

Preface

The vigour and maturity of the field of atomic clusters is well represented by the contributions to ISSPIC14. This book contains the abstracts of the contributions to this Conference: plenary talks, invited talks, selected oral contributions (hot topics) and poster contributions. 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-08 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). Within each topic, the posters have been ordered according to the surname of the presenting author. An author index is provided at the end of the Book. We acknowledge support from Junta de Castilla y León for the edition of this Abstracts Book.

A-01. Structure and thermodynamics of free clusters

A-02. Fullerenes, nanotubes and nanowires

A-03. Clusters in external fields

A-04. Molecular electronics and transport

A-05. Electronic structure and quantum effects in low dimensional systems

A-06. Nanomagnetism

A-07. Nanocrystals and self-assembly

B-01. Experimental production of clusters

B-02. Helium clusters and spectroscopy

B-03. Clusters on surfaces

B-04. Nanoparticles in biology and medicine

B-05. Cluster reactivity and catalysis

B-06. Spectroscopy and dynamics with short laser pulses

B-07. Optical properties

B-08. Technological applications

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Monday, Sep. 15th

Plenary Talks

U. Landman

Structure, Dimensionality and Properties of Supported, Suspended and Interfacial Clusters

Invited Talks

D. J. Wales

Energy Landscapes of Atomic, Molecular and Biomolecular Clusters

C. Barth

Imaging Nanoclusters with the Non-contact AFM and Kelvin Microscope: Cluster Structure and Chemistry at the nm Scale

T. Tsukuda

Ligand-Protected Gold Clusters: Synthesis, Structures, and Stabilities

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Partial Oxidation Reactions on Size-Selected Clusters

Hot Topics

J. Pénuélas

Non-equilibrium CoPt Nanoparticles Structural Transitions

G. Pastor

Tuning the Magnetic Moments and Anisotropy Energy of CoRh Nanoparticles

G. H. Wang

Strong Magnetoelectric Effect in Tb-Pb Cluster-based Thin-Film Heterostructures

H. Häkkinen

Ligand-Protected Gold Cluster Superatoms

I. L. Garzón

Chirality, Optical Activity and Enantiospecific Adsorption in Gold Clusters

S. Dobrin

Mechanisms of Reactions on Pt Nanoclusters used in Electrocatalysis. The Role of Organic Surfactants

Structure, Dimensionality and Properties of Supported, Suspended and Interfacial Clusters

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Gaining insights into the nature of physical and chemical systems of highly reduced sizes, and developing experimental and theoretical methodologies aimed at probing, manipulating and controlling them on the atomic and molecular level, are among the major challenges of current basic interdisciplinary research. Emergent physical and chemical phenomena at the nanoscale regime and the use of atomistic simulations as tools of discovery in this area [1] will be discussed and demonstrated through studies focusing on systems involving: (i) surface-supported nanoclusters, (ii) suspended clusters (in the form of interfacial nanowires), and (iii) quantum electron and boson clusters in 2D dots and cold-atom traps.

(i) Nanocatalysis by small gold clusters [2(a-c)]; Structure, dimensionality and chemical reactivity of surface-supported gold clusters; Control of the physical and chemical properties of supported clusters through the selection of support thickness [2(d, e)] and via the use of external electric fields [2(f)].

(ii) Nanowire formation mechanisms; Structural (atomic and electronic) properties, Mechanical response; Shuttling wire-suspended nanoclusters; Quantized electric conductance; Metal-insulator transition and local magnetic moments in oxygenated gold nanowires [1, 3].

(iii) Symmetry breaking phenomena resulting in formation of electron Wigner crystallites and rotating electron molecules in 2D quantum dots, and in the appearance of crystalline arrangements and rotating vortex clusters in atomic traps [4].

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Energy Landscapes of Clusters: From Atoms to AmyloidDavid J. Wales*University Chemical Laboratories, Lensfield Road, Cambridge, UK**dw34@cam.ac.uk*

Coarse-graining the potential energy surface into the basins of attraction of local minima provides a computational framework for investigating structure, dynamics and thermodynamics in molecular science [1, 2]. Basin-hopping global optimisation employs steps between local minima [3, 4], and predicts novel ‘magic number’ structures for clusters in the mesoscopic regime, including links and knots [5]. To treat global dynamics we must include transition states of the potential energy surface, which link local minima via steepest-descent paths. We may then apply the discrete path sampling method [6, 7], which provides access to rate constants for rare events. In large systems the paths between minima with unrelated structures may involve hundreds of stationary points of the potential energy surface. New algorithms have been developed for both geometry optimisation and making connections between distant local minima [8, 9], which allow us to treat such systems. Applications will be presented for a variety of atomic and molecular clusters. Recent results for the aggregation of misfolded peptides illustrate how experimental time and length scales can now be addressed for such systems [10, 11].

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Imaging nanoclusters with the Noncontact AFM and Kelvin microscope: Cluster structure and chemistry at the nm scale

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In the last 10 years, Noncontact Atomic Force Microscopy (NC-AFM) has successfully proven that true atomic resolution can be gained on any clean and almost atomically flat surface of even bulk insulators [1]. However, emerging fields in surface science and nanotechnology like nanocatalysis [2] ask now for an application of this type of force microscope, which leads to new challenges in NC-AFM.

One challenge is the imaging of nanometer-sized metal cluster with highest possible resolution, which permits a precise characterization of the lateral cluster shape. Another challenge is to extend the microscope in such a way that it gets “chemically” sensitive or, at least, sensitive on more specific force channels of e.g. electrostatic nature. Measuring the local work function of a cluster-surface system at the nanometer scale would be of a high interest in many fields of surface science.

In this contribution it will be discussed to which degree NC-AFM can master these two challenges. In the first part of the contribution, the constant height mode in NC-AFM is presented, which is a suitable technique to image the lateral shape of metal nanocluster with high precision [3]. A comparison between experiment and theory explains that only the last nanometer of the tip images the correct shape of the cluster reducing to a large part the tip-surface convolution effect. In the second part it will be shown that the Kelvin modulation technique can be implemented in NC-AFM in such a way that, alongside the topography, also the work function of supported metal nanoclusters can be imaged at nanometer scale [4]. Possible electronic modifications of single clusters by the substrate but also changes of the cluster work function in the presence of adsorbed gaseous species will be discussed.

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Ligand-Protected Gold Clusters – Synthesis, Structures, and Stabilities

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Free gold clusters have been prototypical systems for the study of structures, stabilities and physicochemical properties of metal clusters. For fabrication of cluster-based materials with desired properties, it is essential to understand the effect of protecting ligands on the structures and stabilities of gold clusters. We have developed an experimental method to synthesize a family of ligand-protected gold clusters with well-defined compositions. Crucial step for our precision synthesis is to fractionate as-prepared, polydisperse gold clusters by size using polyacrylamide gel electrophoresis, size exclusion chromatography, or solvent extraction. Charge states and molecular formulas of the fractionated clusters were determined by electrospray-ionization mass spectrometry. In the present contribution, we discuss the structures and stabilities of the gold clusters protected by phosphines and thiolates.

Bidentate phosphine ligand:

It is known that gold clusters protected by monodentate phosphines such as $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ are not so stable because of weak Au-PR_3 interaction [1]. By using a bidentate phosphine ligand, BINAP, we obtained a stable compound $[\text{Au}_{11}(\text{BINAP})_4\text{Cl}_2]^+$ [2]. The formal charge of the Au_{11} core is 3+, so that the preferential formation is due to high stability associated with electronic shell closing.

Thiolate ligands:

Because of a strong Au-SR bonding, as-prepared samples of $\text{Au}_n(\text{SR})_m$ usually contained metastable clusters kinetically stabilized in addition to thermodynamically stable clusters [3-5]. By depopulating these metastable clusters by chemical etching, we could isolate $\text{Au}_{25}(\text{SR})_{18}$ [6-9], $\text{Au}_{38}(\text{SR})_{24}$ [5,10], $\text{Au}_{144}(\text{SR})_{59}$ [10] as stable compounds. Charge states of these clusters were not fixed but could be altered in the range of -1 to +3 dependent on the conditions of preparation and storage [9,10]. Moreover, these $\text{Au}_n(\text{SR})_m$ clusters show reversible redox behavior in contrast to $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$. These results suggest that geometrical factors play more important role in determining the stability of $\text{Au}_n(\text{SR})_m$. Possible geometric structures are proposed for $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{144}(\text{SR})_{59}$ in which highly-symmetrical Au cores are fully protected by $[-\text{SR-Au-SR-}]$ and/or $[-\text{SR-Au-SR-Au-SR-}]$ oligomers, based on the structures of the relevant systems $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^-$ [11-13] and $\text{Au}_{102}(\text{SC}_6\text{H}_4\text{COOH})_{44}$ [14].

Mixed ligands: [15]

Chemical reaction between $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$ and C_nSH ($n=2-18$) serendipitously yielded a stable compound $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_n)_5\text{Cl}_2]^{2+}$. Single crystal XRD analysis revealed that Au_{25} core forms a cluster-of-cluster structure; two icosahedral Au_{13} cores are bridged by thiolates sharing a vertex atom (see Figure).

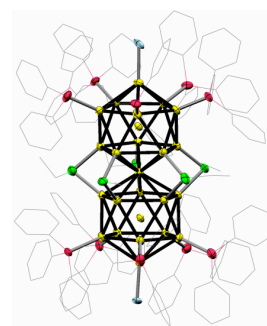


Figure. Ortep drawing of $[\text{Au}_{25}(\text{SC}_2)_5(\text{PPh}_3)_{10}\text{Cl}_2]^{2+}$

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**Partial oxidation reactions on size-selected clusters:
Towards the understanding of the size/shape & function relationship in catalysis**

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This paper focuses on the catalytic properties of size-selected clusters supported on technologically relevant oxide films with the goal to understand the effect of size and composition in complex reactions of high industrial relevance. In particular, partial oxidation reactions of alkanes and alkenes on supported size-selected atomic clusters and up to 20 nm particles are investigated, to our knowledge for the first time, under realistic reaction conditions (at atmospheric pressure and elevated temperatures). The size and shape of the nanocatalysts at work is monitored *in situ* by synchrotron X-ray scattering. The simultaneous detection of reaction products allows to elucidate the correlation between the size&shape and catalytic properties. High-resolution SEM was employed to image the supported clusters before and after the catalytic test; XPS to detect the catalytically relevant states.

Synthesis. The applied synthesis techniques allow for the ultimate control of both: surface composition, as well as cluster size and composition – prerequisites for producing highly uniform active sites on technologically relevant supports for basic catalysis studies. The atomic and several nm size clusters were produced in a laser ablation cluster source and ACIS source, respectively and deposited on thin amorphous alumina films prepared by atomic layer deposition technique on flat as well as nanoporous supports.

Reactions studied. *Epoxidation of propene (C=C bond activation).* The direct oxidation of propene to propylene oxide was studied on size-selected Ag nanoparticles as well as atomic Ag and Au clusters. Pronounced size-dependent reactivity was observed on Ag clusters; the performance of the atomic Au clusters was strongly dependent on additives to the gas mixture. XPS studies found metallic silver; there was no indication of any subsurface chemistry and no surface silver oxide formation. Gold is found metallic (Au⁰) under reaction conditions as well. Theoretical modeling performed on atomic Au and Ag clusters reveals the details of the catalytic steps taking place at the interface of the clusters with the support.

Dehydrogenation of propane (C-H bond activation). It was found that Pt clusters stabilized on high surface area nanoporous supports were highly active in the oxidative dehydrogenation of propane. The subnanometer clusters were by up to two orders of magnitude more active than previously reported platinum and vanadia catalysts, while at the same time maintaining high selectivity towards the formation of propylene. The results of theoretical calculations show that the extraordinary activity and selectivity of the subnanometer clusters is determined by the under-coordination of the Pt atoms.

Non-equilibrium CoPt nanoparticles structural transitions or how the temperature assistance lead to tunable structures

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Co- and Fe-based magnetic nanoparticles (NPs) have attracted a lot of interest because of their applications in ultrahigh density recording media. In particular, FePt and CoPt NPs are especially promising due to the combination of size reduction and alloying effects, which induce large magnetic moment and high magnetic anisotropy [1].

In order to achieve suitable magnetic performances, at this nano-scale, subsequent thermal treatment, during or after the bimetallic NPs growth, is often required. This temperature assistance can lead to morphological changes or important chemical rearrangements in the NPs. Moreover, in case of supported NPs, this thermal treatment can modify the NPs size and dispersion on the substrate surface [2]. The present understanding of fundamental mechanisms, such as driving force for yielding specific NPs structures or morphologies, as well as structure-property correlations, has been hindered by the lack of knowledge of the precise atomic arrangement, especially in the case of few nanometers-size NPs. The challenge is to distinguish during the internal atom rearrangement induced by thermal treatments, between the atom-by-atom mobility and the large motion of atoms induced by the coalescence. Indeed, the coalescence between nanoparticles induces extended defects formation like high angle boundaries, which can act as nucleation center for fast structural transitions, like chemical ordering.

Supported CoPt NPs were studied in the 1-4nm size range by in situ and in real-time X-ray scattering measurements during their co-deposition growth and their annealing. These investigations were performed in UHV conditions at the European Synchrotron Radiation Facility (ESRF) on the BM32 SUV beamline. Grazing Incidence Small Angle X-ray Scattering (GISAXS) provides size, shape and correlation distance between NPs, while X-ray diffraction (GIXD) allows structure identification. In addition, Monte Carlo simulations of relaxed CoPt cluster structures (ordered or disordered truncated octahedral, decahedral and icosahedral) were performed using a semi-empirical tight-binding potential [3], to interpret diffraction experimental results.

Our results show that the evolution of the cluster structure is size-dependant or coalescence-dependant [4]. Dynamical coalescence events in the early stage (<300 atoms) of the growth at 500°C are the main responsables for the fcc NPs formation, while at room temperature, atom-by-atom growth conditions produce the non-equilibrium icosahedral Ih morphology almost exclusively. On the other hand, annealing (400-500°C) leads to the formation of decahedral rather than fcc morphology resulting of the quasi-static coalescence of Ih particles (>300 atoms). Further annealing at 600°C yields partially chemical ordered nanoparticles, by atom-by-atom internal rearrangements.

This opens a new understanding of the coalescence effect versus size effect on bimetallic particle structure transition with the temperature, in a 1-4nm size range.

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Tuning the magnetic moments and anisotropy energy of CoRh nanoparticles

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While the magnetism of monometallic transition-metal (TM) clusters has been largely investigated in past years, very little is known at present about the behavior of binary-metal particles or magnetic nanoalloys. Is it possible to tune the magnetic properties of clusters, in particular the MAE, by alloying as it has been done in the bulk? Can one microscopically design very hard or very soft nanomaterials in a controlled way? What is the role played by the spatial distribution of the chemical species within the particle on the magnetic behavior?

In order to investigate this problem we have determined experimentally and theoretically the spin moments, orbital moments and magnetic anisotropy energy (MAE) of $\text{Co}_x\text{Rh}_{1-x}$ alloy nanoparticles (NPs) as a function of size, structure and composition. The NPs are synthesized by chemical decomposition of organometallic precursors under hydrogen atmosphere and in the presence of a polymer matrix. The magnetic properties are determined using SQUID, Mössbauer spectroscopy, and X-ray magnetic circular dichroism (XMCD). Self-consistent calculations are performed in the framework of a realistic *spd*-band tight-binding Hamiltonian by treating the redistributions of the spin- and orbital-polarized density, as well as the spin-orbit (SO) interactions, on the same electronic level and from a local perspective.

Enhanced values of the average magnetic moment per CoRh unit and of the MAE are observed in alloy NPs, which indicate a significant induced polarization on the Rh atoms. These results are well reproduced by theory and were also confirmed by independent XMCD measurements of the spin and orbital Rh moments. A local theoretical analysis shows that the moments at the CoRh interface are largely responsible for the increase of the average magnetization and MAE. Comparison between theory and experiment suggests that the most likely chemical arrangement is a Rh core covered by a Co shell, with a moderate degree mixing at the interface. Experiment also shows a remarkable non-monotonous dependence of the MAE on Co concentration x with an optimum Rh content that increases with decreasing size. This novel behavior is theoretically explained as the result of the geometrical and chemical environment dependence of the induced Rh moments and the associated enhancement of SO interactions. The *4d* magnetic moments predicted by theory are confirmed by XMCD experiments at the Rh edge. These results not only demonstrate the optimization of the blocking temperature and the dominant role played by *4d* magnetism in *3d-4d* nanoalloys, but they also provide new physical insight on the subtle microscopic mechanisms responsible for the MAE of these systems, that should be very useful as a guide to microscopic material design. Controlling the concentration profile in nanoalloys, for example, by manipulating the kinetics of the synthesis process, opens therefore a variety of new routes in nanomagnetism.

Strong magnetoelectric effect in the Tb-Pb cluster-based thin-film heterostructures

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Magneto-electric films have drawn a continual attention due to the potential application in the microelectro-mechanical devices (MEMS). We have developed low energy beam deposition (LECBD) to prepare the nanostructured thin-films and then fabricate the well-defined multi-layered heterostructures which consist of R-Fe alloy and ferroelectric oxides. Such nanostructured Tb-Fe film possesses higher magnetostriction than the common Tb-Fe films prepared by other methods, for instance, its magneto-striction reaches $\sim 1060 \times 10^{-6}$ at $H_{\text{bias}} = 7.8$ kOe, because of the large magnetic anisotropy in the film. Moreover, in the whole LE CBD process, the phase formation of Tb-Fe nanoclusters is achieved in the condensation chamber with high temperature, while the deposition of Tb-Fe nanocluster beam onto the substrate is performed in the following high vacuum chamber with low energy and low temperature. These two steps are independent of each other. Therefore, even if the substrate is ferroelectric oxide, the degree of the interfacial reaction or diffusion between Tb-Fe alloy and ferroelectric oxide would be greatly suppressed.^[1,2] We have further prepared Tb-Fe/PZT bilayer thin-film heterostructure with clear interface and strong magnetoelectric coupling, i. e., the induced voltage increment $|\Delta V_{\text{ME}}| = 14 \mu\text{V}$ at $H_{\text{bias}} = 5.5$ kOe, in this case the maximum increment of the magnetoelectric voltage coefficient is ~ 140 mV/cm Oe, larger than that of the reported all oxide ferroelectric – ferromagnetic composite films.^[3,4] The experiments demonstrate that this kind of cluster-based heterostructure not only exhibits good ferroelectric and ferromagnetic properties but also the strong magnetoelectric effect, and may open an ideal avenue to manufacture the magnetoelectric composite films, applicable to MEMS devices in future.

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Ligand-protected gold cluster superatomsHannu Häkkinen^{a,b}*Departments of Physics and Chemistry, Nanoscience Center
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Synthesis, characterization, and functionalization of self-assembled, ligand-stabilized gold nanoparticles are long-standing issues in the chemistry of nanomaterials. Factors driving the thermodynamic stability of well-documented, discrete sizes and compositions have been largely unknown. The recent breakthrough in total-structure-determination of an all-thiolate-protected Au₁₀₂ cluster [1] triggered renewed interest in this field.

Herein, we provide a unified view of principles that underlie the stability of particles protected by thiolate (SR) or a combination of phosphine and halide (PR₃, X) ligands [2,3]. The picture has emerged from analysis of large-scale density functional theory calculations of structurally characterized compounds, namely Au₁₀₂(SR)₄₄, Au₂₅(SR)₁₈⁽⁻⁾, Au₃₉(PR₃)₁₄X₆⁽⁻⁾, Au₁₁(PR₃)₇X₃, and Au₁₃(PR₃)₁₀X₂⁽⁺³⁾, where X is either a halogen or a thiolate. Attributable to a compact, symmetric core and complete sterical protection, each compound has a filled spherical electronic shell and a major energy gap to unoccupied states. Consequently, the exceptional stability is best described by a “noble-gas superatom” analogy. The success of our superatom model was highlighted during this work via simultaneous and independent theoretical prediction [3] and experimental confirmation [4] of the same ground-state structure for the Au₂₅(SR)₁₈⁽⁻⁾ cluster.

Traditionally, the “phosphine chemistry” and the “thiolate chemistry” have been regarded as separate branches to prepare ligand-protected gold nanoparticles; no general, unifying theoretical concepts have been available to understand and classify the wealth of experimental information that points to well-defined, discrete compounds. Our work thus provides guiding principles for molecular-precision-synthesis and functionalization of these exciting building blocks of nano-materials that are finding applications in diverse fields of biolabeling, photonics, sensing and nanocatalysis.

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Chirality, optical activity, and enantiospecific adsorption in gold clusters

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Chirality is a fundamental property of many bio-organic molecules and organometallic compounds, with great relevance in several fields like the research on the origin of life, or in the pharmacology industry. Chirality in metal clusters was not expected, however recent experimental results on the structural, electronic and optical properties of size-selected bare and organically-modified gold clusters suggested the existence of chiral structures for these systems [1,2]. Theoretical studies had also provided support on the energetic stability and optical activity of chiral isomers of bare and passivated gold clusters with different size [3-5].

In this work, we present a theoretical study on the structural, vibrational, electronic, and optical properties of chiral gold clusters. Firstly, we consider the case of the Au_{34}^- cluster for which extensive experimental studies on its structural and electronic behavior had been published recently [1,6]. Our results show that the lowest-energy isomers of the Au_{34}^- cluster correspond to two chiral structures with C_1 and C_3 point symmetry groups. The two isomers are nearly degenerate in energy, being the C_1 isomer more stable than the C_3 one by only 0.031 eV. Zero point energies and vibrational entropy at finite temperatures do not produce any change in the energy ordering between these isomers. Moreover, the calculated structure factors, which have been measured using trapped ion electron diffraction [1], can not be used to discriminate between both isomers since they are almost indistinguishable. On the other hand, the electronic DOS of these chiral isomers shows different features around the HOMO-LUMO energy gap, which may be detected through optical spectroscopies. In fact, our calculated absorption and circular dichroism spectra show clear differences in the optical behavior of these chiral clusters. Another important property that distinguishes the C_1 and C_3 isomers is the different spatial distribution of the atomic coordination on the cluster surface, which would generate distinct enantiospecific adsorption patterns with chiral molecules.

Enantiospecific adsorption of a chiral amino acid (cysteine) on a C_1 (chiral) isomer of the Au_{55} cluster had also been theoretically predicted using DFT calculations [7]. The physical origin of this effect is related with the different bond strength and location of the carboxyl group, forming the *L*- and *D*- enantiomers of cysteine, when it is adsorbed on one of edges of the Au_{55} cluster. In this work, the most active sites on the Au_{55} chiral cluster surface for the adsorption of the thiolate, amino and carboxyl groups of the cysteine will be described. The relation of these theoretical results with the optical activity measured on chiral monolayer-protected gold nanoclusters will also be discussed.

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**Mechanisms of reactions on Pt nanoclusters used in electrocatalysis.
The role of organic surfactants.**

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Small Pt nanoclusters (<10nm) are widely used in catalysis and electrocatalysis. In particular, they are of interest in Hydrogen Evolution and Hydrogen Oxidation Reactions (HER/HOR) and in oxidation processes, such as CO and organic molecule oxidation. [1,2] The clusters can be synthesized by the modified inverse micelle [3] technique, which allows one to prepare clusters coated by organic surfactants and to control the size of the clusters. Chemical properties of the clusters depend upon their size and the properties of the surfactants. In spite of numerous studies, these effects are not fully understood yet.

In the current study we focus on the mechanisms of HER and CO oxidation reactions on the Pt nanoclusters, as well as on the mechanisms of attachment of the organic surfactants to the clusters. We also discuss the effect of the surfactants on the catalytic properties of the clusters. Our studies are based on electrochemical experiments and DFT modeling performed using plane wave DFT. Adsorption on the clusters has been modeled using DACAPO. [4]

In the case of Pt nanoclusters stabilized by a non-ionic surfactant, the HER activity has been found to be comparable to that of polycrystalline platinum catalyst. The negligible suppression of the HER indicates that the surfactants may not significantly block the active sites necessary for the HER. This experimental finding agrees with our computational results, which suggest that the surfactants attach preferentially to corner atoms of the clusters, thereby keeping facets of the clusters available for the HER or oxidation reactions.

Experimental studies show that in the case of Pt particles stabilized on carbon substrates the catalytic activity in CO monolayer oxidation decays systematically with the decrease of their size [5, 6]. We use our DFT calculations to model these experimental findings.

Results of this study are of interest for developing new catalysts, which can be used in heterogeneous catalysis, electrochemistry and fuel cells.

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Tuesday, Sep. 16th

Plenary Talks

T. Yanagida

Single-Molecule Nanobiology

Invited Talks

V. Bonačić-Koutecký

Tailoring Functionality of Clusters and their Complexes with Biomolecules by Size, Structures, and Lasers

P. Dugourd

UV Spectroscopy of Gas Phase Proteins and Metal Cluster-Peptide Hybrids

J. -M. L'Hermite

Nucleation and Thermodynamics of Free Clusters

M. F. Jarrold

Melting and Freezing of Aluminum Clusters

Hot Topics

M. E. García

New Approach for Selecting and Designing Fast Folding Proteins

T. Schlathölter

Ionization and Fragmentation of Isolated Biomolecules and their Clusters

M. A. López-Quintela

Towards Atomic Resolution in Colloidal Science: Soft Chemical Strategies for the Synthesis of Metal Clusters

N. Walsh

Production of Aluminum Cluster Polyanions

M. Schmidt

Freezing-Point Depression by Insoluble Impurities: A Finite Size Effect

K. Hansen

Measurement of Absolute Cooling Rates of Fullerene Ions in an Electrostatic Storage Ring

Single Molecule Nanobiology

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Biomolecules assemble to form molecular machines such as molecular motors, cell signal processors, DNA transcription processors and protein synthesizers to fulfill their functions. The reactions and behaviors of molecular machines respond to their surroundings with great flexibility. This flexibility is essential for biological organisms and biological systems. The underlying mechanism of molecular machines is not as simple as that expected from an analogy with man-made machines. Since molecular machines are only nanometers in size and have a flexible structure, they are very prone to thermal agitation. Furthermore, the input energy level is not much different from that of average thermal energy, $k_B T$. Molecular machines can use this thermal noise with a high efficiency of energy conversion for their functions. This is in sharp contrast to man-made machines that operate at energies much higher than thermal noise. In recent years, single molecule detection (SMD) and nano-technologies have rapidly been expanding to include a wide range of life science applications. The dynamic properties of biomolecules and the unique operations of molecular machines, which were previously hidden in averaged ensemble measurements, are now being unveiled. The aim of our research is to approach the engineering principle of adaptive biological systems by uncovering the unique operation of biological molecular machines. Here, I review our SMD experiments designed to investigate molecular motors, enzyme reactions, protein dynamics and cell signaling, and discuss how thermal fluctuations (noise) play a positive role in the unique operation of biological molecular machines allowing for flexible and adaptive biological systems.

Reference: <http://www.phys1.med.osaka-u.ac.jp/>

Tailoring functionality of clusters and their complexes with biomolecules by size, structures and lasers

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Clusters have the potential to be used in creation of tailored materials with desirable optical and reactivity properties. Therefore, the following topics will be addressed and illustrated on selected examples:

- Stoichiometric zirconium oxide cations are potential building blocks for a cluster assembled catalyst with high oxidation activity. We have identified a series of clusters with a radical oxygen center that exhibit enhanced activity and selectivity for three oxidation reactions of widespread chemical importance. These species may promote multiple cycles of oxidation reactions and therefore exhibit true catalytic behaviour.
- Metallic cluster-peptide hybrid systems (e.g. Trp-Ag_n^+ , $\text{Trp-(Ala)}_n\text{-Ag}_n^+$) exhibit unique optical properties such as absorption enhancement and fluorescence which can be tuned by cluster size and the type of hybrid structure. This model systems serve to study the interaction between silver clusters and proteins with the aim to provide basic understanding for developing biosensors and biochips.
- We propose a new “field induced surface hopping” method for the optimal pump-dump control allowing to explore the controllability of dynamics in complex systems. This will be illustrated on Schiff base molecular switches and on laser selective photochemistry in nanoparticle-biomolecular hybrid systems.

UV spectroscopy of gas phase proteins and metal cluster-peptide hybrids

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UV-Vis spectroscopy was used to obtain signatures of geometric and electronic structures of protein and metal peptide complexes. The objective of these gas phase experiments is to provide the bases to construct atomic models of functional molecule in actions.

The experimental set up integrates an electrospray ion source, an ion trap mass spectrometer and one or two tunable UV-Vis lasers. A first series of results was obtained on multiply negatively charged peptides and proteins [1]. Electron emission was observed after irradiation. The electron detachment mechanism and the influence of the repulsive Coulomb barrier will be discussed. Electron detachment yield as a function of the laser wavelength and optical signatures of proton and radical transfers will be presented.

Metal cations are ubiquitous in biology. We will show that gas phase experiments can be used to determine the exact nature of the binding between the cation and the peptide and the influence of the cation on the conformation of the biomolecule. Finally, we will present results on peptide- silver cluster complexes. The surface plasmon of the metal moiety induces a spreading and a strong enhancement of the optical absorption of the complex (see Fig. 1) [2]. These systems can be used as prototypes of biomolecules on surfaces in a well-defined environment.

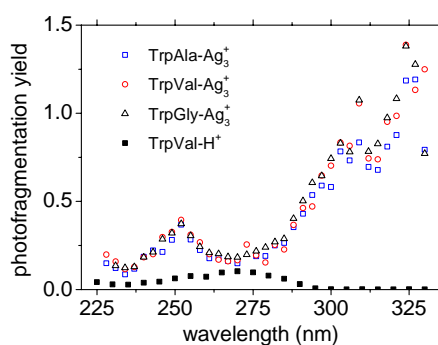


Figure 1: Photofragmentation yields measured for protonated Tryptophane-Valine (TrpVal-H⁺) dipeptide and silver cluster-dipeptide complexes.

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Nucleation and thermodynamics of free clusters

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A novel experimental setup has been developed, which allows controlling the sticking of atoms onto mass selected clusters [1]. It has been applied to sodium clusters so far. The sticking scaling law as a function of the cluster size has been measured for the first time [2]. Beyond the measurement of sticking cross sections, controlled sticking experiment is a powerful tool for determining some thermodynamic properties of clusters. By controlling accurately the collision energy, the caloric curve is deduced from the average number of atoms that can be stuck onto the cluster as a function of its temperature. Unambiguous results are obtained by using a differential scheme. Melting temperatures and latent heat of sodium clusters are, as far as data are available, in good agreement with previous measurements [3]. Nevertheless, our caloric curve for Na_{41}^+ shows a previously unobserved double structure attributed to surface melting. The marked size dependence of melting temperature of clusters has already been extensively analysed. However, in light of a simple two level model, one might also rightfully ask why melting temperatures do not vary much more than they do. Similar experiments on water cluster are in progress.

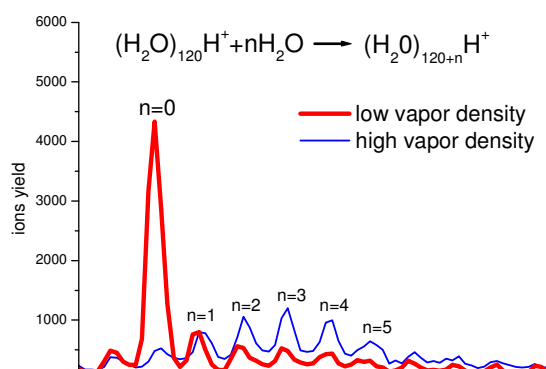


Figure 1: sticking mass spectra of water molecules stuck onto a water cluster.

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Melting and Freezing of Aluminum Clusters*

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Aluminum and sodium clusters have emerged as prototypes for understanding the thermal properties of metal clusters. In this talk I will describe new results for aluminum clusters.

Most of the experimental information on the melting transitions of size selected metal clusters has been obtained from heat capacity measurements. These measurements have now been performed for aluminum cluster cations (and some anions) with 16 to 130 atoms. Results for $n > 80$ are reported here for the first time. Most clusters with $n > 80$ show a single sharp peak in their heat capacities that can be fit with a two state model (i.e., a model that only includes completely solid clusters and completely liquid clusters, and no partially melted intermediates). On the other hand, clusters with 80-90 and 110-120 atoms show two clearly-resolved and well-separated peaks in their heat capacities. The two peaks may be due to partial melting, where part of the cluster melts and then the balance melts at a higher temperature, or it may indicate that there are two structures that melt at different temperatures. I will describe measurements that probe the internal energy distribution of the melting clusters and distinguish between these two possibilities.

Experimental studies of the melting of metal clusters have focused on the thermodynamic behavior (i.e., determining the melting temperature and latent heat). There is virtually no experimental information available on the rates of melting and freezing transitions and how they change with temperature and cluster size. We have performed experiments to investigate the kinetics of metal cluster freezing. In these experiments the clusters are heated to above their melting temperature, rapidly quenched, and then the heat capacity is measured after a fixed time. These studies show that the clusters do not always freeze into the lowest energy structure. At high cooling rates the liquid cluster can bypass freezing into the thermodynamically preferred solid and freeze into a higher energy solid at a lower temperature. In addition, the peaks in the heat capacities measured for freezing are for some clusters shifted to lower temperature than the peaks in the heat capacity measured for melting. This confirms that some of the clusters' super-cool.

* Work performed in collaboration with Baopeng Cao, Anne K. Starace, Colleen M. Neal, Oscar H. Judd, Andrés Aguado and José M. López

New Approach for Selecting and Designing Fast Folding ProteinsDmitry Gridnev and Martin E. Garcia

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ructure Science (CINSaT), Universität Kassel, Heinrich-Plett-Str. 40,
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We propose a general algorithm for predicting good folding proteins and for determining their folding temperature. It uses the Monte Carlo dynamics and tests the rate of convergence of a an amino acid chain in the configuration space. The algorithm can be applied to any kind of models (lattice, off-lattice, go-type, atomistic) and does not require the previous knowledge of the native structure. We tested our approach in the framework of the lattice model and obtained several good folders not found before. The algorithm takes considerably less time than the actual folding time of the proteins.

Ionization and fragmentation of isolated biomolecules and their clusters

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The interaction of keV protons and heavy ions with building blocks of DNA is of particular biological relevance in view of the increasing number of facilities employing MeV proton and heavy ion irradiation for tumor treatment. When the ions traverse tissue and are decelerated to sub-MeV energies, the so-called Bragg-peak is reached where the induced damage is highest due to maximum linear energy transfer (LET) and relative biological effectiveness (RBE) at these energies. The volume selectivity given by the existence of such a well-localized Bragg-peak region renders proton therapy such a promising tool for cancer treatment [1]. Biological consequences of irradiation with energetic protons and heavy ions from galactic cosmic rays and solar particle events are also a limiting factor for human space exploration.

Radiation damage in living cells always involves the condensed phase where the affected molecules are surrounded by a medium. Therefore, ion irradiation studies on nucleobases in the solid phase [2] and on DNA deposited on substrates [3] have been performed. Such studies are however hampered by the great complexity of the systems under study.

A natural solution to avoid these difficulties is the investigation of smaller systems. We investigate the response of isolated DNA building blocks, and their clusters upon keV singly and multiply charged ion impact using high-resolution coincidence time-of-flight mass spectrometry. Kinetic energies of nucleobase and amino-acid fragments exceeding several 10 eV are observed which have the potential to induce subsequent damage in a biological environment [4,5]. Deoxyribose molecules from the DNA backbone are found to be most sensitive to keV ion impact and are subject to statistical fragmentation[6].

To bridge the gap between the biologically relevant condensed phase regime of and experiments on isolated molecules, we investigate systems still allowing intermolecular interactions. Our recent studies on clusters of nucleobases e.g. reveal that intermolecular hydrogen bonds strongly affect the fragmentation dynamics of the DNA building blocks [7].

Currently we are performing irradiation experiments on more complex biomolecular targets, produced by means of electrospray ionization. It is the goal of these studies to investigate well defined DNA oligomers surrounded by a tunable number of water molecules which can be considered good model systems of DNA and its closest environment.

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TOWARDS ATOMIC RESOLUTION IN COLLOIDAL SCIENCE: SOFT CHEMICAL STRATEGIES FOR THE SYNTHESIS OF METAL CLUSTERS

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In the past decade a number of chemical methods have been developed for the preparation of nanoparticles of different metals down to the nanometer/subnanometer range, thus entering into the Cluster region. It has been observed that the properties of these Clusters are very different from their “older brothers”, the colloidal particles, due to the quantum confinement of electrons and holes. The transition from the solid state (characteristics of the Colloids) to the atomic/molecular level (characteristics of the Clusters) can be now observed and studied because new chemical synthetic routes have been/ are being developed. Although this is just the beginning of a very promising area, there are already enough proofs that new interesting properties can come up. Catalytic, fluorescent, magnetic, electronic, optical...properties, very different from those observed with colloidal particles, seem to appear in this fascinating cluster region. Moreover, because the number of superficial atoms is comparable to (or even higher than) the number of those located in the interior, the cluster attached species (capping) may play an important role in the final properties of these nano/subnano-meter structures. This talk will be devoted to introduce different soft chemical approaches recently developed in our lab, which can be used for the preparation of metal clusters

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Production of aluminium cluster polyanions

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Interest in the physics and chemistry of multiply-charged anions has grown considerably during the last two decades. What started with a number of experimental observations of gas-phase dianionic clusters[1] and fullerenes[2,3] in the mid 1980's and early 1990's has since developed into an independent field of research investigating both the production and properties of polyanionic species[4,5,6]. One production method, the "electron-bath" technique[6] involves the exposure of stored cluster monoanions to a 'bath' of low-energy electrons for extended reaction periods. The technique, originally applied to monovalent elements[7] (Cu, Ag and Au) and later to fullerenes[8], has also proven to be suitable for the production of metal cluster polyanions composed of trivalent aluminium[9]. In addition to dianionic species[9], recently tri- (Fig.1(a)) and tetra-anionic (Fig.1(b)) aluminium clusters have been produced. This contribution presents the results of experiments in which both the production procedure and the size-dependence of aluminium cluster polyanion creation have been investigated.

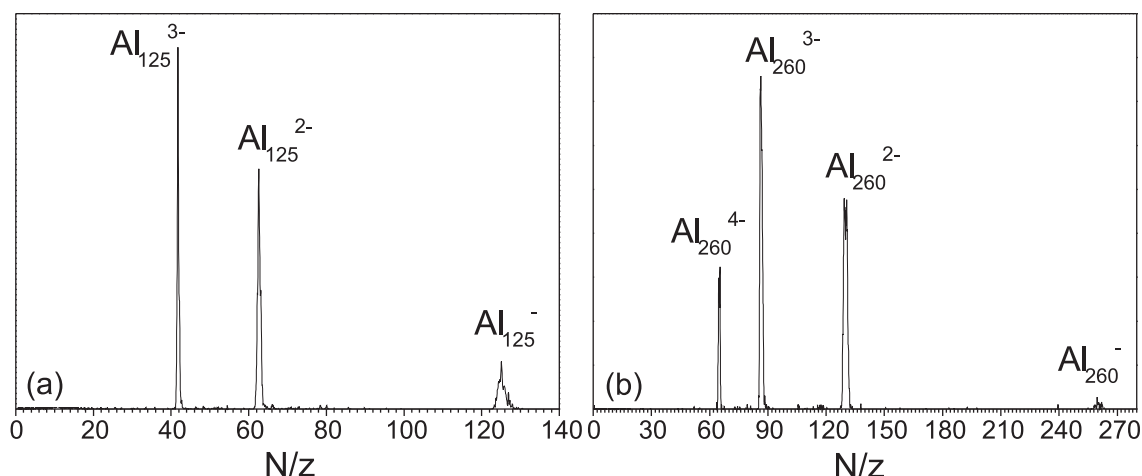


Figure 1: Abundance spectra for (a) Al₁₂₅ and (b) Al₂₆₀ after exposure of the monoanions to an "electron bath".

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Freezing-point depression by insoluble impurities: A finite size effect

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Salt in water is used as anti-freeze protection. The freezing point of the water/salt system is lowered by the effort to transform the homogeneous solution into separated phases of purified ice and concentrated brine. Insoluble impurities, by contrast, cannot influence the freezing point of a macroscopic liquid, which forms instead two separated and independent phases. However, in a nano-sized particle the phases lose their independence, since their interfacial energy can no longer be neglected. Furthermore this surface contribution can change upon melting. Typically, it decreases as a possible lattice mismatch of the solid can be compensated by the higher structural freedom of the liquid, which thus becomes more favorable. It occupies a larger temperature range in the phase-diagram and the freezing points are depressed.

We illustrate this cluster-specific effect by studying nano particles of the sodium – sodium oxide binary system both experimentally and theoretically. First-principles density functional theory is employed. Bulk sodium hardly solves its oxide, which thus cannot depress the freezing point. In contrast our thermodynamic experiments show that the oxide in sodium clusters systematically depresses both freezing points and latent heats and that this effect increases with the size of the oxide. Our calculations confirm that this is due to the surface tension between the oxide and metal in the solid clusters. The surface energy is released under melting and promotes the liquid phase thermodynamically. This causes the observed, cluster-specific freezing point depression.

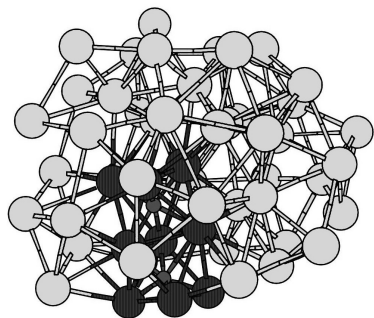


Figure: Na_{55}O_2 at 340 K: The pure liquid metal (light gray circles) forms a well-separated phase that only partially wets the oxide (small dark circles: oxygen; big dark circles: sodium.). Even though the metal cannot dissolve the oxide, its freezing point is depressed by the surface tension between the phases that increases under freezing.

Measurement of absolute cooling rates of fullerene ions in an electrostatic storage ring

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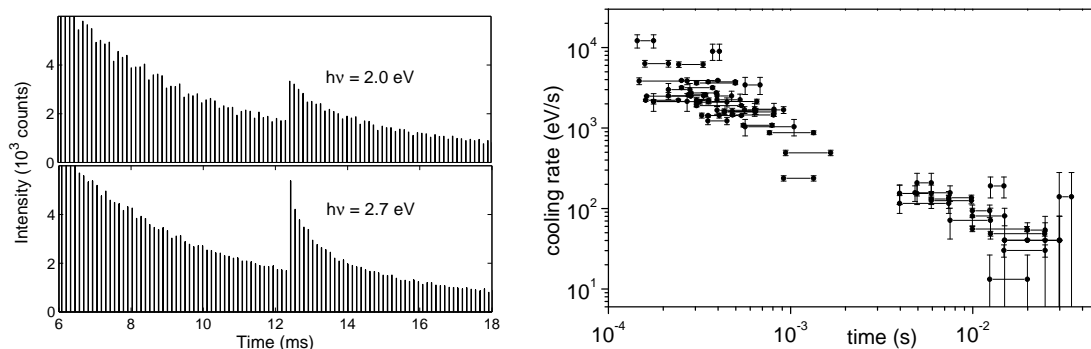
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We have developed a novel method to measure absolute cooling rates of ions, based on the non-exponential decay of ensembles of hot molecules, and applied it to C_{60}^- .

The ions were produced in a laser desorption source and stored in an electrostatic storage ring [1]. The spontaneous decay of the ions is well described by a $1/t$ law for short times [2], while it is quenched by radiative cooling [2] after about 5 ms. One-photon excitation in the energy range of 1.9-2.7 eV induces an enhanced thermionic emission rate. Figure 1 (left) shows examples of the enhanced signal after laser excitation at 12.5 ms after injection. The decay of the enhanced signal is similar to the spontaneous decay, but is shifted backwards in time. The shift depends on the photon energy, as exemplified by the different curvatures of the enhanced signals in figure 1, and can be determined with good precision from the data. Combined with the absolute energy change associated with single photon absorption, the absolute rate of cooling by depletion of the ions can then be experimentally determined [3].

Figure 2 (right) shows the cooling rates extracted from the data. The horizontal bars represent the time interval over which the cooling is averaged. The cooling rate is seen to vary as $1/t$, similar to the decay rate, consistent with a broad initial energy distribution. For values of the rate constant around $10^3 s^{-1}$ one obtains from the plot the value $CT^2/\Phi \approx 12000$ K, where C is the heat capacity, T the effective emission temperature and $\Phi = 2.65$ eV is the electron affinity. This value is consistent with the expected values of the heat capacity and the temperature [4].



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Wednesday, Sep. 17th

Plenary Talks

N. J. Halas

Plasmonic Nanoparticles: Artificial Molecules with Real Applications

J. Jortner

Cluster Dynamics at Extremes (in Memory of Professor Jaroslav Kouřek)

Invited Talks

M. M. Kappes

Determining Structure, Energetics and Fragmentation Behaviour of Mass Selected, Singly Charged, Tin Cluster Anions and Cations

Hot Topics

K. von Haefen

In-Situ Passivation of Silicon Clusters

Plasmonic Nanoparticles: artificial molecules with real applications

Naomi J. Halas

Stanley C. Moore Professor of Electrical and Computer Engineering, Professor of Chemistry, Professor in Bioengineering and Director, Laboratory for Nanophotonics, Rice University, Houston, TX, USA 77005

In recent years we have shown that certain metallic nanoparticles possess plasmon resonances that depend very sensitively on the shape of the nanostructure. This interesting observation has led to a fundamentally new understanding of plasmon resonances of metallic nanostructures- “Plasmon Hybridization”- where the collective electronic resonances in a metallic nanostructure are understood to be a classical analog of the single electron quantum states of simple atoms and molecules. The Plasmon hybridization picture explains the tunability of nanoshells, a dielectric core, metallic shell nanoparticle which is the simplest nanostructure with tunable plasmon resonances. More importantly, it provides a nanoscale “design rule” for understanding the plasmon resonances in an entirely new family of plasmonic nanostructures, and for the coupling of plasmonic nanostructures to meso- and macroscopic structures such as nanowires or thin metallic films. A variety of surface enhanced spectroscopies such as Surface Enhanced Raman Scattering, (SERS) Surface Enhanced Infrared Absorption (SEIRA), as well as fluorescence enhancement of nearby molecules and materials, can exploit these types of designed metallic nanostructures as tailored, high-performance substrates yielding large and highly reproducible enhancements. In addition, by tuning plasmon resonances into the near infrared region of the spectrum, the physiological “water window” can be accessed, where blood is essentially transparent and light penetrates maximally through human tissue. With bioengineers, we have developed a suite of applications for plasmonic nanoparticles in biomedicine, including light-triggered drug delivery and photothermal cancer therapy.

Topics:

- 1. Fundamental Plasmon Hybridization**
- 2. Chemical sensing: SERS, SEIRA and combining both on the same substrate**
- 3. Biomedical applications of Plasmonics: past, present and future**
 - a. nanoscale pH meter based on SERS**
 - b. “turning up” ICG fluorescence**
 - c. Nanoshell-based cancer therapy: tumors and strategies for metastatic disease**
 - d. New vectors for gene therapy**

CLUSTER DYNAMICS AT EXTREMES**In memory of Professor Jaroslav Kouřek**

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The exploration of photoinduced ultrafast response, dynamics, reactivity and function in ubiquitous molecular, nanoscale macroscopic and biological systems pertains to the interrogation and control of the phenomena of energy acquisition, storage and disposal, as explored from the microscopic point of view. We shall focus on recent theoretical, computational and experimental studies of finite systems dynamics under extreme energetic and temporal conditions. Ultrafast and ultrahigh phenomena pertain to extreme cluster ionization in ultraintense laser fields (peak intensities $I_M = 10^{15} - 10^{21} \text{ Wcm}^{-2}$, with $I_M = 10^{21} \text{ Wcm}^{-2}$ constituting the highest light intensity on earth), ultrafast femtosecond dynamics on the time scale of nuclear motion, attosecond–femtosecond electron dynamics, the production of ultrahigh charges in completely ionized molecular or elemental clusters, and the attainment of ultrahigh energies (keV–MeV) in Coulomb explosion of multicharged clusters and nanostructures. Coulomb explosion of clusters and nanostructures transcends chemical–physical dynamics towards the driving of nuclear reactions involving table-top nuclear fusion and nucleosynthesis of astrophysical interest.

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Title: Determining structure, energetics and fragmentation behaviour of mass selected, singly charged, tin cluster anions and cations

Authors: D. Schooss, A. Lechtken, N. Dubrov, N. Crawford, R. Ahlrichs, P. Weis, E. Oger, R. Kelting and M. Kappes

Abstract: We have used a combination of ion mobility spectrometry, trapped ion electron diffraction and density functional theory calculations (with genetic algorithms) to obtain electronic and geometric structural information on mass selected tin cluster ions ranging in size up to several tens of atoms. Results will be discussed in terms of previous knowledge and implications for tin cluster based materials.

In-Situ Passivation of Silicon Clusters

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Bulk silicon is a poor light emitter due to its indirect band gap and a viable method to achieve luminescence is confinement in nano-structures and passivation of the dangling bonds at the surface [1]. Here, we report on the production of clusters by high pressure magnetron sputtering of a silicon target and aggregation in a argon/helium gas mixture [2,3], their subsequent passivation with nitrogen in the gas phase and their deposition on a substrate at flux rates of 1 Å per second. Our apparatus is equipped with an arrangement of cells to focus the cluster beam after the aggregation chamber [4]. One of the cells was filled with nitrogen so that the clusters were undergoing multiple collisions. The cell could be filled with up to 1 mbar nitrogen which guaranteed that the cluster surface was covered completely. Then, the clusters passed through differential pumping stages into ultra high vacuum where they were co-deposited with a gas beam of water onto a liquid nitrogen cooled surface. After the deposition had been completed we melted the ice and obtained a suspension of $\sim 1 \mu\text{l}$ containing silicon clusters.

We characterised samples that were deposited on a carbon grid by transmission electron spectroscopy (TEM) and we also carried out photo luminescence spectroscopy (PLS). The TEM images show spherical clusters with diameters ranging from 2 to 100 nm depending on the growth conditions. For specific growth conditions we also observed flakes and nanowire-like structures. Un-passivated clusters in water suspension showed a yellowish-brownish colour whereas the suspension with nitrogen passivated clusters was clear giving evidence that a silicon nitride layer was formed during the gas phase reaction. The suspension with nitrogen-passivated clusters showed PL at room temperature with a strong peak at 421 nm (90 nm fwhm) when excited at 307 nm.

Our results show for the first time PL from silicon nanoparticles in aqueous suspension and demonstrate the relevance of our approach for applications in biology or nanotechnology, for instance, for jet-printing luminescent quantum dots into nano-structures. Likewise our results show the potential of the pick-up technique to produce alloyed clusters and to achieve radial structural control in the gas phase [5].

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Thursday, Sep. 18th

Plenary Talks

W. A. de Heer

A Quarter-Century of Metal-Cluster-Beam Physics, from the Discovery of Electronic Shell Structure to Quantized Ferromagnetism to Cluster Ferroelectricity

Invited Talks

S. A. Brown

Building Nanoelectronic Devices with Clusters

R. E. Palmer

Cluster Deposition: from 3D Cluster Structure to Excited States and Biochip Applications

S. Montero

Experiments on Small $(H_2)_N$ Clusters

P. Scheier

Electron Driven Reactions in Doped He Droplets

Hot Topics

O. Cheshnovsky

Detection of Heating in Current Carrying Molecular Junctions by Raman Scattering

A. Fortunelli

Interface-Stabilized Exotic Phases of Metal-on-Oxide Nanodots

M. Alcamí

Understanding the Self-Assembly of the Electron Acceptors PCBM and TCNQ on Surfaces

C. Petit

Inorganic Nanocrystals obtained by Wet Chemistry: Control of Composition, Size, Shape and Self-Organization

F. Stienkemeier

Reactivity of Alkalis with Water Clusters Studied in Helium Nanodroplets

M. Di Vece

Hydrogen-induced Changes in a Pd Nanocluster Film

A quarter-century of metal-cluster-beam physics, from the discovery of electronic shell structure to quantized ferromagnetism to cluster ferroelectricity.

Walt A. de Heer, Georgia Institute of Technology

In the Fall of 1983, 25 years ago the first of a series of cluster beam experiments were performed that demonstrated electronic shell structure in sodium clusters. I will give a brief historical overview of these exciting times.

The order provided by the electronic shell model for clusters [1,2] departed radically from the prevailing models: small metal clusters were considered to be molecules, each one had its own identity and there was no reason to expect a systematic order in their properties.

The experimental discovery [1] was followed by years of debate. Electronic shell structure was often incorrectly equated with the spherical jellium model (which treats lithium and gold identically), leading to widespread and lasting confusion.

The electronic shell model (recently renamed the “superatom” model) has now become the prevailing paradigm for the basic electronic structure of diverse metal cluster systems over a wide range of sizes. Yet, why electronic shell structure is a ubiquitous phenomenon in a wide variety of metal cluster systems is still not fully understood.

The early experiments in Berkeley laid a foundation for other directions in cluster physics [3]. I will discuss recent Stern-Gerlach experiments on ferromagnetic clusters [4] including unpublished results on magnetism of Co and Fe clusters in excited states, with important implications for nanomagnetism, including a resolution of the longstanding spin-relaxation problem in free metal clusters [5].

I will further discuss new results [6] on the recently discovered ferroelectric state in low-temperature niobium and niobium alloy clusters with its possible connection to superconductivity [7]. This unusual state is characterized by a phase transition from a normal state to one with exceptionally large electronic dipole moments that exhibit a very large even-odd effect.

Finally, I will present new high-resolution polarizability measurements on sodium clusters as well as their electric dipole moments that are orders of magnitude smaller than predicted.

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Building Electronic Devices from Clusters

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Regular attendees at ISSPIC conferences are well aware of the enormous variety of novel physical and chemical phenomena observed in clusters. Over the years, fundamental studies of gas phase properties have evolved towards more applied studies of clusters on surfaces, and the possibility of “new” materials formed from clusters. A logical continuation of this evolution is the use of clusters as building blocks for electronic devices.

We believe that the ready availability of clusters with sizes ranging from a few atoms up to tens of nanometres makes them ideal building blocks for electronic devices. This size range spans the gap between current integrated circuits (~50nm) and the molecular scale (<1nm), which is presumably the ultimate future of electronics.

We have developed self-assembly / directed-assembly strategies [1, 2, 3, 4] which provide a potentially manufacturable route to fabrication of cluster-based electronic devices. We have focussed on the formation of contacted cluster chains / nanowires because devices containing such nanowires have a wide range of applications (from chemical sensors to transistors). In this paper we will review our work on nanowire formation using templates [1, 2], stencils [3] and percolation methods [4], as well as our understanding of the basic physical assembly processes (enhanced by extensive Molecular Dynamics simulations [5]). We will also discuss prototype hydrogen sensors based on Pd clusters [6], H₂ and NH₃ gas sensors based on oxidised Sn clusters [7], the use of Cu clusters for interconnect applications [8], and progress toward the fabrication of cluster-assembled transistors [9].

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Cluster deposition: from atomic structure to applications

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The controlled deposition of size-selected clusters creates new possibilities for the fabrication of both biochips and model catalysts [1]. Knowledge and control of the 3D atomic structure of the cluster is relevant to these applications, as it is to the fundamental physics and chemistry of the clusters. Direct structural measurements of clusters in the gas phase are very challenging. Here we demonstrate that measurement of the scattered intensity - the high angle annular dark field (HAADF) signal - in the scanning transmission electron microscope (STEM) allows us (a) to count the number of atoms in a cluster on the surface and (b) to determine a 3D atom-density map of the cluster when an aberration-corrected STEM is used [2]. Moreover, size-selected clusters can also be used as a mass standard to "weigh" metal nanoparticles produced by other, less precise but sometimes more practical methods: this is mass spectrometry on the surface.

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Experiments on small $(\text{H}_2)_N$ clusters

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Theoreticians and experimentalists are showing in recent times growing interest on small $(\text{para-H}_2)_N$ clusters for a number of good reasons: low temperature $(\text{para-H}_2)_N$ clusters are non-rigid spinless bosons which have been predicted to show superfluid behavior for $N < 30$ [1]; $(\text{para-H}_2)_N$ clusters are ideal reference systems for quantum Monte Carlo methods; $(\text{para-H}_2)_N$ clusters show magic numbers [2]; spectroscopic data on small $(\text{H}_2)_N$ clusters provide fundamental information for high-quality H_2 - H_2 (6-dim) potential energy surface [3]; $(\text{para-H}_2)_N$ clusters are likely to be the best suited system to understand molecular nucleation in depth; etc, etc.

The formation process of small $(\text{para-H}_2)_N$ clusters has been observed in great detail in a recent experimental survey with space, time, and number size N resolution [4] on the basis of supersonic expansions of the gas through cryogenic axisymmetric nozzles. The diagnostic of the jet medium is based on high-sensitivity (few photon/sec) Raman spectroscopy with very high spatial resolution ($\approx 2 \mu\text{m}$) enabling for quantitative time of flight measurements in the domain of nanoseconds. Temperatures of up to 0.1 K have been attained in the jet at a collisional rate low enough to avoid sudden freezing of the gas. This way clusters between two and eight units appear size resolved, while the gradual transition of larger clusters into the liquid and eventually into the solid has been observed in the experiment.

Exhaustive investigation on nozzle temperature and pressure, and on time scale (position along the jet) have lead us to optimize the sequential formation of clusters from the very beginning of the nucleation process: the formation of dimers, and only dimers, in a bath of monomers. The data obtained from a number of supersonic H_2 jet experiments conducted along well-defined isentropic paths have lead to map the dimer-existing region in the phase diagram. The reaction rate for the three-body collisional process underlying the H_2 -dimer formation has been determined for the first time. Similar experiments have been conducted on mixed H_2 +He jets.

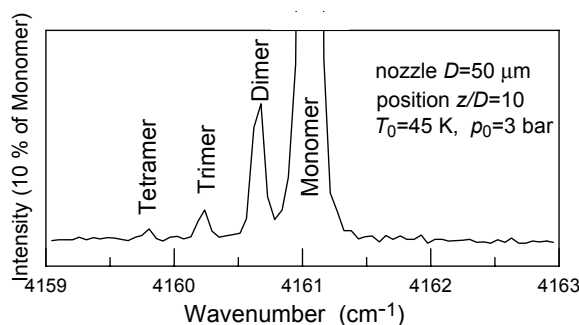


Figure 1: Raman spectrum of small para-H_2 clusters in a $\text{pH}_2(10\%)+\text{He}(90\%)$ supersonic jet.

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Electron driven reactions in doped He droplets

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Formation of positive and negative ions upon free electron collisions with doped nano-droplets of superfluid ⁴He, are studied, utilizing a two sector field mass spectrometer. Simple diatomic molecules such as H₂ and I₂ are used as dopants as well as water, halocarbons, SF₆, CCl₄, amino acids, DNA bases and fullerenes. Molecules that collide with a droplet are picked up by the droplet and in most cases move to its center. Depending on the pressure in the pick-up cell either monomers or clusters of these dopants are formed in the droplet. Positive-ion mass spectra are recorded and compared with results obtained in the gas phase. The high mass resolution and sensitivity of the experimental setup is a prerequisite to identify novel product ions that are stabilized by the surrounding He, e.g., SF₆⁺ and CCl₄⁺.

For many dopants also negative (cluster) ion formation has been observed. The yield of these anions is measured as a function of the electron energy [1]. The molecules chosen for our first study were the nucleobases adenine, thymine and partially methylated or deuterated thymine. The DEA to these nucleobase molecules and clusters in helium droplets (see [1]) exhibits the remarkable site selectivity that we have previously established for these biomolecules in the gas phase [2]. Core excited resonances that lead to low mass fragment anions upon electron attachment in the gas phase are almost completely quenched and instead lead to the formation of dehydrogenated closed shell anions via loss of a neutral H-atom [3]. We have extended these studies to He droplets doped with several other molecules such as CHCl₃ [4], water [5], and ammonia. A surprisingly rich chemistry, driven by electrons, is observed at ultra-low (0.37K) temperatures.

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Detection of Heating in Current Carrying Molecular Junctions by Raman Scattering

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An important consequence of electron-vibration interaction in molecular-junction-transport is heat generation, i.e., energy transfer to the underlying nuclear motions. In balance with heat dissipation, this has important implications on the issue of junction stability. Advancement in molecular electronics necessitates thorough understanding of these processes in molecular junctions [1]. Such an understanding depends on the ability to monitor non-equilibrium occupancy of vibrational levels at current carrying junctions as a function of bias. We report on the realization of such a capability by utilizing the Stokes (S) and AntiStokes (AS) components of Surface Enhanced Raman Spectroscopy (SERS) to probe the effective temperature of current carrying junctions. Home built confocal Raman microscope was used to map the S and AS Raman spectra of edge fabricated conducting molecular junctions [2]. All Raman active modes show similar heating as a function of bias at room temperature, suggesting fast internal vibrational relaxation processes. These results demonstrate the power of direct spectroscopic probing of heating and cooling processes in nanostructures.

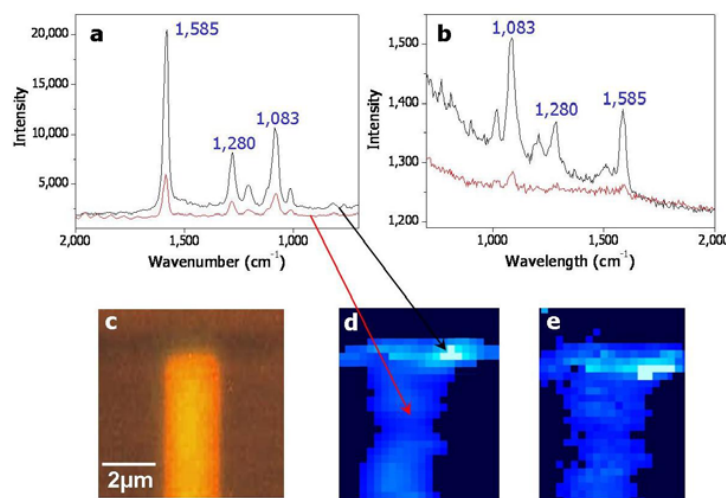


Figure 1: **Raman spectra and maps of a silver molecule junction.** (a) S spectrum (671nm laser) of BPDT molecules in a junction (black) and at an arbitrary spot on the Ag electrode (red). (b) The corresponding AS spectra. Analysis of temperature is based on the AS/S ratios of the indicated modes. (c) An optical picture of a molecular junction. (d) Raman map of the junction (1585cm^{-1} S line) and (e) of the AS 1585cm^{-1} line of the same junction.

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Interface-stabilized exotic phases of metal-on-oxide nanodots

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We discuss a predictive computational methodology which allows one to study the size-dependent epitaxial relationships of metal nanodots supported on (oxide) surfaces. This methodology is first applied to systems with a good epitaxial match, such as Pd clusters on MgO(100), finding results in excellent agreement with experiment [1]. In the presence of a larger lattice mismatch, the possibility of creating unusual metal-on-oxide phases is suggested. In particular, we derive [2] building principles for the formation of “exotic” hcp epitaxies on square-symmetry oxide surfaces, delimiting the values of lattice mismatch, surface and adhesion energy for which hcp phases are expected to be favored even for metals that are not hcp in the bulk. These predictions are supported by available experimental data on Ni/MgO(100) nanodots. Moreover, we are able to rationalize the size-dependent transition from hcp to fcc motifs and to generalize these results to a whole class of metal/oxide systems of great potential interest, such as Pd and Pt on CaO, Ni and Co on MgO. This is the first time that a morphological crossover is quantitatively predicted, a general class of novel nanoparticle phases proposed, and the atomic details of the particle structure fully unveiled for metal-on-oxide particles. Such details in turn suggest that these materials should possess peculiar properties: in particular, the facets exposed by the nanodots reveal adsorption sites with unusual geometry of possible effect on their catalytic properties, while the destabilization of stacking faults and fine details of structural deformations observed for these particles are expected to influence their magnetic behavior.

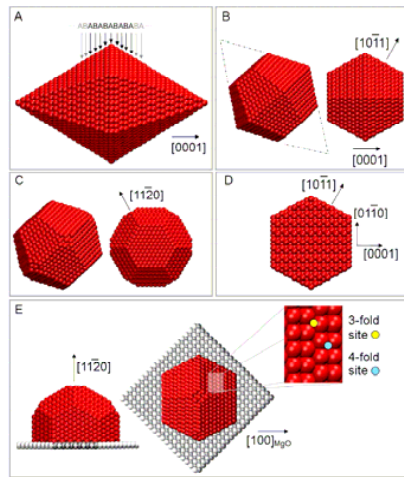


Figure 1: Morphology of the hcp motifs.

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[2] R. Ferrando, G. Rossi, F. Nita, G. Barcaro, A. Fortunelli *Interface-stabilized exotic phases of metal-on-oxide nanodots* (submitted)

Understanding the self-assembly of the electron acceptors PCBM and TCNQ on surfaces

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The adsorption and self-assembly of functional molecular systems on solid surfaces is a powerful tool to fabricate well-ordered structures suitable for potential applications in molecular electronics. In this work we report on the self-assembly of two important electron acceptor molecules widely used on organic solar cells the C₆₀ derivative PCBM (Phenyl-C₆₁-Butyric acid Methyl ester) and TCNQ (Tetra-Cyanoquinodimethane). These systems have been studied with a combination of STM experiments and DFT calculations, which has allowed us to get a complete picture of interactions governing the self-assembly.

It is well known that the 2D self-assembly of organic molecules on solid surfaces is the result of a combination of molecule-molecule and molecule-substrate interactions. In the case of PCBM deposited on Au(111) surfaces we have observed in STM experiments[1] that at low coverages, PCBM self-assembles to create long, parallel, isolated 1D wires, or 2D extended networks, as dictated almost exclusively by the substrate-controlled preference for nucleating at the fcc sites of the reconstruction. However, at higher coverages, intermolecular interactions take over, bypassing the substrate influence, giving islands composed of laterally ordered parallel, 1D double rows of PCBM molecules. In the case of TCNQ on Cu(100) surfaces there exists a strong interaction between the molecule and the substrate, reflected in a large distortion of both TCNQ and the surface. DFT calculations on both systems have been carried out to describe the interactions and the structure of the absorbed clusters of molecules[2] and the different mechanisms that control the self-assembly.

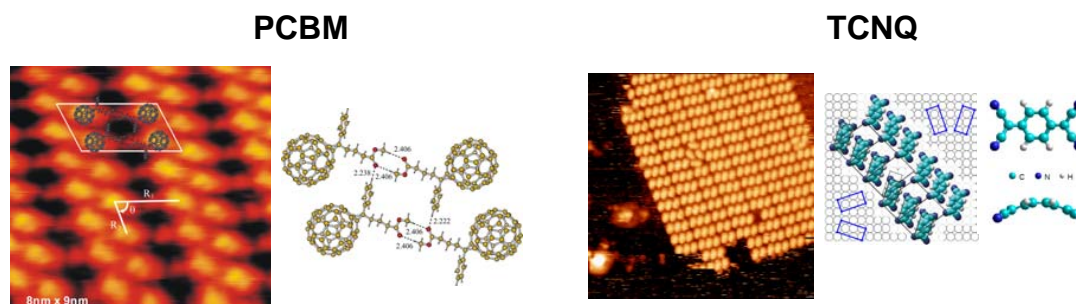


Figure 1: STM images of the self assembly of PCBM on Au(111) surfaces and TCNQ on Cu(100) surfaces. The calculated structures of the corresponding PCBM tetramers and TCNQ molecules on the surface are also shown.

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Inorganic Nanocrystals obtained by Wet chemistry
Control of the composition, size, shape and self-organization into 2D and 3D superlattices

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Research in the field of nanoparticles has grown tremendously during the last two decades. Such inorganic nanocrystals are of interest for a variety of applications such as superparamagnets, semiconductors or catalysis. Thus it is important to have access to methods that give particles in the nanometer range with good control over size, shape and composition but also with the potential for controlled deposition on a solid support in superlattices. Depicted numerous study on these nanomaterials, the understanding of nanocrystal growth is not well defined.

We details here the first use of the liquid-liquid phase transfer to obtain either pure metallic Platinum or Palladium nanocrystals with a control of the size and shape but also magnetic nanoalloys, as CoPt, with a perfect control on the composition and size. We will emphasize on the parameters allowing control the growth process and then the physical characteristic of the inorganic nanocrystals. The low degree of size polydispersity allows these nanocrystals to self-assemble with a long-range ordering in 2D and 3D supra-crystals. According to the nanocrystal shape, simple cubic or face centered cubic supra-crystals are observed. It is remarkable to notice that well-facetted supracrystals with sizes of the order of 10 micrometers may be obtained.

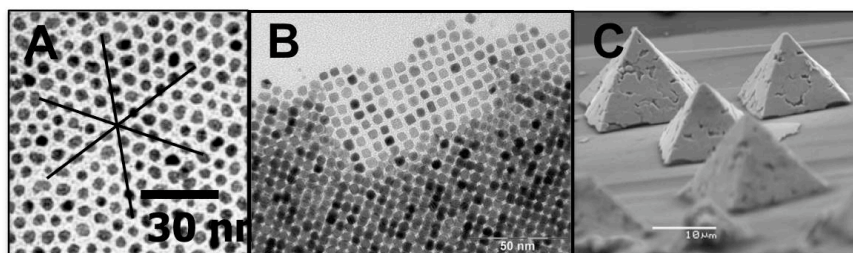


Figure 1: A) 2D self organization of spherical CoPt nanocrystals, B) Quadratic 2D organization of cubic Platinum nanocrystals, C) Pyramidal fcc superlattices on the micrometer scale of cuboocatedron platinum nanocrystals

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- 5--Shape-Controlled Platinum Nanocubes and their Assembly into 2D and 3D Superlattices
 A. Demortière, P. Launois, N. Goubet, P-A. Albouy and C. Petit *J. Phys. Chem C* (2008) to be published

Reactivity of alkalis with water clusters studied in helium nanodroplets

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Molecules attached to superfluid helium nanodroplets have been studied for quite some time in order to study the properties of matter at low temperatures and in the environment of a size limited quantum fluid. Recently, new directions of such studies in terms of short-time dynamics [1] and metal clusters [2] have been reviewed. The variety of dopants has been widely extended. We demonstrated that using kilohertz laser ablation both fragile bio-molecules as e.g. Guanine, as well as refractory metals could be efficiently doped in helium droplets [3]. In order to study reaction processes we successively loaded helium droplets with water clusters and alkali atoms (Fig. 1). Even at the millikelvin temperatures of the droplets we clearly find signatures of chemical reactivity. Analyzing photo-ionization mass spectra we can detect peculiar differences in the reactivity depending on the alkali used (Na, K, Rb, Cs).

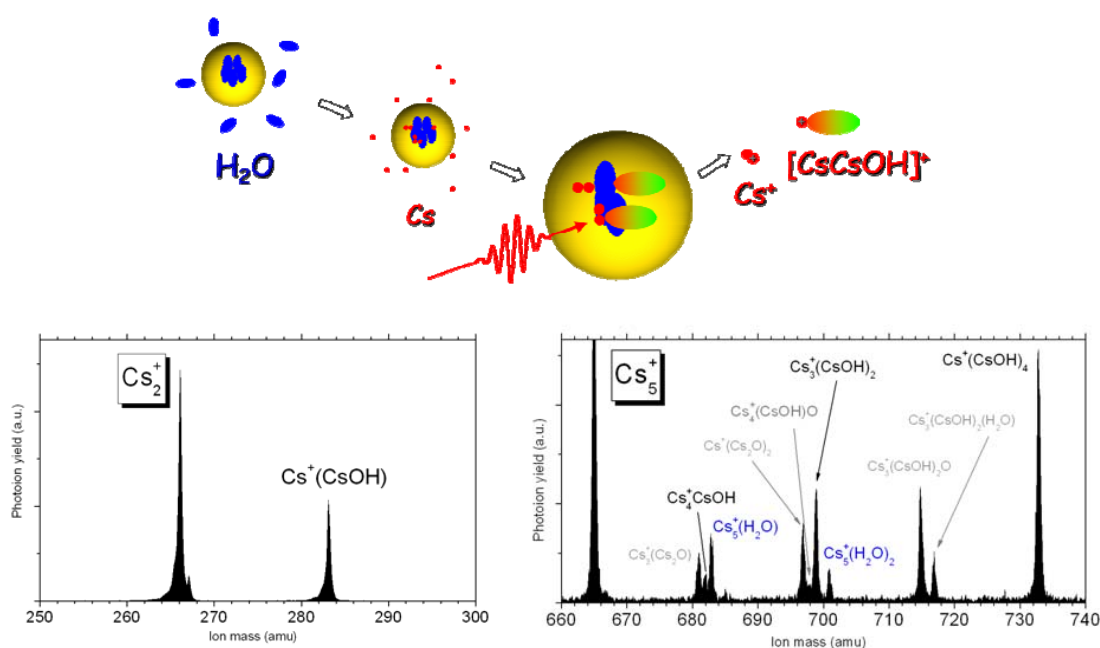


Fig.1: Illustration of an alkali – water reaction inside a helium nanodroplet. The graphs plot mass spectra of all products containing two and five cesium atoms, respectively.

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Hydrogen-induced changes in a Pd nanocluster film

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The pursuit of high capacity hydrogen storage materials started long ago and gained new momentum due to the fossil fuel related problems. The use of hydrogen could contribute to a solution[1]. The main aim is obtaining high hydrogen concentrations in a material that possesses suitable transport properties under ambient conditions. A promising way to alter favorably the properties is by reducing its size to the extent that surface and quantum effects begin to play a major role. The investigation of nanocluster metal hydrides may therefore reveal novel properties.

Palladium is one of the most widely studied metals with respect to hydrogen absorption. We investigated the effect of hydrogen on the structure, morphology and optical properties of a palladium cluster assembled film with various techniques: XRD, EXAFS, STM and electrochemistry. These experiments all revealed changes that may affect hydrogenation properties of nanoclusters in a more general way. By electrochemical means we compared the optical change of palladium nanoclusters with an MBE film. With this novel method we found evidence for a core-shell structure in the palladium-hydride nanocluster. These results demonstrate novel properties which in a general way set boundaries for the use of nanoclusters for hydrogen storage.

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Friday, Sep. 19th

Plenary Talks

B. von Issendorff

Angle resolved Photoelectron Spectroscopy on Simple Metal Clusters

Invited Talks

M. Arndt

On the Cross-Fertilization of de Broglie Interferometry and Cluster Physics

K. Takatsuka

Dynamics of Structural Isomerization and Evaporation of Isolated Small Atomic Clusters

Hot Topics

A. Terasaki

Photon-Trap Spectroscopy of Size-Selected Cluster Ions: “Direct” Measurement of Optical Absorption

M. Tchapyguine

Free One- and Bicomponent Metal Clusters Studied by Synchrotron-based Photoelectron Spectroscopy

V. Kresin

Evaporative Attachment of Slow Electrons to Metal Nanoclusters

Angle resolved photoelectron spectroscopy on simple metal clusters

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Photoelectron spectroscopy is a powerful technique for studying the electronic structure of metal clusters and nanoparticles. Continuous improvements in cluster production, cooling, mass selection and photoelectron characterization in recent years now allow highly resolved measurements on free particles over a very broad size range. A wealth of materials has been studied. A special class here are the simple metals, i.e., alkaline and (to a lesser extent) noble metals, the electronic structure of which is dominated by shell effects. Nevertheless the measurements on such clusters reveal a clear influence of their ion lattice structure, which in combination with DFT calculations in many cases allows an unambiguous determination of the geometric structures of the clusters. Even more detailed information can be obtained by angle-resolved photoelectron spectroscopy. As the angular distribution should depend on the angular momentum of the bound state of the emitted electron, this technique in principle allows a characterization of the electronic wavefunctions. For free, cold, size-selected sodium clusters surprisingly diverse angular distributions have been found, with very similar behaviour for the substates of given electron shells. This demonstrates that lattice-induced mixing between different angular momentum states is not very pronounced. More importantly, it shows that electron emission is a fully coherent process, even for the case of the largest cluster studied (Na_{147}). This makes simple metal cluster interesting model systems for the study of coherent many particle dynamics.

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On the cross-fertilization of de Broglie interferometry and cluster physics

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Matter-wave interferometry with clusters and large molecules, as pursued in our lab, has currently three goals: the exploration of the quantum-classical boundary, the development of new methods for cluster metrology as well as the implementation of new ways of creating surface-bound molecular nanostructures.

Matter-waves were originally introduced by Louis de Broglie in 1923 as a quantum concept for the description of the center-of-mass motion of massive bodies. It has proven correct for all objects studied so far and one may readily find arguments why the intrinsic quantum nature of mice and men will not appear in our everyday world.

However, it remains an open challenge to try and push the experimentally validated limits of de Broglie interferometry as far as possible. This motivated our first quantum experiments with large molecules, i.e. diffraction with fullerenes already several years ago [1]. We were able to show that the internal degrees of freedom may fully decouple from the translational degrees of motion and that large molecules can build up single-particle quantum interference patterns in spite of their high thermal excitation [2]. We will discuss how biomolecular clusters now emerged as intriguing objects for future quantum interference experiments in our lab.

Interestingly, cluster interference is also dependent on all internal cluster properties that couple to translational degrees of freedom mediated by external fields. For instance, the cluster polarizability grows with the volume of the particle and the interaction with both optical and material diffraction elements therefore increases dramatically with cluster size. This requires the implementation of specialized interferometric concepts. One of these, the Kapitza-Dirac Talbot Lau interferometer has recently been successfully realized in Vienna [3]. The sensitivity to external fields turns matter-wave interferometry also in a highly precise sensor, which allows us to measure polarizabilities or susceptibilities with improved accuracy [4]. And it allows us to sort a beam of clusters or molecules according to their polarizability-to-mass ratio [5].

We shall discuss the current status of molecule interferometry and the prospects for experiments on cluster coherence in the mass range of 1.000.000 amu [6] and potentially beyond...

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Dynamics of structural isomerization and evaporation of isolated small atomic clusters as multichannel chemical reactions and their characterization with "temperature"

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Isomerization dynamics of a small atomic (or van der Waals) cluster wandering from one molecular structures to another among many isomers shows many interesting phenomena that gives a link between the deterministic dynamics and macroscopic statistical mechanics [1]: melting (a prototype of the first order phase transition), loss of the memory in structural transitions, liquid-like dynamics that does not care about the so-called transition state, evaporation coupled with structural isomerization, and so on. This isomerization dynamics can be regarded as a prototype of multi-channel chemical reaction, which is far beyond the "transition state concept" having dominated the theory of rate process in the 20th century. In this talk, I discuss the characteristics of these isomerization dynamics from the following view points. (1) "Microcanonical temperature" to characterize the lifetime of isomers. (2) Successive bifurcation of the so-called reaction tube (a geometrical structure in phase space) to characterize the memory-loss rate. (3) Non-Euclidean mechanics inevitably introduced into shape-changing dynamics. (4) Extraction of collective coordinates for the structural change. (5) A novel statistical theory for evaporation of atom or diatomic molecule from the clusters, which coupled with the structural isomerization in a similar time scale. (6) Experimental determination of the canonical temperature in terms of kinetic energy released by the above evaporation.

A particular emphasis is placed on a novel *nonempirical* statistical theory to give reaction rate and the kinetic energy distribution of fragments for molecular evaporation from highly nonrigid atomic and van der Waals clusters, in which an efficient and accurate method to evaluate the absolute value of classical density of states (the Thomas-Fermi density in phase space) and the flux at the so-called dividing surface has been implemented [2]. It is shown numerically that the nonempirical statistical theory gives quite an accurate reaction rate. We also study the kinetic energy release (KER) arising from these evaporations and its Boltzmann-like distribution both for atomic and diatomic evaporation. This provides a general relation between the KER and temperature of the fragments [3].

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**Photon-trap spectroscopy of size-selected cluster ions:
"Direct" measurement of optical absorption**

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A novel experimental technique is presented for optical absorption spectroscopy of size-selected free cluster ions. The technique employs an ion trap and an optical cavity; cluster ions stored in an ion trap interact with photons trapped in a cavity. The storage lifetime of photons in the cavity provides "direct" probe of extinction of light with an extremely high sensitivity (photon-trap spectroscopy [1,2]: an extended scheme of cavity ring-down spectroscopy). The "direct" measurement of photoabsorption is unique to this technique, which is contrasted with conventional action-spectrum measurements relying on "indirect" information from photodissociation or laser-induced fluorescence [3]. In addition, the use of an ion trap instead of ordinary ion-beam experiments allows measurements under controlled experimental conditions such as a temperature and a magnetic field.

We have developed an experimental setup illustrated in Fig. 1(a). The first experiment was performed on the atomic ion of manganese, Mn^+ , which shows ultraviolet absorption due to ${}^7\text{P}_J \leftarrow {}^7\text{S}_3$ ($J = 2, 3$, and 4) transitions. Spectra of hyperfine structures, Zeeman splitting, and Faraday rotation were measured under a magnetic field up to 3 T [2]. The stored Mn^+ ions were even spin-polarized by a circularly polarized light [4]. Very recently, we succeeded in the experiment of silver cluster ions, Ag_N^+ . Preliminary results of absorption measurement of Ag_9^+ are shown in Fig. 1(b), presenting temperature dependence down to 10 K. These spectra are to be contrasted with those assigned to surface-plasmon resonance by photodepletion spectroscopy of hot silver clusters.

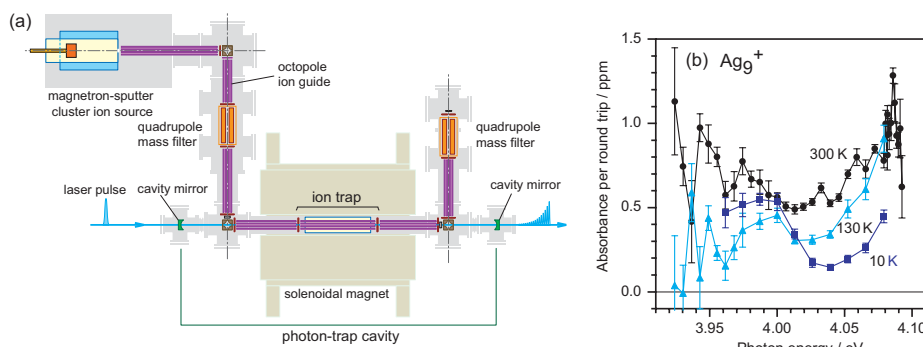


Figure 1: (a) Experimental setup. (b) Temperature dependence of absorption spectra of Ag_9^+ .

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Free one- and bicomponent metal clusters studied by synchrotron-based photoelectron spectroscopy

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In a pair of recent years significant progress has been made by us in the field of *free* metal nanoscale clusters using photoelectron spectroscopy. This progress has been possible due to the combination of an efficient gas-aggregation cluster source, the high-flux tunable x-ray radiation at MAX-lab synchrotron facility, and the versatile end-station of the beamline. The metal vapour in the cluster source is produced either by resistive heating of a furnace or by magnetron sputtering inside a liquid-nitrogen cooled cryostat. So far a number of materials were successfully used by us for *free* nanoscale cluster production and *core-level* spectroscopy on them: Na, K, Pb, Bi, Sn, and –very recently- Mg and Au. Additionally, for Cu, Ag, Na, K, Pb, and Au clusters the electron density of states was mapped by means of the valence photoelectron spectroscopy. Among the most recent achievements one can name successful production and characterization of free metallic core-shell clusters out of sodium-potassium alloy (figure 1,2), and doping of free potassium clusters with favourably chosen gas-phase molecules. For the Na-K clusters our XPS study disclosed the dominating presence of potassium- metal with the lower surface energy – on the surface, and sodium in the bulk of the clusters. This result has been possible to obtain due to the provided by the core-level photoelectron spectroscopy capability to get separate responses from the bulk and surface atoms of a cluster containing a few thousand atoms. Due to the same experimental capabilities it has been possible to record a well-resolved signal from potassium atoms on the cluster surface on which the molecules of the doping gas have adsorbed. Among other achievements of the recent past are the XPS studies of plasmons in free Na, K and Mg clusters, pointing at the overwhelming extrinsic nature of the bulk plasmons. Auger and XPS spectroscopy has been successfully implemented to free potassium clusters what allowed to use the so-called Auger parameter method for estimating the degree of screening of the core-hole by the valence electrons in a free metallic cluster of a few thousand atom size. Among other achievements one can mention the demonstrated possibility to probe the deeper core levels of free metallic clusters. This has been demonstrated for potassium cluster 2p levels and for the lead cluster 4f levels. The presentation will give an overview of the experimental methods, the ways to use the obtained XPS and Auger spectra for deriving information on the cluster size, charge states, energy structure, details of the core-valence electron interaction, multielectron phenomena like plasmons, etc.

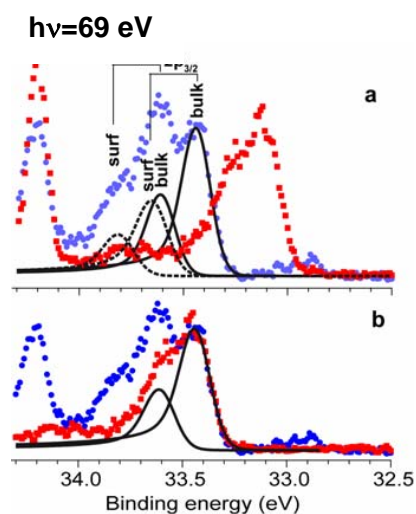
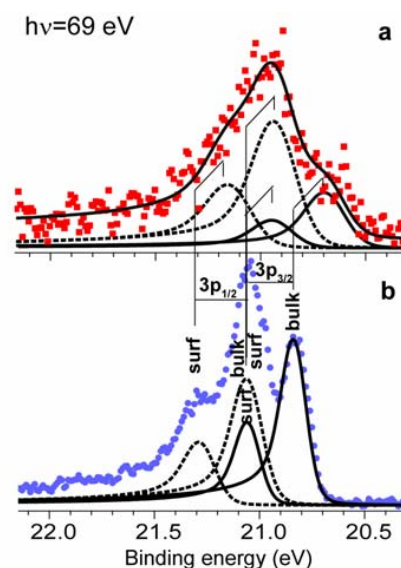


Fig.1 (to the left) Sodium cluster XPS spectrum for the pure case (circles), and for the mixed Na-K case (squares). In the **b** part of the figure the mixed-case spectrum is shifted up to align the lower binding energy flanks, and thus to demonstrate different widths of the features.

Fig.2 (to the right). **a**- “alloy” and **b**- “pure” cluster responses in the potassium 3p binding energy region. The fit for the pure-metal case with the spin-orbit and bulk and surface components is also given.



Evaporative attachment of slow electrons to metal nanoclusters

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We present a measurement of the abundance mass spectra of $\text{Na}^-_{n \sim 7-140}$ cluster ions formed as a result of low-energy (0.1 eV) electron attachment to free clusters. Both the anion (daughter) and the neutral (precursor) cluster mass spectra were acquired simultaneously, making it possible to investigate their transformations without distortions due to beam variations.

The anion spectrum revealed significant restructuring with respect to the neutral precursors, including a downshift in the shell-closing magic numbers, as well as strong changes in the relative intensities of open-shell peaks. Importantly, the latter effect cannot be explained by a simple pattern shift by one electron number, and requires an accurate treatment.

The restructuring of cluster abundances was analyzed on the basis of a three-stage evaporative attachment picture: (1) electron capture by the polarization potential of the cluster; (2) prompt dissipation of electron attachment energy into the internal vibrational degrees of freedom (cluster heating); followed by (3) evaporative cooling. The last stage, comprising a cascade of monomer and dimer evaporations, was described within the statistical evaporative framework. Convoluting the calculated evaporation chains with the mass spectra of the neutral precursors, we obtained detailed agreement with the experimental data without any adjustable parameters. Furthermore, being sensitive to the cluster dissociation energies, the data verified that the prior literature dimer binding energies need to be corrected by $\approx 25\%$.

Thus a complete description of the full process of evaporative electron attachment to metal clusters has been established. The results demonstrate that slow-electron capture offers a useful window into the polarization, statistical and binding properties of nanoclusters. Conversely, they emphasize that in interpreting charge-capture and charge-transfer reactions involving clusters it is essential to account for accompanying evaporative dynamics.

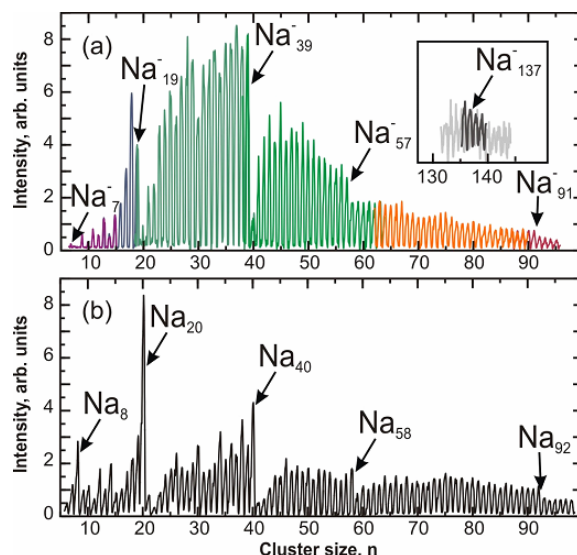


Figure 1: Mass spectra of the electron attachment products (a) and the precursor beam (b).

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