures as well as the possible spin isomers for each homotop in the whole range of composition. Non monotonous dependence of the magnetic properties is observed in the alloys in general.

Properties of stable structures of small TaSi clusters: a DFT studyP.G. Alvarado Leyva¹, E.M. Sosa Hernández² J.M. Montejano-Carrizales³¹ *Facultad de Ciencias, Universidad Autónoma de San Luis Potosí, México*² *Facultad de Contaduría y Administración, Universidad Autónoma de San Luis Potosí, México*³ *Instituto de Física, Universidad Autónoma de San Luis Potosí, México**jmmc@ifisica.uaslp.mx*

The transition metal clusters $3d$, $4d$ and $5d$ are the most studied, theoretically and experimentally, because their electronic and magnetic properties show a dependence with the structural environment and with the chemical environment of the atoms. Small atomic clusters of tantalum are among the most extensively investigated transition metal clusters owing to several features that are experimentally advantageous, such as the relative propensity to form clusters. In this work we present results for detailed systematic investigations of structural and magnetic properties of small Ta_n ($n \leq 8$) clusters. The magnetic order into the clusters presents a dependence with the number of atoms (n). The ground states structures favor higher dimensional configuration and higher coordination number. The study was done by using the Density Functional Theory through the GAUSSIAN 98 software package.

Ferromagnetic resonance and low field microwave absorption as relevant tools to characterize magnetic interactions and anisotropies in micro-scale and composite ferromagnets.

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The purpose of this work is to give an overview of the rich magnetic information that is obtained in the FMR and LFS of single microsize ferro- or ferri magnetic particles, composites and magnetic microwires. In this work we show FMR and LFS results of: a) ferromagnetic wires (L=6 mm, R=5-12 microns); b) Ni and Fe isolated magnetic particles (R= 100 to 4 microns) of arbitrary geometry; c) assemblages of these particles, and d) micrometer samples of military material “mu”. The FMR and LFS measurements were carried out at 300K in a Jeol-JES-R3X spectrometer with zero crossing unit to detect microwave absorption very close to zero field. The FMR spectra showed angular dependence upon rotation of the sample with respect to the applied magnetic field. The angular plots were used to calculate anisotropy constants, K_u , K_K y K_F . It should be emphasised that the physical origins of such anisotropies are quite diverse and yet they all are, very sensibly, detected by FMR and/or LFS. The minimum sample size limit for detection, up to now, is 1 micron at 300k, in our lab. The relative proportion of dipole-dipole forces to magnetic-exchange forces can also be determined for the assemblages of magnetic particles. It was found that the magnetic anisotropies for these “weak” assemblages averaged out to zero. The FMR linewidths showed clear contributions from inhomogeneous broadening factors and dissipative relaxation, Gilbert type, of the magnetization-“small angle” rotation. All these results indicate the richness of information extracted from FMR spectra of a diversity of single micro-size magnetic materials and magnetic composites.

Micro-size Effects on the Microwave Absorption Profile of the Amorphous Metallic Ferromagnet $\text{Fe}_{79}\text{B}_{11}\text{Si}_{10}$

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We carried out Microwave Absorption Profile Measurements (FMR and LFS) in the amorphous metallic ferromagnetic microwire of composition $\text{Fe}_{79}\text{B}_{11}\text{Si}_{10}$ and total diameter $12.4\mu\text{m}$ covered by fabrication with glass-pirex. It is well known that the glass cover retains fabrication stresses that are not necessarily homogeneously distributed, potentially producing, in turn, micromagnetic inhomogeneities. Three samples were cut at lengths of 6mm, 3mm y 1mm and were run in a ESR-JEOL JES-RES3X spectrometer, especially equipped with a zero-cross unit, JEOL ESZCS2, that allows to obtain the microwave absorption at zero magnetic field (LFS), in addition to the Ferromagnetic Resonance (FMR), whenever any is present. We found substantial qualitative and quantitative differences in the FMR and LFS due to the only parameter varied, the length of the microwires. Since changing the length of the wires, amounts to change the shape anisotropy, H_{sha} , Hence; lowering the length of the wires is making H_{sha} changing widely. Such changes are clearly seen in the lineshape that shows more structure- magnetic inhomogeneities as the size of the sample goes down. The smaller the size of the sample, and in consequence its volume, the more pronounced the magnetic fluctuations originated in defects, impurities and local stressed regions. The smaller microwires are not behaving as bulk-magnetic bodies at these sizes with, two dimensions in the micrometric length scale. Other two effects of potential importance in the microwave absorption response are: The closure domains and the demagnetizing fields. We, also observe that the intensity of the signal associated with FMR is diminished whereas the signal associated with LFS is increased as the size of the magnetic microwire is lowered, as can be seen in fig.1.

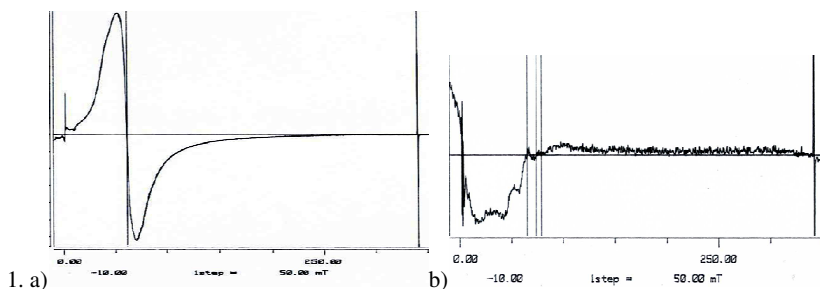


Figure 1. Microwave Absorption Profiles that show the profound changes that appear when the size of the microwires shrink. Length a) 6mm, b) 1mm, respectively.

Giant magnetoresistance and spin torque effects in magnetic Co nanoparticles embedded in a Ag matrix

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In recent years, a significant amount of research has been carried out on the nanogranular Co-Ag system, in single or multilayered form. This interest is due to the observation of the giant magnetoresistance (GMR) effect, which is found to be the highest in the Co-Ag system [1, 2] leading to potential applications in magnetic storage devices. The differences in surface energies of Co and Ag enable the clustering of Co without any traces of alloy formation, allowing the observation of superparamagnetism in these Co clusters embedded in a Ag matrix [3, 4]. The interest has been renewed after the discovery of spin torque effects in granular materials [5].

This study deals with the investigation of the GMR effect and the correlation between structure and magnetism in co-evaporated Co-Ag (Co concentration in the range of 20-40 percent) thin films deposited onto MgO (100) substrates. The samples were grown using molecular beam epitaxy (MBE). The effect of concentration and annealing was analyzed using low temperature transport measurements, SQUID magnetometry and x-ray diffraction measurements. All samples show high GMR (~20-30 percent) at 5 K, which reduces substantially (to ~2-12 percent) when the temperature reaches 250K. The analysis of SQUID measurements, field cooled (FC) and zero field cooled (ZFC) between 5 K and 300 K, as well as MH loops at 5 K and 300 K, show that lower concentration samples have smaller Co clusters. After annealing, the size of particles in all samples increases by a small amount (2-5 nm). SQUID measurements at 300 K show superparamagnetic behavior of the nanoparticles. At 5 K, the particles evidence blocked behavior and a significant contribution from an un-clustered Co (paramagnetic) fraction.

Finally we present results of spin torque measurements, which have been carried out by positioning, using scanning probe techniques, a conductive tip on the sample surface and injecting a high current density into the film.

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Iron Nanowires Inside Finite Zigzag Carbon Nanotubes: Calculation of the Magnetic Properties

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The electronic structure of iron nanowires of 11 and 12 atoms, are calculated using spin polarized density functional theory, with generalized gradient corrections for the exchange-correlation energy. The wires are calculate both as a free clusters and also located inside finite pieces of single walled zigzag, (5,0) and (7,0), carbon nanotubes, CNTs. The main purpose is to analyze the change in the stability and in the magnetic properties of the nanowire due to its interaction with the CNT. Structures of this kind have been synthesized as double wall CNTs filled with 1D nanocrystalline α -Fe [1]; these magnetically functionalized multiwall CNTs have been proposed as useful systems in biomedicine as nano-heaters or as drug delivery systems [2].

First we analyze the bonding energy of the free aggregates, Fe_{11} and Fe_{12} , for different values of the total spin $S=(n_{\alpha}-n_{\beta})/2$, n_{α} and n_{β} are the number of electrons with alpha and beta spin, respectively. For each value of S , we fully optimize the geometry starting always from a linear configuration. We present in Fig. 1 the oscillations of the bonding energy as a function of S . In both cases, the absolute minimum corresponds to a ferromagnetic coupling with magnetic moment per atom larger than $3 \mu_B$. The equilibrium geometries indicate the formation of Fe dimers, and a strong shift between alpha and beta density of states, as can be seen in Fig. 2.

Calculations of the magnetic structure of finite zigzag CNTs [3] show that the ground state is antiferromagnetic, AFM (the edge states are spin polarized at each extreme with an AFM coupling between both sides) and that there is an excited ferromagnetic state FM within thermal energies. When a FM wire is located inside the finite CNT, our results indicate an enhancement of the total spin of the combined system, with respect to that of the free iron nanowire.

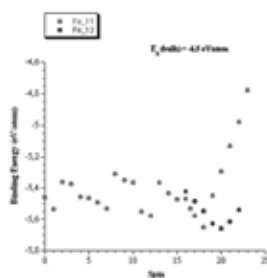


Fig. 1: Bonding energy per atom for Fe_{11} and Fe_{12} nanowires.

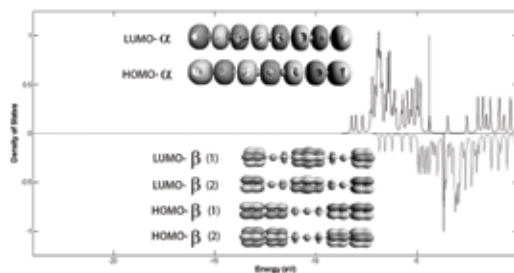


Fig.2: Wave functions of the HOMO and LUMO states and electronic DOS for Fe_{11} nanowire.

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A non-resonant microwave absorption study in Cu-Co nanoparticles prepared by mechanochemical synthesis

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ABSTRACT

In the present work, we report the synthesis of nanoparticles of Cu-Co with 5, 20 and 50% at Co, which are obtained by the reduction reaction between metallic chlorides in solid state, $\text{CuCl}_2 + \text{CoCl}_2 + 4\text{Na Cu/Co} + 4\text{NaCl}$, and that these are activated via the mechanical synthesis in a mill SPEX-D8000 of high energy. Additionally, NaCl is added as an environment to disperse the particles, and obtaining sizes of ~ 5 nm; and that these are dependent on the time of the alloyed mechanic. The nanoparticles are characterized by X-Ray diffraction, these results indicate a reduction of the lattice parameters, and it suggests the formation of the solid solution between both metals.

A study of vibrant sample magnetometry (VSM) shows a typical magnetic response, that it is characteristic of a solid solution formed by nanometric particles [1]. These results show a narrow relation with the spectra of non-resonant microwave absorption, which are obtained in an electron paramagnetic resonance (EPR) spectrometer modified [2]; where this non-resonant signal is associated with magnetic order of the material [3]. Additionally, we compare the results for Cu and Co particles, which are synthesized by the same procedure, with the nanoparticles of the solid solution to give a further knowledge on these materials.

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**SYSTEMS OF GOLD NANOPARTICLES AND ITS APPLICATION AS SERS
SUBSTRATES.**

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ABSTRACT.

Surface Enhancement Raman Scattering (SERS) of Rhodamine 6G at a concentration as lower as 10^6 M were detected using three gold nanoparticles systems: 1) nanoparticles adsorbed on a planar surface, 2) nanoparticles on silica spheres and 3) clusters deposited on planar surface. Deposition of nanoparticles was practiced functionalizing with 3-aminopropyltriethoxysilane (APTES) in the first and second method. A photonic crystal of silica particles is used as a template to obtain gold clusters in the third one. We also investigate the SERS signal as function gold nanoparticles concentration. As expected, gold nanoparticles concentration in these methods is an important parameter for SERS.

Can Au₂S@Au core-shell structures form spontaneously?

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What are the major products of the reaction between AuCl₄⁻ salt and Na₂S? This apparently simple question resulted in much of a controversy. There are two groups whose claims widely differ. Initially observed by Zhou et al [1] and later by Halls et al. [2], believed that chief product in the above reaction is Au₂S@Au core-shell nanostructure. However, Zhang and coworkers [3] did extensive studies and found that the products are gold-aggregates but not core-shell structures. Central to the controversy is the observation of near infra-red absorption (NIR) band, caused surface plasmon resonance (oscillations caused by surface conduction band) by the products of the reaction. Halls and others, by using Mie theory, argued that Au₂S@Au core-shell structure could explain the origin of the bands, where as, Zhang makes a case that gold-aggregates could also result in producing the same effect. In this talk, I will address this controversy in the form of following questions. Can Au₂S@Au core-shell structures form spontaneously? Can the observation of NIR, which is a key piece of evidence, be a result of aggregation of small Au₂S clusters?

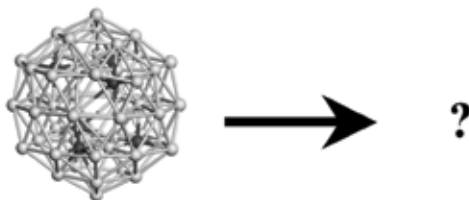


Figure 1. A small Au₂S@Au core-shell structure. Is it stable?

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Optical Properties of Isolated Silver and Gold - Biomolecular Hybrid Systems

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We present a molecular approach of the optical properties of nanohybrids by a joint theoretical and experimental study of the optical properties of tryptophan based hybrid complexed with gold and silver clusters. Our TD-DFT calculations and MD simulations together with experimentally measured fragmentation channels provide insight into the nature of excitations in interacting nanoparticle-biomolecule subunits and allow identifying characteristic spectral features as fingerprints of structures.

Recent results obtained on trapped $Au_n(SG)_m$ (SG : glutathione) polyanions will be presented. Magic-numbered Au_n clusters protected by glutathione monolayers were isolated in the ion trap and activated by collision and laser irradiation. After UV and Visible excitation, an intense electron photodetachment is observed. The electron photodetachment yield will be used to probe the optical properties of these hybrid anions.

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Discrete dipole approximations of Au and Pd nanoclusters

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Nanoplasmonics has received considerable attention in recent times due to technological advances which now allow us to manipulate and structurally characterise clusters on the nanometre scale, and the resulting important applications of these features e.g. sensors. The optical properties of nanoparticles are size, shape and composition dependent, allowing for tunability. Nanorod shapes are of particular current interest due to their display of two axis-dependent surface plasmon resonances (SPRs) [1].

Exact solutions to Maxwell's equations (of classical electromagnetism) were first offered by Mie [2], and are only known for specific geometries. As a result approximate methods are often required. An example is the discrete dipole approximation (DDA), which is a flexible method for computing the absorption and scattering by nanoparticles with an arbitrary geometry [3].

Here, simulations are presented using the DDA for Au_{core}Pd_{shell} nanorods and linearly aggregated Au_{core}Pd_{shell} nanospheres. We hope to find alignment between theoretical [1,4] and experimental results to help explain each resonance appearing in the spectra.

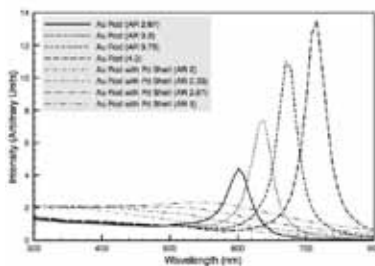


Figure 1: Absorption spectra for Au rods with and without uniform Pd coating.

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The use of atomic hydrogen to control the emission properties of porous silicon layers

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In this work, the evolution on the photoluminescent (PL) properties of etched porous silicon (PS) layer is reported. P-type, (100) oriented silicon substrates were processed by electrochemical method, at room temperature, to develop a porous structure sheet and its PL characteristics determined. Hot filament chemical vapor deposition (HFCVD) technique was used to produce atomic hydrogen for etching the porous silicon layer and modify their luminescent attributes. After that, the porous films were again measured. It was found the maximum in the PL band shifted from its initial position, 720 nm, up to blue-green region, 480-520 nm. The blue shift was ascribed to a reduction on the size of the porous Si cores due to the chemical reaction with the atomic hydrogen. In Addition, regions of PS layer covered with a silicon oxide film were observed. The silicon oxide resulted, in the process, as a principal reaction product. The PL properties drawn in the last regions exhibited a red-infrared shift with the maximum placed at 930 nm. This procedure may be used to improve and stabilize the emission properties of devices based on porous silicon layers.

Surface Enhanced Raman Scattering at the edge of metallic Nanoparticles

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When a molecule is approached to metallic surfaces, metal nanoparticles (NPs), or metal NPs arrays, its Raman spectra intensity is augmented by several orders of magnitude (up to 10^{16} as have been observed in some experimental works). This intensity enhancement is known since as Surface Enhanced Raman Scattering (SERS). It is generally agreed today that there are two main sources of enhancement, the first is due to an amplified EM field at the tiny particles (these could be individual NPs or a set of NPs that form a structure), and the second due to the electrons transport between the target molecule and the substrate. Recently, NPs with very sharp peaks and edges as star-shaped and polyhedral NPs such as icosahedra, tetrahedra, dodecahedra, etc. NPs have been synthesized. At the vicinity of these peaks and edges the electromagnetic field has shown an extraordinary intensity enhancement that favours SERS phenomena allowing probe single molecules.

In this work, we perform a systematic study of the electric field intensity and enhancement factors at the proximity of the edges of different metallic NPs. To understand the influence of the shape, material and environment on the SERS phenomena. We have studied the EM field as a function of the angle and the dielectric functions of the wedge and surroundings, relating those with the geometry of real NPs which are immersed in different host media. In our approach we solve the Helmholtz equation using a power series to represent the electromagnetic field considering the singularity at the edge. The results are compared using numerical calculations of the electric field intensity within the discrete dipole approximation (DDA) for the edges of a cube, a tetrahedron and an icosahedra.

Structural studies of $\text{BaTiO}_3:\text{Er}^{3+}$ and $\text{BaTiO}_3:\text{Yb}^{3+}$ powders synthesized by hydrothermal method.

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Erbium and ytterbium doped barium titanate nanopowders have been prepared by hydrothermal method. Rare earth ions into barium titanate structure improve new characteristics which allow increase the application field in optical devices such as trichromatic tubes, LCD displays, lamps, and infrared laser. In this work, $\text{BaTiO}_3:\text{Er}^{3+}$ and $\text{BaTiO}_3:\text{Yb}^{3+}$ were prepared using barium chloride [BaCl_2], titanium butoxide [$\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$], erbium chloride [ErCl_3] and ytterbium chloride [YbCl_3] as precursors. Anhydrous methanol were employed as solvent. Metallic potassium was used to promote the solubility in the system and increase the pH up to 13. This method let the formation of predominant cubic structure in both Er^{3+} and Yb^{3+} doped BaTiO_3 powders. Characteristic bondings of BaTiO_3 were observed by FT-IR spectroscopy. Predominant cubic structure was confirmed by X-Ray diffraction and Micro-Raman analyses. The particle size (~30 nm) was determined by Scherrer equation from X-Ray diffraction data. The results are presented and discussed.

Excitation spectra of large Ag clusters in He droplets

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We report on the assembly of large molecular and metal clusters containing up to a few thousand particles in liquid He droplets at the ultralow temperature of $T < 1$ K.[1,2] The clusters were obtained via sequential pickup of small hydrocarbon molecules and/or silver atoms by He droplets with average sizes in the range of 10^4 to 10^7 atoms. The size of the clusters and the flux of these transported species are ultimately limited by the evaporative extinction of the entire helium droplet upon capture of particles. The obtained clusters have been studied via laser photo depletion spectroscopy of vibrational and electronic excitations (0.2 – 6 eV). The spectra of neat silver clusters with up to hundreds of atoms are dominated by a strong, relatively narrow ($\Delta\nu \approx 0.4$ eV) resonance close to the well-known surface plasmon frequency of about 3.7 eV and a broad feature in the near-UV due to a higher-energy resonance [3]. However, in clusters having a few thousand Ag atoms there appears strong absorption that extends into the red and infrared spectral range down to about 0.5 eV. This may indicate that large metal clusters formed in helium droplets have open (possibly fractal) structures as compared to a close-packed structure in small clusters.

We also report on the formation of core-shell ethane – silver clusters in helium droplets which have been characterized via electronic and vibrational spectroscopy of their atomic and molecular constituencies.

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Linear optical response of hydrogen-passivated graphene and graphene-like 2D silicon and germanium materials.

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Since 2004, we are witnessing a great interest of research on a new class of a 2D nanomaterial, graphene [1]. Very recently silicon analogue of graphene, silicene, has been produced experimentally [2] while the germanium-based monolayer film analogue has been predicted theoretically [3]. Although graphene (and its Si or Ge analogues) demonstrate a lot of exciting properties, its zero-gap band structure limits graphene application in 2D microelectronics. As it was demonstrated, however, hydrogenation of graphene produces a new stable semiconducting material, graphane [4]. For possible device application of graphene or graphane, a single layer or a bilayer of the material can be formed on the top of, e.g., SiC (0001) [5], or silicene on top of Ag(110) [3]. For such sandwiched systems, experimental geometries might not provide conditions for complete hydrogenation of the 2D sheets. Therefore, it is important to have non-destructive experimental techniques that allow the characterization of the system. We have thus proven theoretically that linear optical techniques can provide detailed access to the properties of 2D monolayers. To reach this goal, we have carried out combined simulation of structural, electronic, optical and spin-current injection properties for graphene, silicene and germanium based 2D nano-sheets with different hydrogen coverages. The optical techniques that are considered are: linear optical response, coherent control of the injection current and of the spin injection.

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Induced aggregation of Ag nanoparticles for SERS sensing

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Due to their unique properties, the noble metals are the most studied among the metallic nanoparticles. The different applications are based, among others, on the surface plasmon of noble metal particles, the biocompatibility of the gold and the bactericide property of silver.

In this work, the most recent results of the surface modification and induced aggregation of silver nanoparticles will be shown. Aminoacids were used to the surface modification of the nanoparticles. It was studied how depend the stability and the optical properties of the metallic nanoparticles in aqueous medium on the metal concentration, the concentration of aminoacids and the pH of the solution.

Varying the pH, the protonation of the aminoacid molecules are changing. At the isoelectric point the amino acid has a neutral, zwitterionic form with protonated amino and deprotonated carboxylic groups. Between the nanoparticles, an attractive force can exist due to the opposite charges of the adsorbed aminoacids. In part for this interaction the nanoparticles can be connect to the others, which finally should cause their aggregation.

The kinetic study of the aggregation was studied by UV-Vis spectroscopy detecting the change of the characteristic plasmon band of silver nanoparticles. Decreasing the pH the cross-linking and finally the aggregation of the nanoparticles was faster, indicating the role of the protonated amine groups.

The nanocomposites also were studied by Infrared and Raman spectroscopy and transmission electron microscopy.

The aggregated nanoparticles can be serving as substrate of SERS application.

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Optical to UV Spectra of Sandwiches of Benzene and Transition Metal Atoms.

Time-dependent DFT and Many-body Calculations.

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The optical spectra of sandwich clusters formed by transition metal atoms (titanium, vanadium and chromium) intercalated between parallel benzene molecules have been studied by time-dependent density functional theory (TDDFT) and many-body perturbation theory (GW approximation and Bethe-Salpeter equation). Sandwiches with different number of layers, including infinite chains, are considered. The lowest excitation energy peaks in the spectra are characteristic of the robust bonding in these complexes. The excitation energies vary in a systematic way with the metal atoms and with the cluster size, and so these materials could be used to tune the optical properties according to specific functionality targets. The differences in the spectra could be used to identify relative abundances of isomers with different spins in experimental studies. As a salient feature we found that the infinite (TiBz)_∞ chain becomes metallic.

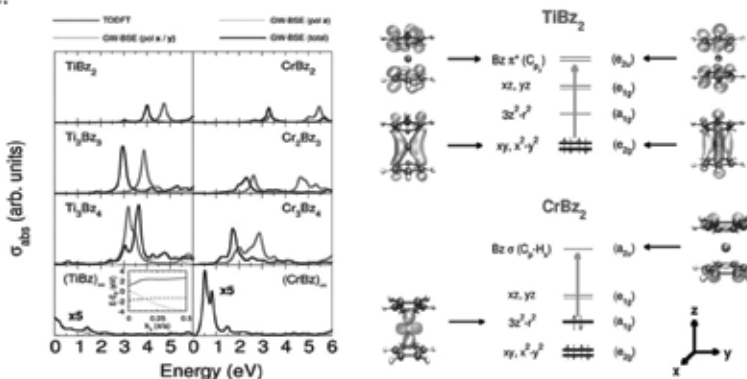


Figure 1: Calculated GW-BSE photoabsorption cross sections of Ti_nBz_{n+1} and Cr_nBz_{n+1} sandwich clusters and infinite chains; and frontier orbitals of TiBz₂ and CrBz₂ (axis set chosen also shown).

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Linear and nonlinear photophysical performance of Ag- and Au/SiO₂ supported nanoparticles embedded in SiO₂-sonogel films

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SiO₂-based hybrid sonogel films were prepared via spin-coating with Au and Ag/SiO₂ supported nanoparticles (NPs). The well-established catalyst-free (CF) sonogel route [1] was successfully implemented to produce these optically active hybrid films by doping the liquid sol-phase with Au and Ag/SiO₂-NPs. Au/SiO₂-NPs were synthesized according to the [Au(en)₂]³⁺-cation-adsorption method [2], whereas the Ag/SiO₂-NPs were obtained by the deposit precipitation with NaOH method, using AgNO₃ as precursor. Prepared Au and Ag/SiO₂-NPs exhibited low 2D-HCP crystallinity with diameters below 12nm and homogeneous size distribution. The easy NPs loading within the dielectric sonogel network evidenced the huge chemical affinity between the highly pure CF-SiO₂-sonogel host environment and the guest Au and Ag/SiO₂-NPs. This fact allowed us to fabricate stable hybrid films suitable for linear and nonlinear photophysical characterizations. Indeed, the host system provided thermal and mechanical stability protecting the active metallic NPs from environment conditions and diminishes their tendency to form aggregates; hence, preserving their pristine optical properties and producing hybrid sol-gel films appropriate for optical applications. Comprehensive morphological, structural, spectroscopic and cubic nonlinear optical (NLO) characterizations were performed to the obtained hybrids. Results show that Au and Ag/SiO₂-NPs were satisfactorily embedded within the highly pure SiO₂-sonogel network with homogeneous distribution, random orientation and low guest-host interactions. Thus, improved cubic NLO-properties such as nonlinear refraction and third harmonic generation (THG) were measured in the developed amorphous-based hybrid films according to the Z-Scan and THG-techniques.

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Optic characteristics of silver nanoparticles incorporated into erioniteG. Odegova¹, N. Bogdanchikova², V. Petranovskii², M. Avalos Borja², A. Pestryakov³¹ Borekov Institute of Catalysis, Novosibirsk, 630090, Russia² Centro de Nanociencias y Nanotecnología - UNAM, Ensenada, B.C., 22800, México.³ Tomsk Polytechnic University, Tomsk 634050, Russia

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Recently the methods of obtaining and the optical properties of the diverse materials, which ensure modulation of refractive index with the period of the order of light wavelength, attract the great interest. Stabilization of silver nanospecies on erionite microcrystal of different forms has been studied by the methods of UV-visible diffuse reflectance spectroscopy (DRS), XRD, TEM.

The experiments revealed that silver was stabilized in the pores of carrier in the form of clusters Ag_8^0 and Ag_8^{n+} (absorption bands at 33800 and 30900 cm^{-1} in UV-vis. spectra, Fig.1); and in the form of nanoparticles with size of 2-3 nm on the external surface (peaks at 22100 cm^{-1} and 14300 cm^{-1}). A rise of reduction temperature up to 300-500°C led to the decrease of the silver clusters concentration, the formation of the larger Ag particles and their partial oxidation in air. DRS and TEM analysis showed that relatively regular form of the erionite microcrystals created conditions for the formation of the partially ordered medium Ag/erionite with the unusual optical properties. As a result of the interference of the waves, repeatedly scattered on such ordered systems, the appearance of localization of states and formation of the "forbidden photon band", whose position in the scale of photon energy is determined by the period of the lattice of photon crystal and by the relative refractive index of particles become possible.

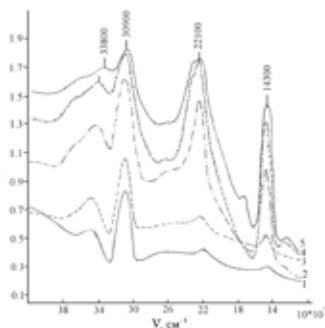


Figure 1: UV-visible spectra of the samples Ag/erionite reduced in H_2 at 110°C.

Ag concentration: 1 - 0.6%, 2 - 1%, 3 - 5%, 4 - 12%, 5 - 23%.

The investigations showed that highly dispersed medium Ag/erionite can be considered as one-dimensional photon crystal for which the interference effects are observed in the visible region of the spectrum. The presence of optical effects makes the application of such materials in optics and optical electronics possible.

Scintillating properties of $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$ nanopowders obtained by sol-gel process

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Lu_2O_3 has emerged as one of the most promising scintillator material to be incorporated in X-Ray devices, due primarily to its high density and effective atomic number, allowing to absorb almost all the radiation diminishing all off the problems related to a long exposition time. Furthermore, when it's codoped with Eu^{3+} and Tb^{3+} , presents highly efficient scintillating properties, emitting in the red region of the visible spectrum (611 nm). In this work, $\text{Lu}_2\text{O}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$ nanopowders were prepared by the sol-gel process, using as precursors lutetium, europium and terbium nitrates, and ethanol as solvent. The system was heat-treated at different temperatures in order to determine the crystal structure by means of X-Ray diffraction. The sample heat treated at 700°C presented the expected cubic structure, this sample was studied by Transmission Electronic Microscopy with the aim to analyze the morphology and establish the size of crystallites. The scintillating properties were analyzed in function of the Tb^{3+} atomic content (0.005, 0.075 and 0.01) with a fixed Eu^{3+} level (2.5 at.%), monitoring the well known ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ europium emission band. The results shown that at higher Tb^{3+} contents, a quenching process between Eu and Tb occurs, however, the lowest Tb^{3+} content exhibits an increased scintillation light yield compared with a monodoped sample.

**SYNTHESIS OF CDSE NANOPARTICLES IMMERSSED IN A
POLYMERIC MATRIX OF AMYLOPECTIN BY MEANS OF R.F.
SPUTTERING**

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Abstract

CdSe nanoparticles immersed in a polymeric matrix of Amylopectin have been synthesized by means of the r.f. magnetron sputtering growth technique. The target was elaborated employing high CdSe and Amylopectin powders. X-ray diffraction (XRD) shows that the amylopectin thin film is amorphous, spectrum reveals that the organic material crystalline structure (at short range) is not affected by the sputtering process, in addition the optical spectrum shows the band gap energy of the CdSe is greater than bulk one.

CdSe nanoparticles grow with the hexagonal wurtzite structure. The average radius of the grains, calculated by using the Scherrer's formula radius in XRD peaks, is of the order of 10 nm. The band gap of CdSe nanoparticles measured from optical absorption measurements is 1.9 eV. Atomic force images allow observe well defined spherical regions scattered in a uniform background of the organic material, which indicate the location of CdSe nanoparticles. Synthesis of semiconducting nanoparticles in organic biocompatible matrices is an important topic of research due to its important applications in biological area.

Use of organic solvents as dispersing grinding for obtaining nanoparticles natural pozzolan

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The natural pozzolan is used as inorganic admixture to replace part of the clinker in the Portland cement manufacture due to low activate temperature in an alkaline medium, it is advantageous because it increases the strength of hydrated Portland cement. Previous studies have reported that the reactivity of the pozzolan increases as particle size decreases. In this work were used some organic solvents as dispersion medium in the grinding of pozzolans. In the present work were used ultrafine mill and balls with different natural pozzolans in order to reduce the average particle size. Acetone was the most appropriate dispersion medium. Were characterized the final particle size distribution of the pozzolan. The results a trimodal distribution of particle size with 10% of particles below 1 μm , and the presence of SiO_2 limiting factor the reduction of particle size

Optical and thermal characterization of solutions containing gold nanoparticles at different pH values

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Abstract

Thermal lens spectrometry (TLS) and Photoacoustic Spectroscopy (PAS) techniques were used to obtain respectively the thermal diffusivity and optical absorption spectra of solutions containing gold nanoparticles (diameter of 20 nm) with variable pH values. The results show that, as the pH of these nanofluids increases, the thermal diffusivity also increases. Also it was possible to observe changes in their optical absorption spectra when compared with the characteristic reported spectrum of gold nanoparticles solutions. It was observed that the pH values of the solutions influenced the superficial density of charges in the nanoparticles and thus the stability of the solutions. These results will be compared with report studies of nanofluids with variable pH. These measurements were performed at room temperature. TLS was used in a mode-mismatched dual beam configuration that provides a reliable alternative measuring with high sensitivity, the thermal diffusivities of semitransparent materials and low thermal diffusivities on the other hand the optical absorption spectra for these samples were obtained by using a photoacoustic spectrometer.

A new Magnetron based gas aggregation source of metal nanoclusters

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A new magnetron based gas-aggregation source [1] for continuous production of metal nanoclusters has been built and coupled to a double time of flight mass spectrometer system [2-3]. The capability of the source to produce neutral, positive and negative nanoclusters within one production cycle has been tested. The source remains steady for continuous long operations and has high beam intensity. This kind of source is preferable for size selective measurements on individual nanoclusters in gas phase. Mass abundances of neutral and charged copper clusters have been investigated. The experimental isotopic distributions of ^{63}Cu vs. ^{65}Cu of individual clusters have been derived and compared to corresponding theoretical profiles [4]. Figure 1 shows the mass abundance of negative copper clusters and the isotopic distribution of neutral 34 atom cluster detected in the same cycle of operation.

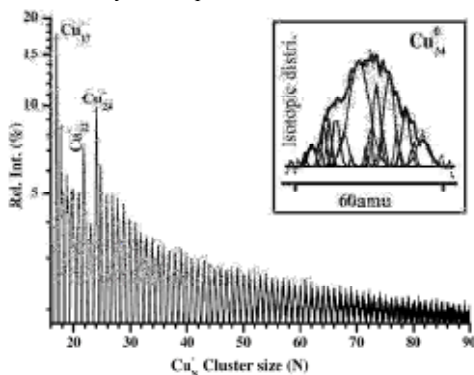


Figure 1 Mass abundance of negatively charged copper cluster from the magnetron based gas aggregation source. Inset shows the individual mass peak of neutral 34 atom copper cluster. Experimental isotopic distribution derived by Gaussian fitting are plotted within.

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Growth and Characterization of Nanostructured CuInSe₂ Particles and Films

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In recent years nanostructured semiconductors have received considerable attention because of their application in solar cells and photoelectrochemical hydrogen production. CuInSe₂ has emerged as a candidate for solar energy conversion, due to its favorable characteristics as the absorber material for solar radiation. High absorption coefficient and low cost methods for deposition of thin films make CuInSe₂ a promising material for photovoltaic devices. Various preparation techniques have been employed to prepare CuInSe₂ thin films including flash evaporation, single source evaporation, multiple source evaporation, three-source evaporation, spray pyrolysis and electrodeposition. It has been reported that the copper indium diselenide films can be prepared by chemical bath deposition technique. Though it is difficult, authors have successfully prepared the CuInSe₂ thin films using chemical bath deposition technique. In this study we employed chemical synthesis and physical vapor deposition to prepare the nanostructured CuInSe₂ films. Various characterization techniques were used to analyze the films.

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