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Report on DOE Travel Support Award DE-SC0014605

The aim of the aforementioned award (Program director: Dr. Mark Pederson) was to facilitate the attendance of researchers, students, and postdocs from the U.S. at the international workshop co-organized by the undersigned.

The award succeeded in making it possible for a number of US attendees to present their work and participate in the meeting, which was a significant event in the research community at the interdisciplinary interface of physical chemistry, nanoscience, atomic and molecular physics, condensed matter physics, and spectroscopy.

The workshop did not issue proceedings, but the attached pages present the schedule, the abstracts, and the attendance list of the July 2016 Workshop. DOE sponsorship is gratefully acknowledged on the last page, and we sincerely appreciate this support.

If you need additional information or further comments, please don't hesitate to contact me.

Sincerely yours,

Vitaly Kresin
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Friday, July 22: arrival

Invited talks: 35 minutes + 5 minutes for discussion; "Hot topic" talks: 20 minutes + 5 minutes for discussion

Saturday, July 23		Sunday July 24		Monday July 25		Tuesday July 26		Wednesday July 27	
Commemoration of T. P. Martin and reflections on the 1987 Erice School						XLIC COST Action session			
Session chair: V. Kresin		Session chair: A. Kirilyuk		Session chair: I. Shuttleworth		Session chair: L. Ma		Session chair: J. Gspann	
9:00-9.10	Welcome	9:00-9.40	R. Antoine	9:00-9.40	T. Zeuch	9:00-9.40	L.-S. Wang	9:00-9.40	M. Arndt
9:10-9:20	G. Benedek								
9:20-10.20	G. Pacchioni	9:40-10.20	H. Häkkinen	9:40-10.20	P. Slavíček	9:40-10.20	K. Hansen	9:40-10.20	G. Gribakin
10.20-10.40	K. Hansen	10.20-10.50	break	10:20-10:45	J. Lengyel	10.20-10.50	break	10.20-10.50	break
10:40-11:10	Break	10:50-11:30	K. Bowen	10:45-11:15	break	10:50-11:30	J.-M. Rost	10:50-11:30	X.-J. Liu
11:10-11:50	W. de Heer	11:30-12.10	T. Azuma	11:15-11:40	J. Bakker	11:30-12:10	F. Lepine	11:30-12:10	F. Stienkemeier
11:50-12:30	B. von Issendorff	12:10-16:00	Lunch, free time	11:40-12:00	G. Benedek (History of Erice)	12:10-16:00	Lunch, free time	12:10-16:00	Lunch, free time
12:30-16:00	Lunch, free time			12:00	Lunch				
Session chair: G. Seifert		16.00-19:00	Posters	*departure 14:00* Excursion and excursion dinner		Session chair: M. Nakamura		Session chair: M. Fárník	
16:00-16.40	K. A. Jackson					16:00-16.40	M. Pederson	16:00-16:45	V. Kresin
16.40-17.05	E. Krotschek					16:40-17:05	R. Delaunay	16:40-17:05	L. Kranabetter
17:05-17:35	break					17:05-17:35	break	17:05-17:35	break
17:35-18:15	L. Schweikhard					17:35-18:15	J. Fedor	17:35-18:15	A. Mauracher
18:15-18:40	E. Roduner					18:15-18:40	M. Kuhn	18:15-18:40	D. Merthe
	Dinner		Dinner				Dinner	19:30	Banquet (informal)

Thursday, July 28: departure

Nature and Consequences of Electron Localization or Delocalization in Oxide Nanoparticles

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The properties of oxide nanostructures largely depend on the presence of holes, electrons, electron-hole pairs, etc. The localized or delocalized nature of the excess electrons and their mobility are crucial for the understanding of the optical, magnetic, photo-chemical, and transport properties of these systems. Particularly challenging is the characterization and identification of the nature of excess electrons in oxide nanoparticles.

We will introduce the problem by discussing the consequences of electron localization or delocalization in phenomena like photo-catalysis by titania nanoparticles. We will address the question of how to identify excess electrons by combining electron spin resonance experiments with density functional theory calculations. We will address the formation of small and large polarons and the role of low-coordinated sites at the surface of nanoparticles for electron localization. Finally, we will discuss under which conditions localized electrons in oxide nanostructures can result in magnetic interactions and eventually in magnetic ordering.

Two state cluster ferromagnetism
and the evolution of itinerant bulk ferromagnetism

Lei Ma[1], John Indergaard[2], Walt A. de Heer[1,2]

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Molecular beam Stern-Gerlach deflection technique has been an indispensible tool to interrogate cluster ferromagnetism. Little has changed in the basic measurement methods since the early 1990's when the first measurements were made on Fe, Co and Ni clusters [1]. Since then, significant technological advances have been made so that these measurements can be made from cryogenic temperatures up to 1000 K. Improved laser vaporization cluster sources, high-resolution position-sensitive mass spectrometry, coupled with F_2 excimer pulsed-laser photo-ionization have significantly improved the quality of the data. With these improvements surprising new effects have come to light. In particular, we have found that the 3D metal clusters of Cr, Mn, Fe, Co and Ni exhibit two magnetic states for all sizes. Fe, Co and Ni exhibit a high magnetic moment at low temperature (the magnetic ground state). As the temperature is increased a second, low magnetic moment peak emerges (the magnetic excited state). For these clusters, the average magnetic moment approaches that of the bulk as the cluster size increases. This contrasts with the original observations, at lower spatial resolution, for which a single, broad deflection peak was observed. Since its deflection corresponds to the average of the two peaks that are observed in the recent high-resolution measurements, the evolution of the magnetic moment from the atom to the bulk was properly measured in the earlier measurements [1]. However, the physics is clearly different than previously assumed. Moreover, Cr and Mn, that are antiferromagnetic in the bulk, also exhibit two peaks, however the low moment corresponds the low temperature ground state, and the high moment to the excited state. In this case the per-atom magnetic moments of both states diminish with increasing size. These observations suggest that the evolution to the bulk involves these two states that have an energy gap that vanishes with increasing size. In this way, molecular magnetism evolves into itinerant magnetism.

In this talk, I will review these results, and, time permitting, also address some intriguing recent results on the electric and magnetic deflections of Cu, Ag, and Au clusters.

[1] *Magnetism from the Atom to the Bulk in Iron, Cobalt and Nickel clusters*, I. Billas, A. Chatelain, W. A. de Heer, *Science* **265**, 1682, (1994)

Photoelectron spectroscopy of simple and not so simple metal clusters

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Simple metal clusters like alkaline or noble metal clusters exhibit an electron shell structure, the discretized electron density of states resulting from the boundary conditions the cluster surface constitutes for the free electron gas. In close to spherical clusters the electrons consequently occupy wavefunctions which are approximately angular momentum eigenfunctions, as can be nicely demonstrated by angle resolved photoelectron spectroscopy [1]. Nevertheless there is a significant interaction between the ionic structure of the cluster and the delocalized electrons, which lifts the degeneracy of the angular momentum eigenstates. The resulting patterns in the electronic density of states reflect the symmetry of the cluster, and therefore can be used as a very sensitive tool to determine their geometrical structure.

A much more profound interaction between the ionic structure the electronic system can be found in divalent metal clusters. These clusters exhibit a nonmetal-to-metal transition as a function of size: while small clusters exhibit a bandgap as could be expected for semiconductors, larger clusters exhibit an electron shell structure similar to that of simple metal clusters [2-4]

A combined experimental/theoretical study recently demonstrated, however, that the structure of divalent clusters (namely zinc clusters) is much more complex. Zinc clusters in the size range of a few ten atoms form atomic shell like structure, where the electrons are delocalized within the atomic shells, but not between them. This leads to exotic geometries structures like core and shell structures with different symmetries. Consequently medium sized zinc clusters could rather be seen as representatives of layered 2D-metals than of homogenous 3D-metals.

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Polarizability and Metallicity in Silicon Clusters

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The electric dipole polarizability is an experimentally accessible measure of the response of a cluster to an applied electric field. It can also be accurately calculated within density functional theory (DFT) and such calculations can give insight into the physical significance of observed data. Our computational approach decomposes the total polarizability into site-specific contributions from individual atoms (or groups of atoms) in a cluster. This provides a direct look at effects such as electrostatic screening – or to what extent charge transfers at the cluster surface shield the interior from the effects of an external field. The approach also allows an additional partitioning into charge transfer and local dipole polarizability that further enhances its interpretive power. We have used this methodology to study trends in a variety of molecules and clusters.[1-3] In this talk we will compare and contrast cluster size trends in the polarizability of metal (Na_N, Al_N, Mg_N, etc), semiconductor (Si_N), and insulator (NaCl, KCl) clusters. We will describe how shape and surface-related effects are manifested in the size evolution of the polarizability and how the per-atom polarizability approaches the corresponding bulk value. Silicon is a particularly interesting case. We will present the results of new calculations of the polarizabilities of Si_N and show that they are in excellent agreement with values obtained in recent experiments.[4] We will show that the cluster-size trends and the site-specific analysis present a consistent picture of metallic behavior at small and intermediate sizes in these clusters.

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Trapped polyanionic clusters

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Storage of ions gives access to a large variety of studies of cluster reactions with various interactions particles (Fig. 1) [1]. In particular, the Penning-trap setup ClusterTrap (Fig. 2) has been extended over the years for studies of the production and properties of poly-anionic metal clusters [2,3]. The singly charged anionic clusters can pick up further electrons when exposed to an “electron bath” [4,5]. Thus, provided the clusters are large enough, (meta-)stable polyanions can be formed. The necessary cluster sizes depend on the charge states as well as on the cluster material.

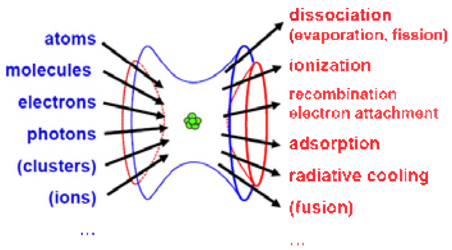

Fig.1 Interaction partners and corresponding reactions of stored cluster ions (from ref. 1).

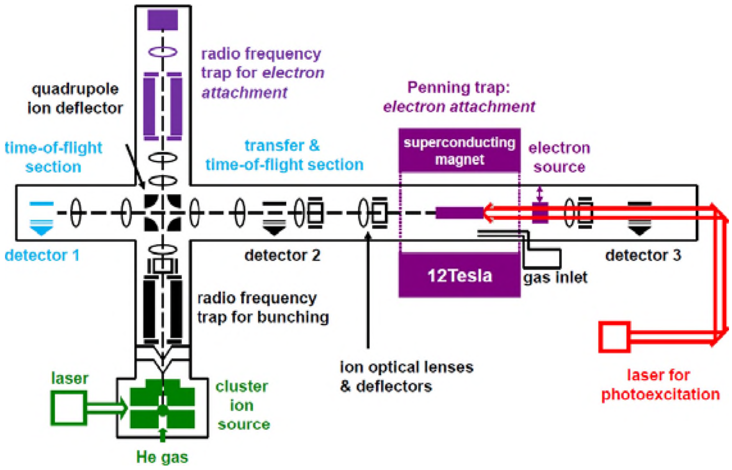

Fig.2 Schematic overview of the ClusterTrap setup

Upon photoexcitation the clusters (re-)emit an excess electron or decay by neutral atom evaporation. The behavior depends, again, on the cluster size. In addition, it seems that in some cases a simultaneous emission of two excess electrons may occur [6]. And very recently, strong indications for a further decay pathway have been found: Some photoexcited dianionic metal clusters seem to undergo fission, i.e. they decay into two smaller singly charged anionic clusters.

The presentation will review cluster-ion trapping and describe the formation of polyanionic clusters by electron attachment in Penning and Paul traps. The decay behavior of various metal clusters will be described. If time allows, alternative production and storage techniques for polyanionic clusters will be touched upon.

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Ligand-protected gold and silver nanoclusters:
Towards a new class of nonlinear optics nanomaterials

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Atomic clusters of metals are an emerging class of extremely interesting materials occupying the intermediate size regime between atoms and nanoparticles. Nonlinear optical (NLO) characteristics of atomically precise clusters of gold and silver revealed remarkable features. The two-photon absorption cross section of protected noble metal nanoclusters is several orders of magnitude larger than that of commercially-available dyes. However, the fundamental photophysical mechanisms underlying those two-photon processes in ligand protected clusters with few metal atoms are not fully understood yet.

Theoretical models to explain the experimental observations will be introduced and the possibility to deduce the key ingredients to propose new classes of nanoclusters with large NLO efficiency will be discussed. Additional case studies, on silver and gold liganded clusters will be presented to emphasize their NLO properties making them promising candidates for various imaging techniques such as fluorescence microscopy or Second-Harmonic Generation microscopy.

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HOW MANY GOLD ATOMS MAKE GOLD METAL ?

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A major challenge in nanoscience concerns understanding behavior of systems when their size increases from a few atoms towards bulk. The properties of small molecules and bulk matter are well understood while nanoclusters and small particles present significant challenge to uncover their size-dependent properties. Nanometer-scale, ligand-stabilized gold clusters have emerged in recent years as a novel form of nanoscale matter with potential applications in molecular electronics, optics, sensing, drug delivery and biolabeling. Tremendous advances have been achieved in discovering their structures due to contributions from synthetic work, X-ray crystallography and density functional theory computations. This talk discusses recent progress in understanding the development of their “metallicity” as a function of the increasing size.

Dipole Bound Anions, Quadrupole Bound Anions, and Double Rydberg Anions

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In this talk, we will present the anion photoelectron spectra of several newly discovered dipole bound anions, quadrupole bound anions, and a double Rydberg anion, all delocalized electron systems. Two different formation mechanisms were used to form the dipole bound anions, i.e., nozzle-ion and Rydberg electron transfer. The quadrupole bound anions were made by Rydberg electron transfer, and the double Rydberg anion was made via laser vaporization. The capabilities of our new Rydberg Electron Transfer-Photoelectron Spectrometer will be illustrated and discussed.

Recurrent fluorescence:
fast cooling mechanism of clusters and molecules

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Our group has been studying dynamics of negatively-charged small carbon cluster ions (C_n^-) stored in an electrostatic ion storage ring. This type of the storage rings is suitable for observing their slow dynamical behavior in the long timescale. We have focused our attention to the energy relaxation process of hot ions prepared by visible laser irradiation. For polyatomic molecules, internal conversion (IC) is a common phenomenon, by which electronic excitation energy is dissipated into the vibrational modes in the time scale on picosecond timescales, and vibrational radiative cooling by IR photon emission follows. Radiative stabilization is important particularly for anions with their low activation energies for electron loss, and for small clusters with their small heat capacities.

We recently found new efficient radiative stabilization mechanism referred to as recurrent fluorescence (RF). The reversed process of IC, i.e. the inverse internal conversion (IIC) is followed by visible photon emission from low-lying electronic excited states. We experimentally obtained evidence of RF's contribution to the cooling process for C_6^- [1] and C_4^- [2] from the fast decay time of the neutral yield resulting from electron detachment. We elucidated the contribution of such electronic radiative cooling especially to the C_4^- ions with internal energy far below the detachment threshold by a novel approach, observing the laser-wavelength and storage-time dependences of the total yield of the photo-induced neutrals. In addition, very recently, we have succeeded in direct detection of visible RF photons emitted from the thermally populated electronic excited state of C_6^- [3]. Clear evidence is provided to distinguish RF from normal fluorescence, based on the temporal profile of detected photons synchronized with the revolution of C_6^- in the ring, for which the timescale is far longer than the lifetime of the intact photo-excited state.

The energy relaxation process is heavily affected by the existence of the available low-lying electronic excited state. This finding is particularly important from the viewpoint of astrochemistry, because the presence of the IIC and RF will have a significant influence on the abundance of small carbon cluster anions and related species in the diffuse interstellar clouds in space.

References

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Sodium doped water clusters: From solvated electrons to the smallest ice crystals

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The interaction of a sodium atom with clusters containing 5 to 10 water molecules reduces its ionization energy from 5.14 eV to values around 3 eV. This observation has been interpreted as the formation of a fully solvated electron in surprisingly small water clusters [1]. The corresponding solvation of the positively polarized Na atom results in similar Na centered local structures for neutral and cationic clusters fully suppressing fragmentation upon photoionization [2]. The photoionization spectrum of $Na(H_2O)_n$ clusters is very broad for n>15 with the first ion signals appearing around 2.7 eV and signal saturation at around 4.1 eV. Most of the clusters have ionization energies above 3.4 eV indicating a high fraction of clusters, in which the sodium atom and its 3s electron are not solvated. Heating of the clusters by IR absorption of the OH stretch oscillators enhances sodium solvation and solvated electron formation increasing the ion yield when photoionization is performed near the appearance ionization energy [2]. The combination of all these properties enables a size-selective IR action spectroscopy with neutral water clusters providing an IR spectrum of the structure sensitive OH stretching region for each size of the distribution in a single IR laser scan. With this method the structural transition from amorphous to crystalline water clusters containing 100 to 500 water molecules was for the first time traced with precise size control [3]. Very recently we explored the dependence of the ion signal on the delay time between IR and UV laser pulse. This analysis revealed IR frequency specific components of the signal with different time scales. There are a) "fast" (<5 ns) and b) "slow" (20 – 200 ns) positive and c) "slow" (τ~45 ns) negative components. For cluster sizes in which crystalline structures are present the time dimension of the ion signal allowed an isomer distinction between a surprisingly large fraction of vaporizable amorphous clusters with a pronounced negative signal component peaking around their absorption maximum of 3400 cm^{-1} and rigid crystalline clusters without negative signal component at their absorption maximum around 3200 cm^{-1}. The analysis further revealed that largely crystalline water clusters without amorphous sub-surfaces are already present at the critical size for the onset of crystallization (n = ca. 200 in this experiment). These highly rigid clusters are discriminated by their slow positive signal component indicating delayed sodium solvation. Both, the high fraction of amorphous clusters and the absence of clusters with small crystalline cores suggest that water clusters feature a broad temperature band in which very rigid, highly crystalline and vaporizable liquid-like clusters are the two dominating minima in the free energy landscape [4]. Due to the time scale of cooling in our experiment crystallization can only occur in the upper range of this temperature band in which the equilibrium is dominated by liquid-like clusters.

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Structure and Dynamics of Hydrated Electron: Computational Perspective

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[2]Jaroslav Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, Prague 8, 180 00, Czech Republic

Hydrated electron remains to be one of the most enigmatic species in chemistry; on the one hand, it is the simplest chemical species, even simpler than hydrogen atom. On the other hand, it owes its existence to the solvation which complicates the theoretical description. Even now, the degree of delocalization of the species remains controversial.

In my talk, I will focus on the formation and reactivity of a hydrated electron in or on finite-size particles as results from quantum-chemical and molecular dynamics calculations. In the first part, I will deal with solvated electrons formed upon deposition of alkali metals (sodium in particular) on water clusters. Here, an ion pair of the $Na^{+}\cdots(e^{-})_{H2O}$ type is formed and the properties of these clusters depend both on the position of the sodium ion and on the structure of the hydrated electron.[1,2] The question of isomerism and its control will be discussed. I will also focus on the process of formation of these systems within the pick up procedure, describing the energy transfer and gradual formation of different isomers of a solvated electron. The formation of a solvated electron on clusters composed of other polar molecule will be briefly discussed.

Tagging of molecular clusters with a hydrated electron became recently a viable way for sizing molecular clusters and even its characterization via IR spectroscopy.[3] I will discuss the foundations of the approach and also its limitation. In this context, I will pay attention to the reactivity of a hydrated electron on the surface of molecular clusters. I will discuss properties of anionic water clusters as they appear from the molecular simulations.

In the last part of my presentation, I will discuss the transition from finite-size molecular clusters to a hydrated electron in bulk water. In particular, I will discuss structure and reactivity of a hydrated electron in liquid water.

The work was supported by Czech Science Foundation, grant numbers 14-08937S and and 15-12386S.

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Electron Delocalization in Size-Selected Boron Clusters: From Planar Structures to Borophenes and Borospherenes

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Photoelectron spectroscopy in combination with computational chemistry over the past decade has shown that boron clusters possess planar or quasi-planar structures [1-3], in contrast to that of bulk boron, which is dominated by three-dimensional building blocks. All planar or quasi-planar boron clusters are observed to consist of a monocyclic circumference with one or more interior atoms. The propensity for planarity has been found to be a result of both σ and π electron delocalization over the molecular plane, giving rise to concepts of σ and π double aromaticity.

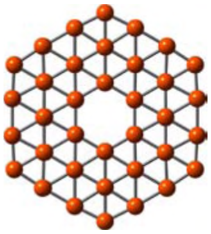

Fig. 1. The B_{36} cluster.

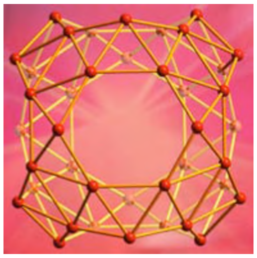

Fig. 2. The B_{40} cluster.

Because of its electron deficiency, boron cannot form graphene-like structures with a honeycomb hexagonal framework. Computational studies suggested that extended boron sheets with partially filled hexagonal holes are stable. We have found that B_{36} is a highly stable planar boron cluster with a central hexagonal hole (Fig. 1). This finding provided the first indirect experimental evidence that single-atom layer boron-sheets with hexagonal vacancies, which we named "borophene" [4], are potentially viable. We further found that the B_{35}^- cluster also possesses a hexagonal structure with two adjacent hexagonal holes and can be a more flexible motif for borophenes with different atomic arrangements [5]. More interestingly, our photoelectron spectroscopic studies revealed that the B_{40}^- cluster consisted of two nearly degenerate isomers competing for the global minimum: a quasi-planar isomer with two hexagonal holes and an unprecedented cage isomer (Fig. 2). In the neutral, the B_{40} cage is overwhelmingly the global minimum, which is the first all-boron fullerene to be observed and is named "borospherene" [6]. Further studies showed that the B_{39}^- cluster consisted of two nearly degenerate chiral cage structures [7], suggesting the possibility of a family of borospherenes. Finally, I will also discuss our recent progress to investigate transition metal doped boron clusters [8] and the possibility for metallo-borophenes [9]. It will be shown that electron delocalization plays critical roles in the structures and chemical bonding of both bare and doped boron clusters.

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Single Photon Hot Electron Ionisation of Molecules

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One photon molecular ionization is conventionally understood as emission of an electron in state-to-state processes, involving only a few and well defined electronic states. In contrast, multiphoton ionization may proceed *via* several different mechanisms, such as above threshold ionization, field ionization and thermionic emission. In addition, electrons can be emitted in a quasi-thermal process where the electronic degrees of freedom act as a thermal subsystem which is heated by e.g. laser pulses while the vibrational motion remains cold for a good fraction of a picosecond [1].

This mechanism has been shown to be responsible for the ionization of a number of large polycyclic aromatic hydrocarbons exposed to light with photon energy far below the ionization energy [2]. The ionization requires a laser pulse of duration on the order of the electron-vibration coupling time or shorter, to avoid the premature dissipation of excitation energy into the vibrational motion.

We have recently shown that C_{60} also ionizes with this mechanism after absorption of a *single* photon [3]. The measurements were performed at the ELETTRA Synchrotron Light Source in Trieste (Italy) with photons of energies between 13.5 and 60 eV. The primary experimental evidence is a persistent and strong component of low kinetic energy electrons in the photoelectron spectra. The electron momenta are spherically distributed with no remaining sign of the light polarization and can be described with a Boltzmann factor with a temperature of 1-2 eV, or $1\text{-}2 \cdot 10^4$ K. Additionally, the threshold and channel (viz. single and double C_2 loss from C_{60}^+) for subsequent fragmentation of the produced cation agrees quantitatively with the previously measured thermal behavior. The presence of this type of ionization for photon energies above 30 eV which reach beyond the valence band requires that the photon creates a particle-hole state with at least two particles and two holes.

The observation of this process expands the picture of light-matter interaction with a fundamentally new type of ionization process. It will be of special and immediate importance in astrophysics, e.g. by providing a novel mechanism for producing low energy electrons in the dense interstellar medium close to nascent stars.

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From illumination with midinfrared to x-ray pulses: The changing role of the nanoplasma in clusters and large molecules.

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Clusters of atoms or molecules are an ideal target to probe the interaction of high density matter with light of high (energy) density, available from lab-based laser sources for long and facility free-electron-laser sources for short wavelengths.

Although initial photon coupling to the bound electrons as well as subsequent energy absorption from the laser pulse differs dependent on the wavelength of the pulse and its duration, a universal feature is the formation of a transient electronic nano-plasma. We will discuss its role which differs for IR, VUV and X-ray pulses. In the latter case, proton ejection occurs for hydrogen-rich molecules [1]. Consequences for the nanoplasma will be illustrated for hydride clusters as well as a large molecule, lysozyme..

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Attosecond and femtosecond XUV induced dynamics in carbon based large molecules using electron momentum spectroscopy

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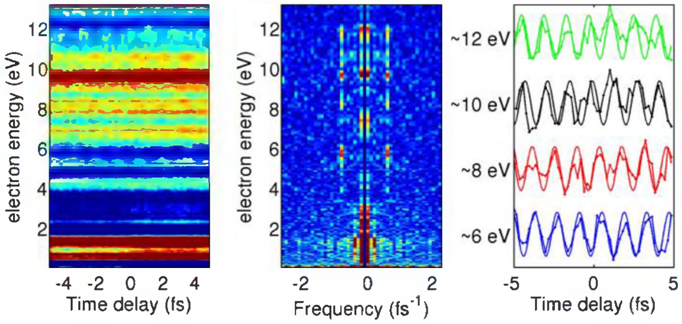
Short XUV pulses provide new means to interrogate matter on ultrafast timescale with femtosecond and even attosecond accuracy. With the improvement of this technology, experiments that were so far limited to atomic-like targets are becoming accessible for investigating increasingly large and complex isolated species using pump-probe schemes [1]. We present investigations of XUV induced processes in carbon based molecules, such as polycyclic aromatic hydrocarbons (PAH) and fullerenes using time-resolved electron momentum spectroscopy. Following XUV excitation, both independent electrons and Born-Oppenheimer approximations are broken which determines the evolution of the molecule. We have investigated scattering phases in the photoemission process using attosecond interferometry, and how electron correlation determines the photoemission delay on the attosecond timescale. Following the electron ejection, coherent charge dynamics can be produced [2] and vanishes through electro-nuclear couplings that are measured on few tens of fs [3]. This offers new opportunities to investigate matter on nanometric scale, especially relevant for a large number of interaction electrons.



Photoelectron spectrum as a function of the XUV-IR delay, the Fourier transformation of the signal indicates periodic attosecond oscillations of the electron signal from which scattering phase and photoemission delay can be extracted (example: PAH).

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Löwdin Orthonormalized Fermi Orbitals for Self-Interaction-Corrected Density-Functional Approximations with Unitary Invariance

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This talk will introduce a new formulation [1] for removing self-interaction errors that are present in most approximate density functionals and present recent applications using this method. Specific focus will be on the localization-delocalization transition in simple systems containing transition metals. The formulation relies on a new procedure for constructing a set of localized orbitals that are unitarily equivalent to the Kohn-Sham occupied orbitals, but are determined from N optimized quasi-classical electronic positions and the one-electron density-matrices. This allows one to modify the original formulation of the Perdew-Zunger self-interaction corrected density-functional approach so that the resulting expression for the total energy is explicitly unitarily invariant and size extensive. Derivatives of the total energy associated with the quasi-classical "electronic geometry" are calculated and the localizing unitary transformation is determined in a manner that is entirely analogous to optimization of the atomic geometries from Hellmann-Feynman forces in molecules and solids [2]. Recent benchmark applications, within the PW92 local density approximation, will be presented. In small molecules we find that atomization energies are significantly improved especially for cases where pi-bonding is important [1]. In atoms [2] and intermediate-size molecules [3,4] we find that the underestimate of the Kohn-Sham orbital energies, relative to ionization energies, is corrected. In molecules containing under-coordinated transition-metal ions, which may be of interest to catalysis, we find that this version of SIC predicts larger spin moments than LDA and GGA and that this appears to be in accord with experiment [5].

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Influence of elementary aggregation on electron-induced molecular fragmentation

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Electron-molecule collisions often efficiently cause cleavage of chemical bonds even at collision energies that are lower than electronically exited states of the neutral molecule. Such reactions proceed via dissociative electron attachment (DEA): formation of a temporary anion state (resonance) that can be repulsive and lead to the molecular fragmentation. This process drives chemical changes in environments with high abundance of low-energy electrons, typically originating from a secondary electron avalanche generated by radiation passing the matter. Probing such bond-breaking reactions both in the gas phase and in various types of clusters enables to unravel the effects of elementary environment on the triggered chemical changes. In this contribution we show, that these effects can be dramatic and that a caution has to be taken when extending the gas-phase knowledge to processes occurring in bulk.

I will discuss two distinct topics. In the first part, I will focus on experiments with iron pentacarbonyl, $Fe(CO)_5$, a common precursor molecule used in the electron-induced deposition (FEBID). It is commonly accepted that the deposition process in FEBID is driven by secondary and back-scattered electrons whose distribution peaks well below 10 eV. The gas-phase experiments show that the molecular decomposition via DEA proceeds at very low electron energies (< 1 eV). We have performed experiments with two different types of clusters: (i) pure $Fe(CO)_5$ clusters and (ii) $Fe(CO)_5$ clusters deposited on argon nanoparticles with the size of several hundreds of atoms. The presence of environment completely suppresses the low-energy features and pronounced bands appear in the 5-15 eV energy range [1]. We attribute this change to electron self-scavenging: a two-center excitation/attachment process which drives the synthesis of complex anions of mixed Fe/CO composition.

In the second part, I will describe the changes in DEA to uracil and thymine that occur upon adding several water molecules to these nucleobases. Our novel approach allows for a significant control over the hydration of target molecules in the beam. While for isolated nucleobases the DEA efficiently causes the N-H bond cleavage, the presence of already few water molecules around both uracil and thymine prevents their fragmentation and stable molecular (and hydrated) anions are formed instead.

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Matter-wave interferometry with nanoparticles and biomolecules

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I will report on two perspectives of quantum delocalization of electrons in atomic and molecular nanoclusters. First, we are exploring the quantum wave nature of atoms, (bio)molecules, organic and ligand-stabilized nanoclusters, where each particle can be delocalized as an intact object, even though it may be composed of several hundred atoms and several thousand electrons.

Second, while de Broglie diffraction and interferometry is primarily about the quantum wave description of the center of mass motion of massive objects, the translational motion is also affected by the internal molecular dynamics in the presence of external fields. This, in turn, depends on delocalization of electrons *inside* the molecule or cluster.

I will present different matter-wave interferometers and discuss, how they allow to assess internal molecular properties from measuring de Broglie wave fringe shifts in external fields.

Our work in the Quantum Nanophysics Group at the University of Vienna profits from a close collaboration with the teams of Marcel Mayor/University of Basel, Ori Cheshnovsky/Tel Aviv University, Klaus Hornberger/University of Duisburg-Essen and Bernd von Issendorff/Freiburg.

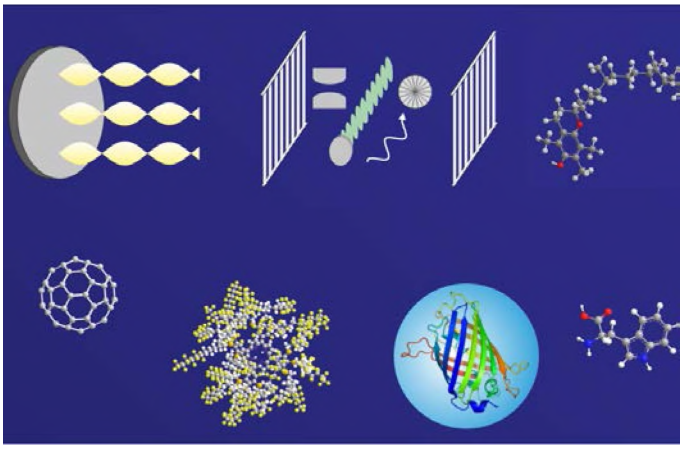

Fig.1 Gallery of interferometer arrangements and molecules that can elucidate the delocalization of both the molecule as an intact massive particle and of the electrons inside the cluster or molecule.

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Quantum chaos in excited electronic states of heavy open-shell atoms and ions

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In heavy open-shell atoms, such as lanthanides, several valence electrons can occupy a number of orbitals (4f, 6s, 5d, 6p) that lie in close proximity. This gives rise to a dense spectrum of multiconfigurational electronic states. The degree of configuration mixing in these systems is so high that the behaviour of the system can be described as many-body quantum chaos. In this regime, the many-electron eigenstates become chaotic, nearly random superpositions of very large numbers of configurational basis states. The eigenstates largely lose their individual features, electron orbital occupation numbers differ strongly from integers, and the only quantum numbers that can be used to classify the eigenstates are the exact ones, i.e., the total angular momentum, parity and energy (see the detailed study of Ce [1], as an example).

Direct, brute-force computation of the properties (e.g., energy eigenvalues or transition amplitudes) for many-body quantum-chaotic systems becomes increasingly difficult, effectively impossible, because of the extreme sensitivity of these quantities to any small perturbation, such as trancation of the basis or some higher-order corrections. In many cases the sheer size of the Hamiltonian matrix in these systes is so large that its diagonalisation becomes prohibitively expensive. On the other hand, the strong level mixing and quantum chaos allows one to develop a statistical theory [2] which can be used to calculate mean-squared values of transition amplitudes between chaotic eigenstates in terms of underlying one- and two-electron matrix elements [3,4].

A most spectacular manifestation of this physics is orders-of-magnitude enhancement of electron recombination with heavy multicharged ions, such as Au25+, U28+ or tungsten ions, such as W20+. It occurs due to extremely dense spectra of electronic excitations in these ions [5], which leads to effective trapping of the incident electron by the target ion. Besides its fundamental interest, strongly enhanced electron recombination rates can be critical for the feasibility of nuclear fusion. Tungsten is the material of choice for the plasma-facing components of the TOKAMAK reactors, such as ITER, which also makes it a major contaminant of the fusion plasma. High electron recombination rates can lead to plasma cooling or even instability. Direct calculations of the recombination rates for many tungsten ions are simply impossible because of the complexity of the system, while the statistical theory based of the quantum-chaotic nature of the eigenstates provides, reliable estimates and explains experimental findings [6,7].

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Short wavelength radiation-matter interaction: a playground for fundamental phenomena

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Synopsis The essence of Einstein–Bohr's debate about wave–particle duality was whether the momentum transfer between a particle and a recoiling slit could mark the path, thus destroying the interference. We realized this recoiling double-slit gedanken experiment by resonant X-ray photoemission from molecular oxygen. For geometries near equilibrium (coupled slits), the recoil momentum is shared by two O atoms and the interference is observed. While in a dissociative state far away from equilibrium (decoupled slits), the recoil momentum transfer is localized on one O atom and the interference is quenched.

Double-slit experiments not only illustrate the fundamental wave–particle duality, but also founded the X-ray diffraction method. Einstein–Bohr recoiling double-slit gedanken experiment [1,2] reveals one of the most intriguing deviations from classical concepts. In a double-slit experiment one can infer that achieving information about the particle path via momentum transfer erases the interference pattern characteristic of the wave behavior [3]. However, when using macroscopic slits, momentum transfer from the particle to the slit is too small to be measured. For this reason, coherence and decoherence in double slit experiments have also been studied using ultra-light atomic slits.

Our experiment, based on resonant X-ray ionization of the O_2 molecule (Fig. 1) using synchrotron radiation and a state-of-the-art coincidence set-up, offers the possibility to distinguish the momenta imparted to each of the two slits materialized by identical atomic sites: during the X-ray-induced ultrafast dissociation, the symmetry is broken owing to a site-specific momentum exchange between the ejected electron and the dissociating molecule.

We demonstrate the occurrence of symmetry breaking in the dissociating O_2^+ cation by a direct measurement of the momenta of co- and counter-propagating O+ ions with respect to the ejected electron momentum. Which-path information (WPI) about the recoiling atomic slit is thus revealed, and the interference fringes are washed out through the measurement of the opposite Doppler shifts of two paths—the 'left' and 'right' dissociating oxygen ions.

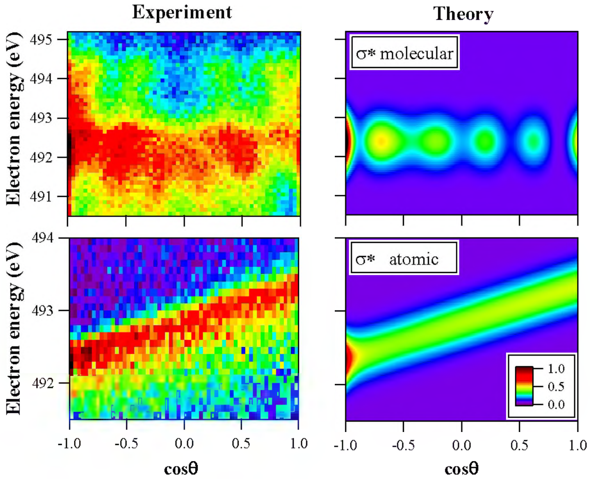

Figure 1. By both experiment and theory, the interference patterns show up when O_2 molecular geometry near equilibrium (upper part), while they disappear when O_2 dissociate far away from equilibrium(lower part).

We thus provide a consistent experimental proof and corresponding theoretical support showing a Doppler marker eliminates the interference pattern, in full agreement with Bohr's complementary principle [4].

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Superradiance, singlet fission and triplet annihilation processes of organic molecules attached to rare gas clusters.

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Charge and excitation transfer and corresponding decay and loss mechanism are the key aspects to be understood in connection with the function of light harvesting, organic photovoltaics and optoelectronic devices. In our studies we probe aggregates of organic molecules formed and isolated on rare gas clusters in order to understand collective processes of electronically excited systems. Superradiance is a collective effect where all excited states simultaneously emit radiation. This can lead to a reduced effective lifetime and an enhancement in the radiative intensity, which has been observed in a variety of interacting systems such as hot dense gases, films and Bose-Einstein-Condensates. We observed a new superradiative system where large immobile chromophores (e.g. antracene, tetracene, pentacene, PTCDA) attached to rare gas clusters exhibit characteristic lifetime shortening. Such complexes are ideally suited to probe the role of e.g. the number and the intermolecular distance of interacting systems. Furthermore, we observe at the same systems singlet fission and triplet annihilation processes, depending on the substance and the aggregate properties. Results are discussed in the context of the spectroscopy and collective effects of the complexes and decay mechanism of the aggregates.

Evidence for pairing at *T*≳100 K in size-selected nanoclusters

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The electronic shell levels of metal nanoclusters are highly degenerate and therefore represent sharp peaks in the density of states. This may enable exceptionally strong electron pairing in certain clusters composed of just tens to hundreds of atoms.

A photoionization spectroscopy study of size-resolved free aluminum nanoclusters, Al_n, has revealed a novel phenomenon: a rapid rise in the near-threshold density of states of several specific clusters with decreasing temperature. The characteristics of this behavior are fully consistent with a pairing transition, implying a high-temperature superconducting state with Tc≳100 K [1,2].. This value exceeds that of bulk aluminum by two orders of magnitude, and can be plausibly raised even higher.

The results highlight the potential of novel pairing effects in size-quantized systems and the promise of bare and ligand-decorated metal nanoclusters as high-T_c building blocks for materials and networks.

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Charge transfer reactions in helium droplets: Theory and experiment

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Helium droplets provide experimental means to investigate atoms and molecules at very low temperature. Helium droplets have an equilibrium temperature of 0.37 K and most atoms and molecules are picked up and transferred to the centre of a helium droplet upon collision which leads to rapid cooling of the dopant. With decreasing temperature, the number of quantum states with significant occupation probabilities decreases substantially. In addition, working at low temperature makes it possible to form chemical species which would be unstable at room temperature.

An important issue in mass spectrometric investigations of doped helium droplets is the process of charge transfer upon electron impact. In case of electron energies above 24.6 eV, i.e. the ionization energy of helium, resonant charge hopping from the surface of the helium droplet towards the dopant takes place. In case the charge gets close to the dopant within a certain amount of steps it will ionize the dopant, otherwise He_2^+ will be formed [1]. For electron energies below 24.6 eV an electron bubble is formed inside large enough helium droplets which can move towards the dopant and eventually interact with it. However, for electron energies around 22 eV it was experimentally shown that atomic and molecular helium anions can be formed [2]. In this presentation we discuss the formation of these anionic species on ground of quantum chemical calculations and discuss their implications for charge transfer processes within helium droplets [3,4]. We will show that both single and double charge transfer reactions from the atomic helium anion to embedded molecules in helium droplets can occur [5].

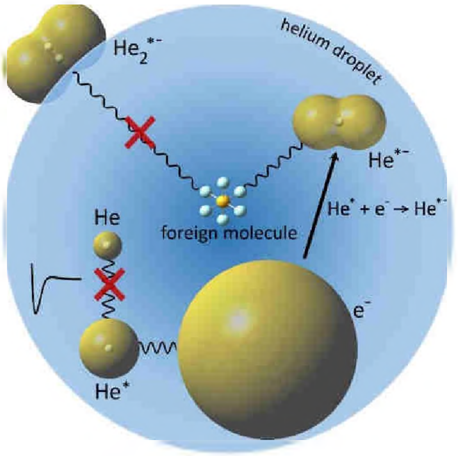

Fig.1 Properties of atomic and molecular helium anions in helium droplets.

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Metallic Clusters: New Computational Methods and Applications to Pure and Embedded Alkali Clusters

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The first part of this presentation describes a public domain package for DFT calculations of metallic clusters. The computational algorithms are formulated entirely in coordinate space and therefore make no assumptions on the electronic structure. New high-order real-space methods for solving the Kohn-Sham equations and carrying out the density update are rapidly converging and highly parallel. A specific form of discretization permits calculations in homogeneous magnetic fields without being plagued by the notorious gauge-origin problem.

In the second part we describe the application of our method for calculating the ionic structure of Mg and Na clusters up to N=30 as well as a few Mg calculations up to N=120. We then use the annealed configurations for computing the structures properties of small ^{4}He droplets and examine the sensitivity of the properties of the ^{4}He droplets on the cluster structure and the cluster-helium interaction.

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Magnetic Properties and the Superatom Character of 13-Atom Platinum Nanoclusters

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13-Atom platinum nanoclusters have been synthesized quantitatively in the pores of the zeolites NaY and KL. They reveal highly interesting magnetic properties like high spin states and super-diamagnetism, depending heavily on the loading of chemisorbed hydrogen.[1,2] Also EPR active spin-½ states are observed. All these magnetic properties are understood best if one considers the near-spherical clusters as analogs of transition metal atoms with low-spin and high-spin states, and with delocalized electrons in molecular orbitals which have a similar structure as atomic orbitals. These clusters are therefore called superatoms, and it is their analogy with normal atoms which is in the focus of the presentation.

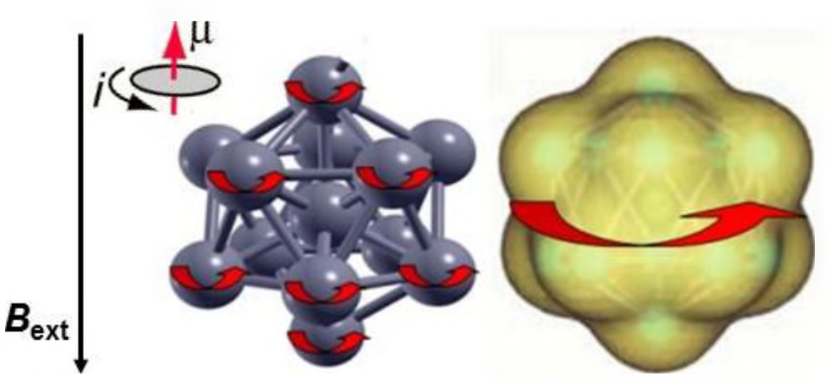

Fig. 1: Ring currents giving rise to diamagnetism on atoms and to super-diamagnetism on superatoms

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Reactions of hydrated electrons with CF_2Cl_2 and HNO_3 related to atmospheric chemistry

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In the present work, we report a systematic study on the reaction mechanism between hydrated electrons $(H_2O)_n^-$ ($n \leq 86$) and atmospherically related molecules, such as CF_2Cl_2 and HNO_3, using Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. We observed that fully thermalized hydrated electrons are able to induce bond cleavage in these molecules. While collisions with CF_2Cl_2 result in the formation of $(H_2O)_mCl^-$ (Fig.1 *left*), a more complex mechanism was observed for HNO_3 (Fig.1 *right*). This yields $(H_2O)_mOH^-$ and $(H_2O)_mNO_3^-$, with secondary reactions of $(H_2O)_mOH^-$ generating $(H_2O)_mNO_3^-$. Multiple collisions of $(H_2O)_mNO_3^-$ cluster ions with HNO_3 lead to $(HNO_3)_2NO_3^-$ formation as a final product ion.

Applying nanocalorimetry, we extract the reaction enthalpy from the experimental data. Both reactions are efficient and very exothermic. Nanocalorimetry combined with condensed phase literature thermochemistry yields thermochemical data that is consistent with published values, as well as our own quantum chemical calculations. All these arguments together are consistent with the interpretation that these molecules undergoes dissociative electron attachment in condensed aqueous environments, if thermalized hydrated electrons are present. Whether or not this mechanism is actually relevant for atmospheric chemistry on ice particles is to be discussed.

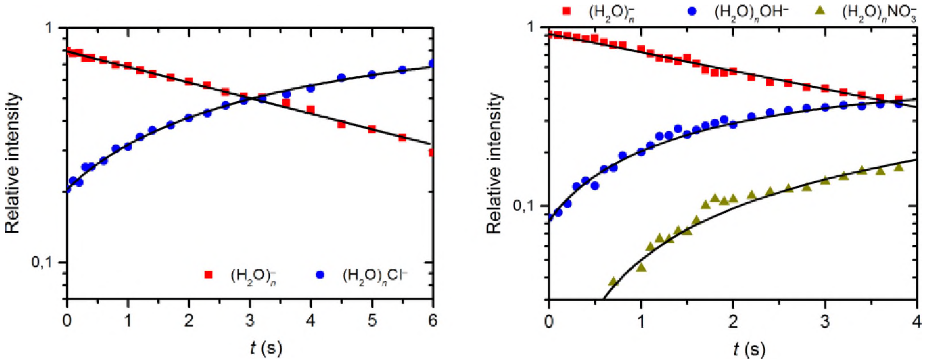

Fig.1 Kinetic analysis of the reaction of CF_2Cl_2 (left) and HNO_3 (right) with hydrated electrons.

Probing the electron-phonon coupling in clusters through resonant vibrational excitation

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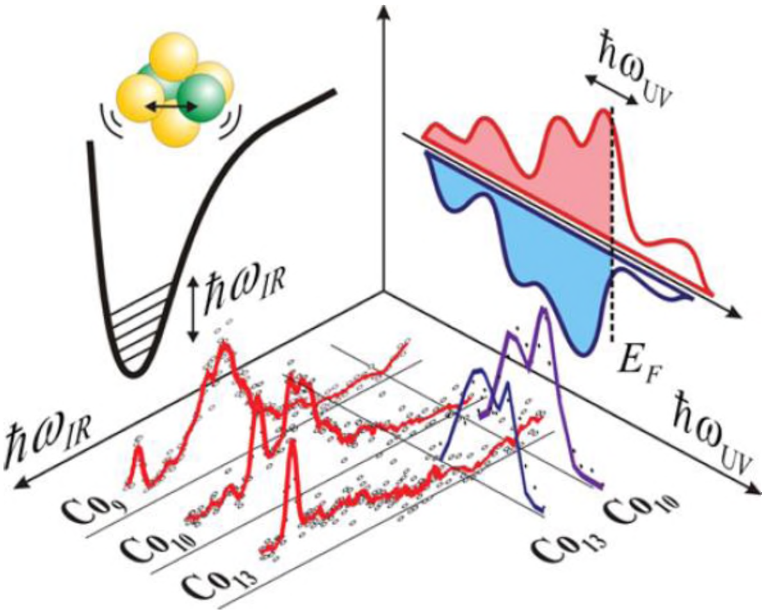
Atomic clusters uniquely bridge the gap between the discrete electronic levels of atoms and the correlated band structure of bulk matter. As a well-defined and fully controllable system free from outer influences, gas phase clusters provide an excellent opportunity to explore such fundamental properties of matter as the electron-phonon coupling, responsible for important physical phenomena like superconductivity, polarons and the acoustoelectric effect. We study the e-ph interaction by exciting the nuclear coordinates of a cluster with an IR laser and register the response in the electronic system above the Fermi level, with UV photoionization. We here present the electronic response from metal and metal carbide clusters on pure vibrational excitation and discuss the feasibility for ps-domain time-resolved experiments, revealing a real-time view of the energy flow from a selectively excited vibration to the electrons.



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Ion-induced molecular growth inside of carbonaceous clusters

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An atomic ionic projectile interacts both with the electronic cloud and the nuclei of atoms constituting matter. The relative importance of these processes strongly depends on the projectile mass and velocity. The nuclear energy loss which stems from elastic collisions is higher for heavier and slower projectiles. In this case of binary collisions, the transfer of momentum to the nuclei is prompt and localized. This could open specific non-statistical fragmentation pathways as already observed in collisions with C_{60} clusters [1] or Polycyclic Aromatic Hydrocarbon (PAH) molecules [2].

Time-of-flight mass spectrometry experiments were realized at the low-energy ion beam facility ARIBE in GANIL (Caen, France). Besides the standard fragmentation of molecular clusters due to ion collisions, the results show that non-statistical fragmentation channels lead to the formation of highly reactive species. The latter promptly react with neighboring molecules before the cluster dissociates (ps timescale). Thus, a distribution of growth products is observed (see figure 1) showing that intra-cluster reactivity can initiate a growth mechanism inside of molecular clusters. The formation of a rich molecular growth have been observed in clusters of C_{60} and pyrene [3,4]. More specifically, the intra-cluster growth mechanism can also lead to a hydrogenation of the PAH molecule. The role of the nitrogen substitution on the hydrogenation will be discussed comparing clusters of anthracene $[C_{14}H_{10}]_k$, acridine $[C_{13}H_9N]_k$ and phenazine $[C_{12}H_8N_2]_k$.

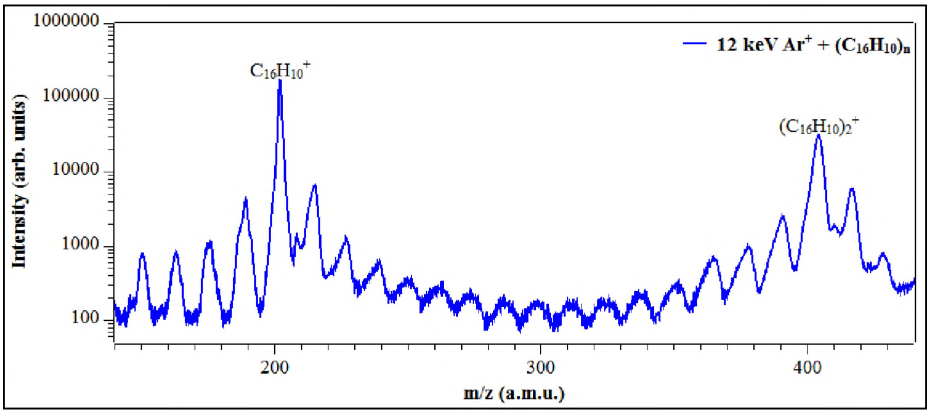

Fig.1 Mass spectrum of 12 keV Ar^+ ion collisions with pyrene clusters $[C_{16}H_{10}]_k$.

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Phase transition of fullerene cations solvated in He nanodroplets

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The measurements of Campell,et al.[1] confirmed C_{60}^{+} as the carrier of two diffuse interstellar bands by photofragmentation of complexes of C_{60}^{+} and He atoms. Here we confirm independently the position of these absorption lines and extend the measurements to $C_{60}^{+}He_{n\ (2<n<100)}$. In this range we investigate an atomically resolved solid-to-liquid phase transition of physisorbed helium atoms on fullerene ions. In our case we use, instead of a radio frequency ion trap, helium nanodroplets to form the $C_{60}He$ complexes[2]. We excite the helium covered fullerenes after ionization with a narrow linewidth tuneable ring laser (fig.1). This results in fragmentation of He near the respective resonance frequencies (fig.2) which is measured as a signal loss of the corresponding ion via mass spectrometry utilizing a high-resolution reflectron time-of flight mass spectrometer system. We observe a remarkably linear redshift of 0.07 nm / He up to $C_{60}^{+}He_{32}$ where all faces of C_{60} are occupied with one He atom[2] (fig.3). The addition of more He atoms leads to the loss of He attached to the pentagonal faces and results in a pronounced blueshift. Neglecting power broadening we can perform fast scans through large frequency ranges searching for unknown resonances of fullerene containing ionic complexes that might be of relevance in the interstellar medium.

Acknowledgement: This work was supported by the FWF projects I978 and P26635

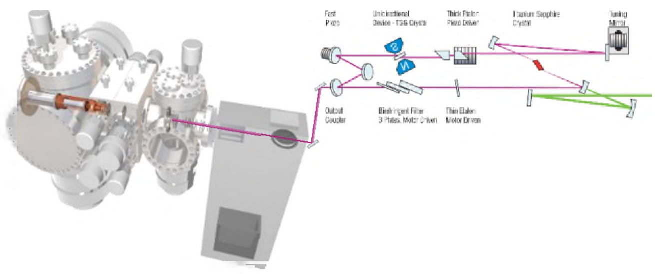

Fig.1: Experimental Setup.

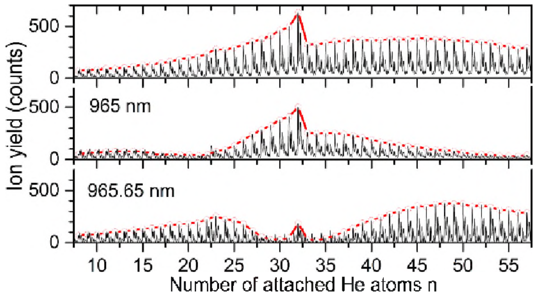

Fig.2: Hole-burning at 965 and 965.65 nm

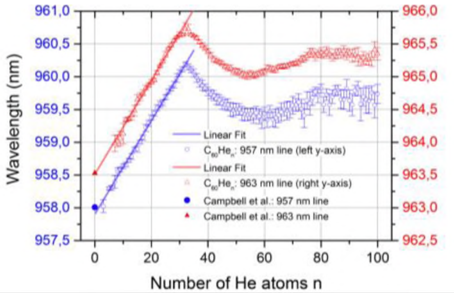

Fig.3: Center positions for the absorption of $C_{60}^{+}He_{n}$ around 958 nm and 963 nm

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Fission of multiply-charged alkali clusters in helium droplets

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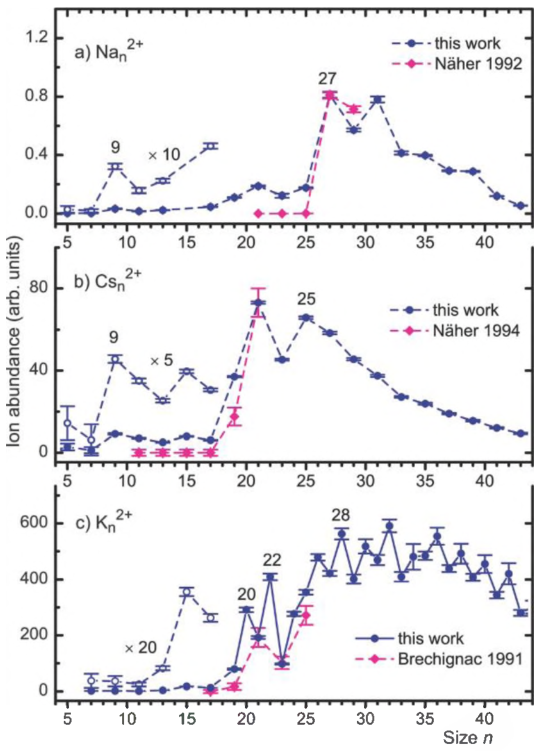

Cluster abundances for a) Na b) Cs and c) K[1,2,6].

Superfluid helium nanodroplets are doped with sodium, potassium or cesium and then ionized via electron bombardment. This process can yield doubly- and, for cesium, triply-charged cluster cations as has been measured with a high resolution time of flight mass spectrometer. The smallest observable doubly-charged clusters are Na$_9^{2+}$, K$_{11}^{2+}$ and Cs$_9^{2+}$. These clusters are a factor two to three smaller compared to ions produced via photoionization of conventionally formed clusters, i.e., gas aggregation or supersonic expansion[1,2]. For sodium and potassium the presently obtained smallest cluster sizes approach the calculated Rayleigh limit n_{ray}, where the fission barrier vanishes. Therefore the fissilities of these cluster ions are close to X=1. Cs$_9^{2+}$ is even smaller then n_{ray}, which implies that their fissilities have been significantly overestimated. Triply-charged cesium cluster ions as small as Cs$_{19}^{3+}$ are observed which also pushes the lower limit of observed cluster sizes. According to Huber and coworkers[3] the formation of multiply-charged clusters near fissilities of X = 1 is limited by the initial temperature of the cluster. Therefor we propose, that the enhanced production of small multiply-charged alkali cluster can be attributed to special ionization processes and the ultra-cold helium matrix environment. In this model the small neutral alkali clusters reside on the surface[4,5] of the droplet and are ionized via Penning ionization. Afterwards the singly-charged clusters will submerge into the droplet where they are Penning ionized once more via collisions with He* or He*$^-$ which are formed by a second electron hitting the doped He droplet. Effective cooling by the surrounding He matrix is essential to suppress Coulomb explosion.

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Electrostatic Deflection of Doped Helium Nanodroplets

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Controlling the orientation and dynamics of polar molecules has been the goal of many recent experiments[1]. Helium nanodroplets offer a very cold (0.37 K), superfluid and inert environment[2], which enhances the average response of polar molecules to external electric fields. This property may be exploited to orient single molecules, influence molecular assembly and enhance chemical reactivity. As a preliminary demonstration, we show that helium nanodroplets containing single molecules with permanent electric dipole moments can be deflected by a modest static electric field. Electrodes in the Rabbi "two-wire" configuration establish the deflecting field. We demonstrate the deflection of nanodroplets with $\sim 10^4$ helium atoms and containing cesium iodide, water, dimethylsulfoxide, formamide or histidine. We obtained deflections of up to 0.5 mm. This technique can be used to sort helium nanodroplets by size or measure permanent electric dipole moments that elude other methods.

Acknowledgment: Work supported by the U.S. National Science Foundation under grant CHE-1213410.

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Spectroscopy of $Na(H_2O)_n$-clusters containing solvated electrons

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Singly sodium doped water clusters show a significant decrease in the binding energy of the sodium excess electron which has been linked to the formation of solvated electrons [1-3]. The photoionization spectrum $Na(H_2O)_n$-clusters shows an interesting size dependence featuring two isomer classes with different appearance ionization energies (aIE) of 2.8eV for clusters with $n \geq 10$-15[1] and 3.2 eV for $n \geq 4$.[2] *Ab initio* molecular dynamics simulations showed that the isomer class with an aIE of 2.8 eV results from clusters where sodium atom and solvated electron exhibit solvent separated ion pair properties. This work aims at size-selectively determining the ionization energy at which the ion signal is saturated in order to better understand the Na – $(H_2O)_n$ interaction and thus deduce the mechanism of an action-spectroscopy approach [4,5] exploiting sodium solvation upon vibrational excitation of OH-stretching vibrations.

The key result is that the energy at which the ion signal is saturated does not depend on the size of the clusters for $n \geq 9$-10 and is at the relatively high level of around 4.1 eV. The resulting breadth of the photoionization spectrum from 3.2 eV (aIE of isomer class I) to 4.1 eV (sIE) cannot be explained by the two known isomer classes. This suggests the abundance of a third isomer class with ionization energies significantly above 3.4 eV. Theoretical modelling indicates that for $Na(H_2O)_n$-clusters with ionization energies higher than 3.5 eV the 3s-electron is most likely unseparated from the sodium atom and located on the cluster surface. The physical state of the clusters only subtly affects the photoionization spectrum indicating an increasing portion of cluster with IEs higher than 3.76 eV with increasing cluster size as soon as crystalline clusters are observable with vibrational IR-UV action spectroscopy.

The IR-UV action-spectroscopic signal shows the following effects: a) spectra of cationic species can be measured as depletion spectra only for the largest clusters of the cluster size distribution, b) the signal increase due to electron solvation occurs on a timescale shorter than few nanoseconds, c) subsequent depletion due to evaporation of water molecules from the cluster occurs with a lifetime around 40-50 ns.

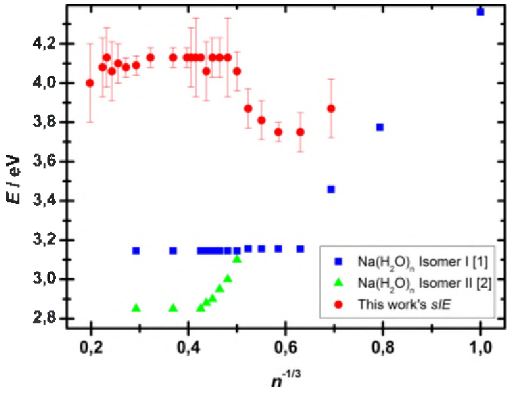

Fig.1 Appearance and saturation ionization energies of $Na(H_2O)_n$-clusters.

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Charge localization and stability of van der Waals clusters

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The stability of multiply charged clusters is determined by the balance between the Coulomb energy and the surface energy. Therefore, a multiply charged cluster with charge z is stable if its size n is larger than the appearance size $n_c(z)$. Echt et al. [1] estimated the appearance sizes for many kinds of multiply charged van der Waals clusters using the liquid drop model. In the model, it is assumed that the excess charge distributes uniformly in the cluster. Their calculation reproduced the appearances sizes of many multiply charged clusters measured in experiments. However, a recent experiment [2] has shown that the observed appearance sizes for doubly and triply charged neon clusters are much smaller than those expected by the model. There have been some attempts to shed light on this problem. Nakamura [3] has calculated the appearance size with including the geometrical shell effects. The discrepancy between the model and experiments has been improved. Still the model cannot sufficiently explain the discrepancy for the case of Ne clusters. Calvo [4] introduced quantum corrections to explain for the discrepancy. However, significant improvement was not found. Here we make a different assumption [5] that the excess charge distributes uniformly on the *surface* of clusters, for it is plausible that it locates on the surface of the cluster because of the electron correlation. As shown the Table, the appearance sizes calculated by this model are much smaller than those given by the previous models. The present model gives the appearance sizes for doubly and triply charged neon clusters within a considerable accuracy.

Table: The appearance sizes $n_c(z)$ of multiply charged clusters with charge z: measured and theoretical values. Values in parentheses are results of calculation with including geometrical shell effects.

Rg	z	Experiment[1,2]	Echt[1]	Nakamura[3]	Present model [5]
Ne	2	287	868	635(657)	257(257)
	3	656	2950	2209	660(667)
Ar	2	91	122	92(97)	61(61)
	3	226	333	251(255)	134(135)
Xe	2	46	51	40(36)	26(30)
	3	107	114	87(83)	50(53)

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Reactivity of solvated electrons in ice nanoparticles

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Large water clusters (ice nanoparticles) $(H_2O)_N$, $N \approx 10^2$-10^3, produced in molecular beams in vacuum can serve as model systems for various species and processes [1], e.g., to mimic ice particles in the atmosphere [2,3] or ice grains in the space [4] or for investigation of solvation phenomena in photochemistry of biomolecules [5], etc. In our versatile CLUster Beam (CLUB) apparatus, Fig. 1, we can dope the ice nanoparticles by various other molecules and subsequently we can probe the doped species by Velocity Map Imaging (VMI) or different mass spectrometric techniques. The mass spectrometry includes positive ionization of the nanoparticles by electron (EI) or photoionization (PI), or negative ionization by electron attachment (EA), or Na-doping (NaPI).

In the later method, NaPI, the nanoparticle is doped by a sodium atom resulting in the ion pair generation: Na^+ plus *solvated electron* e_s^-. Subsequent photodetachmnet of the e_s^- by a UV radiation of fairly low energy (~3 eV) produces positively charged clusters with a fairly low degree of fragmentation. This method has been proposed as fragmentation free ionization for cluster mass spectrometry [6,7].

However, we have shown that the situation is much more complicated in cases, where the ice nanoparticles are doped by electronegative molecules such as HNO_3 [8], N_2O [9,10] which can react with the solvated electron. Such reactions scavenge the solvated electrons leading to further ion chemistry in the clusters. These experiments will be discussed.

Recently, we have complemented our experimental toolbox on the CLUB apparatus by electron attachment and negative ion mass spectrometry [11,12]. This allows us to generate the solvated electrons in the ice nanoparticles without the Na^+ counterion which can influence the ion chemistry in the case of Na-doping. The comparison of the two methods of solvated electron generation in the same species can provide an unprecedented detailed insight into the e_s^- reactivity and dynamics in these species as will be demonstrated in the presentation.

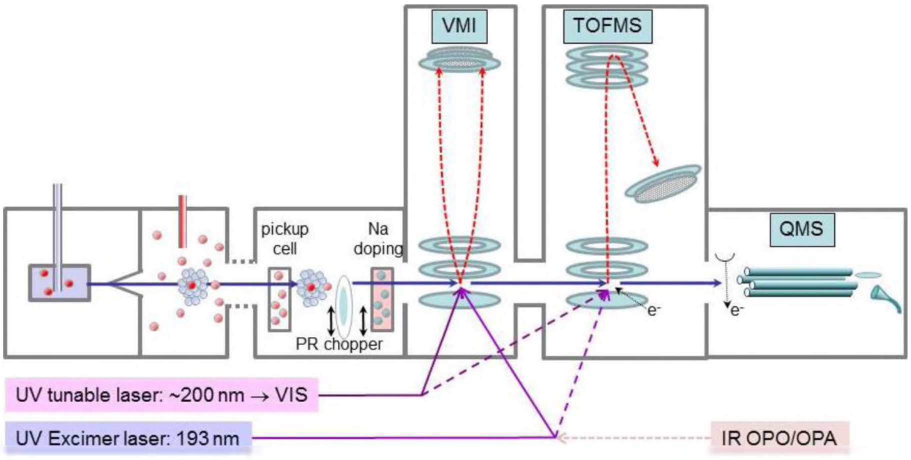

Fig.1 Schematic picture of CLUster Beam (CLUB) apparatus.

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Magnetic deflection of V, Nb and Ta clusters

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Sub-nanometer clusters are attracting significant interest, due to their unique properties, where they offer the advantages of size-selection, in the regime where every single atom counts and can change significantly the properties of the cluster. Molecular beam experiments on free clusters can give information on the geometries [1], electric dipole moments [2], and magnetism [3] of small metal clusters.

Magnetic properties of gas-phase clusters are studied with a magnetic deflection setup, where the cluster beam passes an inhomogeneous magnetic field resulting in the deflection of clusters. Further, a position-sensitive time-of-flight mass spectrometer is used for the detection [3]. In our setup, variable temperature (25-160 K) cluster source was used.

In this work we studied the magnetic deflections of vanadium, niobium, and tantalum clusters. The results showed double sided deflections for most clusters containing an odd number of atoms [4] and no deflection at all for an even number of atoms. The deflected profile are however rather different for the three studied metals. In particular, for Nb, most odd-numbered clusters show an atomic-like behavior, splitting in two maxima corresponding to $\pm 1\ \mu_B$. In contrast, V and Ta clusters also show an undeflected component. There are some exceptions however, namely single sided deflections for clusters containing both even and odd number of atoms. The exact number of atoms at which this happens is different for different materials. Analysis of these deflection profiles using Langevin formula and assuming the cluster temperature estimated from their velocity, magnetic moments of the order of 3-5 μ_B are obtained. Interestingly, the Kramers theorem should in principle prevent the spin-lattice relaxation in the odd-numbered clusters. While this is visible in the clusters with single unpaired electron, the relaxation does occur when the magnetic moments are larger.

We also studied cobalt doping vanadium and niobium, in order to see whether the large magnetic moment of the impurity can induce magnetism in these almost-magnetic clusters. The results, however, are different from what is expected, and are rather in agreement with the screening of the Co moment by the electrons of the host [5].

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Geometric structure determination of neutral clusters with IR-UV spectroscopy

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The determination of the geometric structure of clusters is the first step in investigation of their electronic, magnetic or catalytic properties. The most direct, reliable and thus popular approach is to employ an infrared (IR) vibrational spectroscopy technique in a combination with Density Functional Theory (DFT) calculations.

Obtaining IR spectra for cationic clusters is often performed by dissociation of a loosely attached messenger atom (cluster) at a resonant frequency (IR Multiple Photon Dissociation Spectroscopy [3]). Application of this method for neutral species is not only complicated by difficulties in bonding of a messenger, but also by unwanted breaking of the cluster-messenger bond under UV radiation required for ionization of a neutral cluster for detection. For some systems the IR Resonance Enhanced Multiphoton Ionisation (IR-REMPI) [2] technique allows to directly ionize a cluster by absorbing a very large number of IR photons. However, in the rare cases it works, the high power required for such experiment may result in broadening and shifting of the vibrational bands.

Here we use IR-UV double resonance spectroscopy [4], where a cluster is only slightly excited by an infrared light pulse, produced by the Free Electron Laser for Infrared eXperiments (FELIX). This excitation transfers the cluster from a ground to a relatively low-lying vibrationally (or electronically) excited state. The excited system is then ionised by the UV pulse with the photon energy tuned below the ionization energy of the cluster. The approach requires substantially less IR power in comparison to IR-REMPI. Therefore, it results in the substantially better defined vibrational bands and one is able to record vibrational spectra for those types of clusters where IR-REMPI does not work at all.

Here we present the vibrational spectra and derived geometries for Nb_nC_m and Ta_nC_m carbides, as well as for Fe_n, V_n and Co_n transition metal clusters.

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Metallic and insulating antiferromagnetic states in radical anion fullerene complexes

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$(MDABCO^+)(C_{60}^{\bullet -})(TPC)$ (**1**) ($MDABCO^+$ is *N*-methyldiazabicyclooctanium, TPC is triptycene) is a rare example of fullerene based quasi-two-dimensional (2D) metal, which contains closely packed hexagonal fullerene layers (Fig. 1). A layered complex $(MQ^+)(C_{60}^{\bullet -})(TPC)$ (**2**) (MQ^+ is *N*-methylquinuclidinium) with a hexagonal arrangement of $C_{60}^{\bullet -}$ was also obtained (Fig. 1). Bulkier MQ^+ cations increase the interfullerene distance in **2**. As a result, in contrast to metallic **1**, **2** exhibits nonmetallic spin-frustrated state with an antiferromagnetic interaction of spins (the Weiss temperature is –27 K) and no magnetic ordering down to 1.9 K. It was supposed that **2** has Mott-Hubbard insulating state with antiferromagnetically frustrated spins [1].

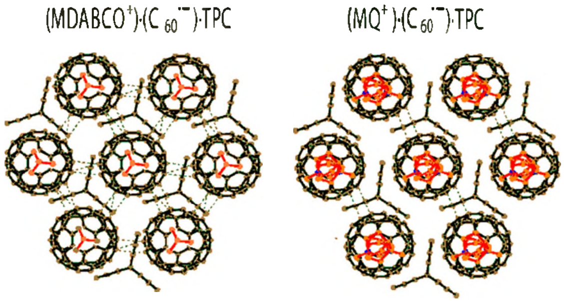

Fig. 1. Projection of organic $(C^+)(TPC)$ layers on hexagonal fullerene layers in **1** and **2**.

Complexes with noninteger –0.33, –0.5 and –1.33 charge on C_{60} were obtained: $\{Cryptand(Na^+)\}(C_{60})_3^- \cdot 2C_6H_4Cl_2$ (**3**), $\{Cryptand(Na^+)\}(C_{60})_2^-$ (**4**) and $\{cryptand(Na^+)\}_8(C_{60})_6^{8-}$ (**5**). Complex **3** with closely packed 3D structure formed by fragments of hexagonal fullerene layers shows metallic conductivity down to 120 K even on air. It manifests a band in the IR range with maximum at 2000 cm^{-1} and a Dysonian EPR signal characteristic of highly conducting materials. Complexes **4** and **5** do not show metallic conductivity due to charge disproportionation [2].

Fullerene salts with the cations having C_{3v} symmetry $\{(Ph_3P)_3Au^+\}_2(C_{60}^{\bullet -})_2(C_{60})\cdot C_6H_4Cl_2$ (**6**) and $\{Ph_3MeP^+)(C_{60}^{\bullet -})\cdot C_6H_5CN$ (**7**) show charge disproportionation and dimerization of $C_{60}^{\bullet -}$, respectively [3,4]. In the absence of these phenomena strong antiferromagnetic coupling of spins with spin frustration is observed in $(Ph_3MeP^+)(C_{60}^{\bullet -})$ (**8**) [4].

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Non-Heisenberg covalent magnetism in iron oxide clusters

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In magnetism, the most popular model used to describe microscopic magnetic interactions is the Heisenberg model. Its basic assumptions, namely localized magnetic moments with fixed magnitude and interaction strengths which are independent of the magnetic state considered, appear strongly restrictive. Nevertheless, the Heisenberg model is successfully used for a wide range of physical systems such as spin wave excitations in metals [1], transition metal oxides, and molecular magnets [2,3].

Atomic clusters, having highly non-monotonous behavior as a function of size, are a promising model system to study fundamentals of magnetism at the nanoscale and below. Therefore, in this work we use $Fe_xO_y^{+/0}$ clusters as a model system to study magnetic exchange from the atom to the bulk.

We theoretically consider gas-phase $Fe_xO_y^{+/0}$ clusters using Density Functional Theory (DFT). As a starting point, we determined the relation between the geometry, electronic structure and magnetic state of these Fe_xO_y clusters [4]. Next, we map the DFT calculations onto a tight-binding model and use the magnetic force theorem to calculate the corresponding magnetic moments and exchange interactions [5].

We show that, opposite to the bulk hematite Fe_2O_3, as well as NiO and MnO, the exchange interactions in clusters heavily depend on the magnetic state considered, resulting in strong non-Heisenberg behavior. In particular, for the $Fe_3O_4^+$ cluster, we exclude the double-exchange mechanism and attribute the non-Heisenberg effects to covalent magnetism and unusually strong oxygen spin polarization.

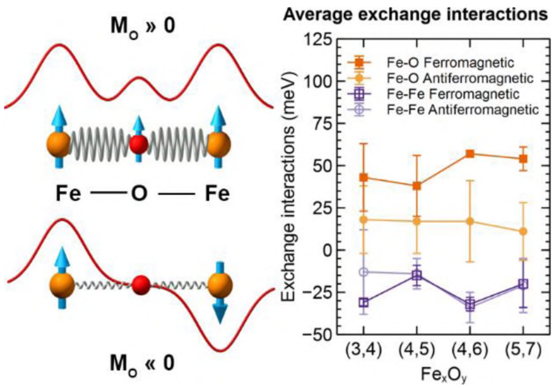

Fig.1 (left) a schematic representation of the spin polarization and exchange interaction dependence on the magnetic field created by the Fe atoms. (right) The average exchange interactions in Fe_xO_y clusters as function of cluster size (x,y).

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Measured atomic ground-state polarizabilities of 35 metallic elements

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Advanced pulsed cryogenic molecular-beam electric deflection methods involving position-sensitive mass spectrometry and 7.87-eV ionizing radiation were used to measure the polarizabilities of more than half of the metallic elements in the Periodic Table. Concurrent Stern-Gerlach deflection measurements verified the ground-state condition of the measured atoms. Comparison with state-of-the-art calculations exposes significant systematic and isolated discrepancies throughout the Periodic Table.

Magnetic deflection of small (bi)metallic clusters

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The magnetic properties of small atomic clusters differ greatly from both the bulk and the single atom. Stern–Gerlach experiments on small clusters are of great interest to address fundamental questions about composition and size dependent magnetism in confined systems. It was for instance predicted that the magnetic coupling between the magnetic dopants in a transition metal oxide cluster oscillates with the number of oxygen atoms [1] and that the magnetic anisotropy energy is enhanced in 3d/4d transition metal alloy clusters [2].

In the past years, a magnetic deflection set-up was developed in Leuven. By using a position sensitive detector this set-up allows direct and simultaneous measurements of both the spatial cluster deflection profile and the cluster size. The nozzle temperature can stabilized and tuned between 20 K and 300 K (±2 K), the detector has an position accuracy of 0.04 mm, the field gradient can be as high as 350 $^{T}/_{m}$, and a dual-target source allows for the production of bimetallic clusters. A chopper system is implemented for velocity selection.

Recently the magnetic deflection profile of the aluminum atom was measured for calibration purposes. Also first measurements on the magnetic deflection of Co_n (n=7-21) clusters, and preliminary measurements on Co_mO (m=10-15,18,20) clusters were done. These prove the proper operation of the set-up. The derived magnetic moments for Co_n are compared with previously measured values for Co clusters [3-8].

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Optical nanopore integrated with Au particle By using electron beam irradiation

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There have been strong interests about the optical nanopore platform due to its possible characterization of a single molecule such as DNA, RNA, and protein [1, 2]. The Au nanopore on pyramid with its diameter less than 5 nm can be fabricated with either a diffusion technique under electron beam irradiations, or a drilling technique by a focused electron beam irradiation [3]. During electron beam irradiation, the diffused nanometer thick membrane will be formed, followed by several Au cluster formation on the diffused membrane via Ostwald ripening as in Figure 1 [4]. In addition, the Au nano-hole with its diameter less than 5 nm was also drilled by using focused electron beam irradiation at 200 keV as in Figure 2. The fabricated nanopore array platform can be utilized as a biosensor device with optically driven technique.

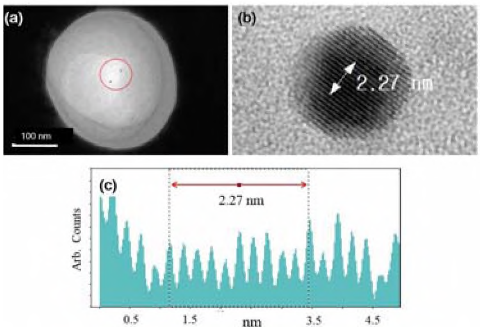

Fig.1. An Au cluster with Au crystal lattice spacing formed on the diffused membrane via Ostwald ripening

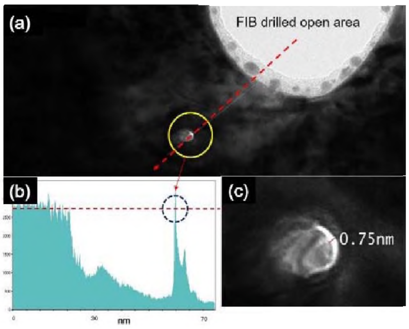

Fig. 2 Electron beam drilled Au hole by using 200 keV TEM

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Photoelectron Spectra of Succinonitrile and Dicyanocyclohexane Anions Made by Rydberg Electron Transfer (RET)

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We have combined Rydberg Electron Transfer (RET) and anion Photoelectron Spectroscopy (PES) techniques for the first time. In the photoelectron spectrum of the succinonitrile (SCN) anion, both the dipole bound and the quadrupole bound states are apparent. The vertical detachment energies of the dipole bound and quadrupole bound states are 129 meV and 14 meV, respectively, which agree with previous experiments [1] and theory [2,3]. Additionally, the dipole bound and quadrupole bound states of the dicyanocyclohexane (DCCH) anion have been observed at vertical detachment energies of 120 meV and 17 meV, respectively, which are in good agreement with calculations [4]. This combination of RET and PES has given rise to spectroscopic data that was previously unattainable.

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The Study of O and Graphene on the Zr(0001)-1x1 surface.

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Atomically resolved STM and PES were applied to study a surface of Zr(0001)-1x1 single crystal. The surface was cleaned with ion bombardment and annealing at 750°C. LEED shows a simple 1x1 patterns. Different degree of surface contamination with C and O was detected with PES. The amount of both species was less than one monolayer and the C1s and O1s spectra did not show the presence of carbide or zirconia forms. On the other side, relatively high background of LEED patterns signalises a certain disorder at the surface. STM images give a more complex view of the "clean" surface. We found a high density of steps that separate terraces no bigger than 1 µm in diameter. Most of the step edges are decorated. In the interior of the terraces, three different regions are found: i) Small ones with hexagonal ordering, typical for a metallic surface. We identified it as the Zr(0001)-1x1 clean parts. ii) Some terraces or their parts are covered with a layer showing a well-known feature ? Moire patterns. Atomic resolution at such layer shows hexagons in the form of benzene ring i.e. strong covalent bonding. On the base of these data and narrow C1s peak, we prescribe it to graphene formation at 750°C. iii) The third region is covered with chain like structure formed either from the single atoms (first stage) or massive rope like agglomerates. This feature is time dependent and increases at the same rate like O1s signal. We believe that it is an initial stage of the Zr oxidation.

Electron Ionization of Tungsten Hexacarbonyl Clusters

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Low-energy (<100eV) electron interactions with tungsten hexacarbonyl in the gas phase have been reported in the past [1, 2] although we note lack of comprehensive studies in aggregates. Thereby the electron ionization mass spectrum and appearance energies of the most abundant cations were recorded and analyzed, as well as the dissociative electron attachment reactions. Recently we have investigated the interaction of tungsten hexacarbonyl clusters with low-energy electrons utilizing a double focusing two-sector field mass spectrometer [3]. The bare W_2^+ metal cation was observed and a mechanism for the formation of this fragment upon electron impact ionization of the weakly bound $W(CO)_6$ dimer was proposed: this metal cation can be observed due to fast conversion of the weak cluster bond into a strong covalent bond between the metal moieties. In addition to this finding, further investigations were performed with a setup where an electron beam with high electron energy resolution was crossed with tungsten hexacarbonyl embedded in ultra-cold (0,37 K) helium droplets. Cations formed in the ionized droplets were observed with a quadrupole mass spectrometer. A remarkable difference between fragmentation of bare clusters and clusters embedded in helium droplets was found and the formation of tungsten hexacarbonyl dimer is suppressed in helium droplets.

Acknowledgment: This work has been supported by FWF, Wien, Austria (I1015).

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Electron attachment to 2-nitrophenol: Effects of clustering

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Electron attachment (EA) plays an important role in various natural and technological processes, which has drawn researchers' attention to this phenomenon. These processes can be found in the atmosphere or in the interstellar space; they may be induced in the living matter by ionizing radiation or in technical applications such as focused electron beam induced deposition. They typically occur in a complex environment; it is, therefore, essential to understand the influence of the surroundings on the electron attachment. Measurements in large bulk systems are, however, often hard to interpret, so it is desirable to reduce the system's complexity. Such simplification can be conveniently achieved in molecular clusters, which represent an intermediate stage between isolated molecules and bulk matter.

In this work [1], we investigate the EA to 2-nitrophenol. 2-Nitrophenol attracted our attention because of its functional groups: the nitro group is known to have good electron scavenging properties while the OH group represents an important electron attachment site in biological molecules. Here, we mainly focus on the influence of cluster environment on the electron attachment. For this purpose, we compare attachment of low-energy electrons (0-13 eV) to three different systems generated in molecular beams (Fig. 1): isolated molecules and dimers (I), homogeneous 2-nitrophenol clusters (II), and mixed clusters of 2-nitrophenol with argon and water (III). For EA to isolated molecules and dimers we observed several new fragments that were not reported previously [2,3]. On the contrary, clustering significantly reduced the fragmentation. Furthermore, electron-energy-dependent ion yields provided deep insight into changes in EA dynamics induced by clustering.

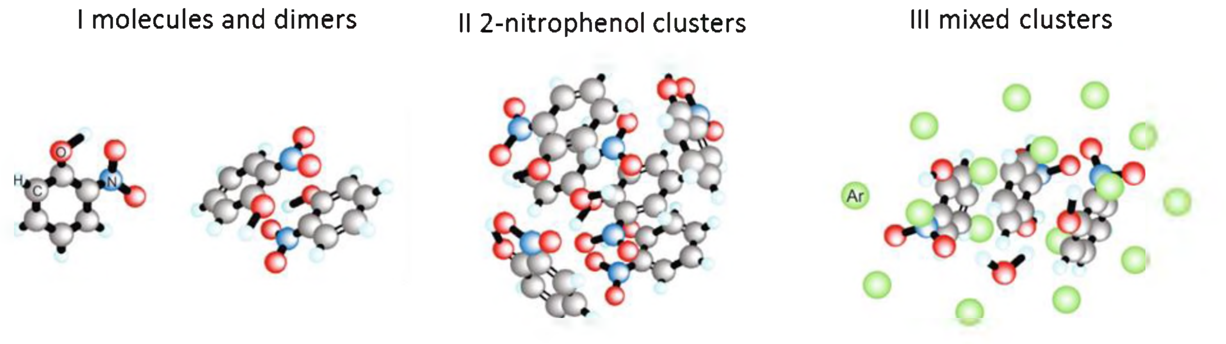

Fig. 1. Sketch of systems studied in this work. The structures were not optimized.

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Electron Induced Proton Transfer in the Anion of Acetoacetic Acid

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Anoin photoelectron spectroscopy (PES) allows for the determination of electron affinity (EA) and vertical detachment energy (VDE) of a neutral molecule via interrogation of its anion. Through the coupling of theoretical calculations with our experimental results, the geometries of the neutral and anion are predicted. In the case of acetoacetic acid, it is shown that the valence anion undergoes intramolecular proton transfer upon binding an excess electron. The experimentally measured and theoretically calcualted VDE of acetoacetic acid is found in to be in good agreement [1].

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Abstract template for July 2016 Erice workshop

[Polyaniline-based Nanostructured Materials for Optical and Electrochemical Formaldehyde Sensenig]

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Nowadays nanotechnology attracts great attention and promising future for interdisciplinary and applied science due to the small size and precise characters of the nanomaterials. The aim of this study was to develop an efficient formaldehyde sensor. Polyaniline nanoparticles and gold-polyaniline nanocomposites were prepared, characterized and evaluated independently to be used as formaldehyde sensors. Sensing process were carried out either optically using microplate assay or electrochemically using potentiostat, it was found that, polyaniline nanoparticles have the desired properties required for efficient sensor whereas it can detect low concentrations of formaldehyde starting from $3\text{x}10^{-5}$ ppm. On the other hand, gold-polyaniline nanocomposites showed no significant sensitivity for the detection of low concentrations of formaldehyde. Therefore, polyaniline nanoparticle could be used as a rapid, cheap, stable and sensitive formaldehyde sensor.

Abstract template for July 2016 Erice workshop

Metallic Nanocluster materials: Separation, pressure and magnetism.

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The fulcrum of intrigue of metallic nanoclusters is the electronic shell structure known to be present [1], resulting in discrete and molecular like energy levels, where the valence electrons of the core can occupy a new set of "superatomic" orbitals, analogous to atomic orbitals where a closed shell confers stability and the same spherical harmonics are exhibited [2]. The molecular like state of these clusters opens up the possibility to form new types of materials based on cluster building blocks. Various organically passivated metallic clusters are known to exhibit this electronic shell structure and crystallize into superstructures. How the superatomic orbitals interact with one another under close proximity or how they are effected by external stimuli is of great interest for the development of these materials. Furthermore, improving the purity and separation of said building blocks is thus important for manufacture of high quality crystals for examination. Our work looks into these three subjects for the advancement and development of cluster materials.

We show a simple and highly efficient method for separating mixed size passivated gold nanoclusters, improving the purity of the clusters and allowing for effective crystallization of clusters for further examination. We present the first experimental investigation of the effect of (isotropic) high pressure on the superatomic electronic structure of metallic clusters in the molecular state (Figure 1-center). Highlighting how the increased pressure upon the core of the cluster can affect the splitting of the superatomic orbitals and destabilize ligand states, ultimately causing shifts in the unique electronic spectra of these clusters. Finally, we present the low temperature magnetic response of metallic nanoclusters crystals of increasing core size. Interestingly, the crystal phase of the samples was shown to have an effect on the magnetic response of the same clusters, shifting the system from diamagnetic to paramagnetic. Furthermore, antiferromagnetic behavior was observed for the largest cluster examined thus long range order interactions between clusters are shown to occur (Figure 1-Right).

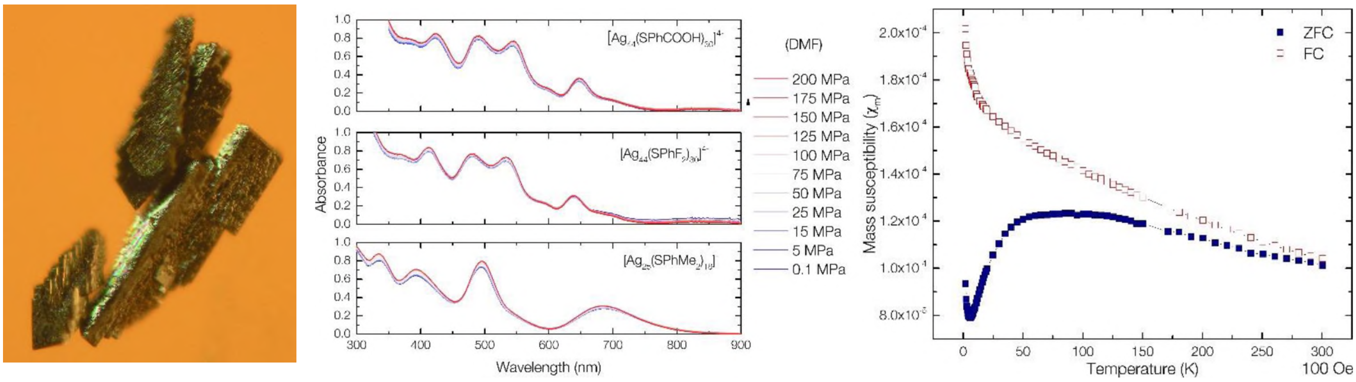

Fig.1: left to right: optical image Crystal of Au_{25}^0 clusters, Molecular absorption spectra of three clusters under isotropic pressure, Magnetic susceptibility of Au_{144}^0 cluster crystals at low temperature.

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Towards matter wave interferometry & quantum metrology of nanoparticles and biomolecules

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Quantum delocalization of very massive particles is interesting as it allows one to explore the boundary between quantum and classical physics[1] and it provides new methods for molecule metrology[2].

Here, we present new efforts to extend the range of matter-wave experiments both to functionalized metal nanoparticles as well as to complex biomolecules.

Even though advanced near-field matter-wave interferometers[3] are compatible with de Broglie wavelengths as small as 200 fm, they require the particle momentum to be smaller than 20'000 amu × 100 m/s. For that purpose we have characterized different particle sources, including laser induced acoustic desorption[4] (LIAD), laser desorption into cryogenic effusive[5] or cold supersonic seed gases[6] as well as evaporation sources for nanoparticles up to 100.000 amu. Apart of velocity measurements, we are also interested in the probability of 157nm photoionization of biomolecules that are volatilized in buffer gas beams.

This is important for the molecule detection and crucial for the working principle of our time domain matter wave interferometer[3] (OTIMA). In this experiment, VUV laser beams are retro reflected to form three standing light wave gratings. This near field interferometer is well suited for high mass interference, and compatible with many of the aforementioned biomolecular sources. Here we will present the achievements with regard of molecular source development and experiments proposed to be performed in OTIMA interferometry.

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Fabrication and characterization of a single cluster transistor

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Small atomic objects such as molecules and atomic clusters play a key role in bottom up approaches to tailor properties of matter and constitute fundamental building blocks for the synthesis of new advanced materials. Due to quantum confinement effects, small clusters with a countable number of atoms show entirely new physical phenomena without equivalent in bulk materials [1]. The strong size dependence of the properties of atomic clusters opens up a so-called third dimension for all elements of the periodic table [2]. This represents a tremendous space of exploration with important interdisciplinary potential.

With the final goal to exploit the unique properties of clusters in integrated circuits, we propose a novel fabrication method to create a single electron transistor (SET) based on the charge transfer through a single cluster deposited from a gas phase (Fig.1, left side). The methodology includes junction electromigration (Fig.1, right side), clusters deposition and simultaneous current measurement from drain to source. Metal clusters are produced by a magnetron sputtering source, size-selected in flight, and then soft-landed on the device. Electrostatic focusing is used to direct the clusters towards the junction. The main motivation to create such device is to investigate how the electronic transport is modified by the discrete electronic structure of the size selected clusters.

For the purpose of SET tailoring, the electromigration technique was further developed in means of controllability and reproducibility. The technique was also successfully applied in our group to study the superconducting properties of nanosized aluminium junctions [3].

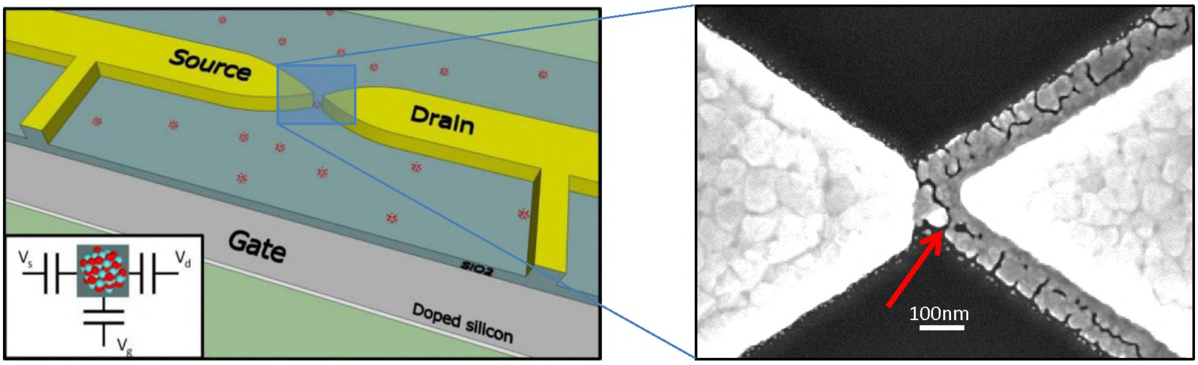

Fig.1 Sketch of the envisaged transistor based on a single cluster (left) and scanning electron microscopy image of an Au junction after electromigration (right). The red arrow points to a gap of the smallest size, which is a few nm wide.

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Deciphering chemical bonding in clusters and molecules: Application of Fermi-Löwdin orbitals as a tool to elucidate valency and bond order.

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The recently developed Fermi-Löwdin orbital based method for the correction of the self-interaction error within Density Functional Theory [1,2] does provide improved orbital eigenvalues and more realistic level ordering [3]. We demonstrate the versatility of this method to provide details of chemical bonding by applying it to several systems featuring localized and many-center chemical bonding. We present recent results on representative systems with varying structural complexity: Boron clusters, compounds containing planar tetra-coordinated carbon as well as prototypical aromatic and anti-aromatic molecules. The Fermi-Löwdin orbitals yield a localized and inherently "chemical" representation of bonding in terms of localized Lewis-type lone pairs and two-center bonds as well as delocalized multi-center bonds in a natural, chemically-intuitive fashion. We anticipate that this novel and parameter free methodology provides a powerful tool to obtain insights into the fundamental origins of structure, properties, and reactivity of clusters and molecules also in circumstances where multi-center bonding plays a crucial role.

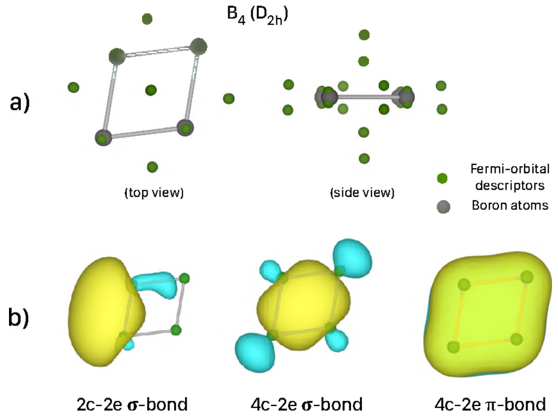

Fig.1 a) Structure and positions of the Fermi-orbital descriptors of the B_4 cluster. b) Isosurfaces of the Fermi-Löwdin orbitals as obtained from the FLO-SIC DFT calculation. The valence bonding can be described by four 2c-2e B-B bonds, one delocalized 4c-2e σ-bond and one delocalized 4c-2e π-bond.

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High-throughput Fermi-Orbital Descriptor Screening and The Application on Chromium

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An improved density-functional formalism[1,2] proceeds by adopting the Perdew-Zunger expression for a self-interaction-corrected (SIC) density-functional energy but evaluates the total energy based on Fermi-Lowdin-Orbitals (FLOs). Each localized electron is represented by an FLO, determined from the occupied Kohn-Sham orbitals and a semi-classical FO descriptor (FOD). The SIC energy is then minimized through the gradients of the energy with respect to these descriptors. The initial configurations of FODs are highly related to the efficiency of energetic convergence. The work here is to provide efficient strategies of sampling and prioritizing initial sets of FODs, which may reach the global energy minimum. Applications on chromium are presented.

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The role of delocalized charge in effective Oxygen Reduction Reaction (ORR) catalysts

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Nanoscale particles are the most common materials currently used to construct heterogeneous catalysts, and a significant amount of research has focused on the mechanisms by which these materials function catalytically. Accurate theoretical modelling of these processes, however, requires a reduction of the catalytic system to focus on a range of particular facets that arise across the surfaces of the nanoparticle. In the current work [1] the exceptionally ORR-active core-shell Pt/Pt_3Ni nanoparticle is reduced to a sequence of low-index surfaces and the binding of typical ORR intermediates (O, H, and OH) to these surfaces has been analyzed using Density Functional Theory (DFT). The results indicate that the directionally-bonded oxygen-bearing intermediates do not significantly change their binding under surface loading, whereas the nature of the delocalized H-surface bond changes dramatically. Analysis of the H-bond shows that the diffuse H s-Pt s interaction plays a key role in this mechanism.

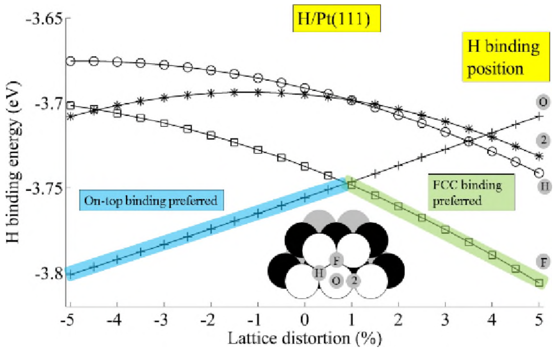

Fig.1 Strain-controlled binding in H/Pt(111)

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ELECTRONIC AND OPTICAL PROPERTIES OF 2D TMD NANOCLUSTERS

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In addition to Graphene nanostructures of layered semiconducting 2D transition metal dichalcogenides (TMD), as for example MoS_2, are promising materials for applications in electronics and photovoltaics Though the structure of these materials results in a highly inert surface with a low defect concentration, edge and finite size effects can strongly influence the properties of these nanostructures. Therefore, a basic understanding of the interplay between structural, electronic and optical properties as a function of the cluster size and the role of the edge states is needed.

We demonstrate on the basis of quantum mechanical calculations of 2D MoS_2 clusters how the size, topology and edge structure influence the electronic and the optical properties of such systems. Especially, the size dependence of the optical absorption spectra - obtained by time-dependent density-functional theory (TD-DFT) based calculations - will be discussed. The experimentally observed quantum confinement behavior of such nanoparticles could be confirmed, as well as the coexistence of metallic like and semiconducting properties of such particles is demonstrated. The observed strong photoluminescence of MoS_2 platelets is discussed in a qualitative manner.

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