Satellite meeting of XXVIII International Conference on
Photonic, Electronic and Atomic Collisions, ICPEAC 2013

The Sixth International Symposium
"Atomic Cluster Collisions"

第六届原子团簇碰撞国际研讨会

Wuhan-Chongqing, China

18-23 July, 2013

Wuhan Institute of Phys. & Math.
Chinese Academy of Sciences

FIAS Frankfurt Institute
for Advanced Studies

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Preface

The sixth International Symposium "Atomic Cluster Collisions" (ISACC 2013) will take place in July 18-23, 2013, in Wuhan, China. The venue of the meeting will be Wuhan Hongyi Hotel and the cruise liner traveling along the Yangtze River. The ISACC 2013 is organized by Wuhan Institute of Physics and Mathematics (WIPM) and Frankfurt Institute for Advanced Studies (FIAS).

ISACC started as an international symposium on atomic cluster collisions in St. Petersburg, Russia in 2003. The second ISACC was held at the GSI, Darmstadt, Germany in 2007. Both first and second symposia were satellites of the International Conferences on Photonic Electronic and Atomic Collisions (ICPEAC). The third ISACC has returned to St. Petersburg, Russia in 2008 and was organized as a separate conference. The fourth ISACC took place in Ann Arbor, Michigan in 2009, USA; and the fifth ISACC took place in St.-Michaels-Heim, Berlin in 2011, Germany; both were satellite of the ICPEAC.

The ISACC2013 will promote the growth and exchange of scientific information on the structure, properties and dynamics of complex nuclear, atomic, molecular, cluster, nanoscopic and biological systems studied primarily by means of photonic, electronic, heavy particle and atomic collisions. In the symposium, particular attention will be devoted to dynamical phenomena, many-body effects taking place in clusters, nanostructures, molecular and biological systems, which include problems of fusion and fission, fragmentation, collective electron excitations, phase transitions, radiation damage and many more. Both experimental and theoretical aspects of cluster physics uniquely placed between nuclear physics on one hand and atomic, molecular and solid state physics on the other will be subject of the symposium. The sixth symposium will again be a satellite of the ICPEAC2013, which will be held in Lanzhou, China, soon after the ISACC2013 (July 24-30, 2013).

Important Dates

Distribution of the first announcement	February 26, 2013
Distribution of the second announcement	April 24, 2013
Deadline for early registration	May 30, 2013
Distribution of the third announcement	June 27, 2013
Deadline for abstracts	June 15, 2013

Scientific Program

The scientific program for the symposium will consist of interdisciplinary sessions, which will include invited lectures, review talks and progress reports. A number of contributed papers will be chosen as special reports by the International Advisory Committee of the ISACC2013. Other contributed papers will be presented in the poster session. Suggestions about possible candidates for invited speakers should be sent to the Chairmen of the ISACC2013.

Topics

- Structure and dynamics of atomic clusters and nanoparticles
- Ion-cluster collisions
- Cluster structure and dynamics on a surface
- Electron and photon cluster collisions
- Clustering in systems of various degrees of complexity
- Cluster-molecule interactions, reactivity and nanocatalysis
- Structure and dynamics of biomolecules
- Clusters and biomolecules in external fields: electric, magnetic, laser etc.
- Collision processes with biomolecules
- Cluster and bimolecular research at Free Electron Lasers (FEL)

Symposium Venue

The conference venue is Wuhan Hongyi Hotel at No. 136 Donghu Road, Wuchang District, Wuhan, Hubei, 430071, PRC.

The opening ceremony will be held at the Wuhan Institute of Physics and Mathematics (WIPM), which is located at West No.30 Xiao Hong Shan, Wuhan, 430071, China. The following meeting will be held during the cruise liner traveling along the Yangtze River.

Symposium Language

The language of the conference is English.

Social Program

Event	Date/Time
Vist WIPM	Friday, July 19, 2013, 10:30-12:00
Going to Yichang (by bus), boarding the boat	Friday, July 19, 2013, 13:30-18:30
Three Gorges Dam sightseeing (by bus)	Saturday, July 20, 2013, 14:00-17:30
Welcome Performance	Saturday, July 20, 2013, 20:00-22:00
Shennong Stream sightseeing (by boat)	Sunday, July 21, 2013, 8:30-13:00
Fengdu Ghost Town sightseeing (walking)	Monday, July 22, 2013, 9:00-12:00
Banquet	Monday, July 22, 2013, 19:00-22:00

Meals

Meals (lunches and dinners) will be served at the symposium venue. Breakfasts and lunches are buffet meals. Participants should inform the local organizing committee their dietary taboos. The local organizing committee recommends the participants to take the organized catering service because there are no other choices once boarding the ship.

Official Invitation and Visa

Letters of invitation to attend ISACC2013 will be sent upon request. Both an electronic copy and a hard copy can be requested. This invitation implies no obligations, financial or otherwise, by the symposium organizing committee. Conference participants should check the visa requirements well in advance. The Chinese Visa Application Service Centre at local Chinese embassy or consulate provides helpful information on how to apply for a Chinese visa. More information regarding the visa matters can be found on the ISACC2013 web pages.

Symposium Program

Thursday, 18 July 2013

9^{00} - 20^{00}	Participants registration in Hongyi Hotel

Friday, 19July 2013

7^{30}- 8^{30}	**Breakfast at Hongyi Hotel**
8^{30}	Taking bus to WIPM
8^{45} - 9^{00}	*Opening ceremony (WIPM)* *Location: conference room on the 1st floor of Pinbiao Building in WIPM* Welcome by **Bing Zhang,** ISACC2013 LOC Chair Speech by **Maili Liu**, Director of WIPM Greeting by **Andrey V. Solov'yov,** ISACC 2013 IAC Chair
9^{00} - 10^{30}	*Morning session I: Clustering in systems of various degrees of complexity* *Chair:* ***Andrey V. Solov'yov*** *Location: conference room on the 1st floor of Pinbiao Building in WIPM* **Jean-Patrick Connerade**, Imperial College, London, UK *Collaborative experiments between China and the UK on atoms in strong external fields.* **Gordon W.F. Drake**, University of Windsor, Canada *Clustering in halo nuclei as probed by atomic spectroscopy: An overview.* **Guanghou Wang,** Nanjing University, China *Novel properties of some cluster-based nanostructures by low energy cluster deposition.*
10^{30} -12^{00}	Visiting WIPM;
12^{00}	Taking bus to Hongyi Hotel
12^{00} -13^{30}	**Lunch**
13^{30} - 18^{00}	Going to Yichang (by bus), boarding.
18^{00} -19^{30}	**Dinner**
20^{00} - 21^{30}	*Evening session I: Structure and dynamics of atomic clusters and nanoparticles* *Chair:* ***Jean-Patrick Connerade*** *Location: the 5th floor* **Lai-Sheng Wang**, Brown University Providence, USA *Probing the structural and electronic properties of atomic clusters using photoelectron spectroscopy.* **Cheuk-Yiu Ng,** University of California, Davis, USA *State-to-state spectroscopy and dynamics by vacuum ultraviolet laser photoionization and photoelectron methods.* **Min Han,** Nanjing University, China *Controllable fabrication of closely spaced nanoparticle arrays with low energy cluster beam deposition.*

Saturday, 20 July 2013

$7^{00} – 8^{30}$	**Breakfast**	
$8^{30} – 10^{00}$	*Morning session I-1: Structure and dynamics of atomic clusters and nanoparticles* *Chair:* ***Gerardo Delgado-Barrio*** *Location: the 5th floor* **Vadim Ivanov,** St. Petersburg State Polytechnic University, St. Petersburg, Russia *Stability of electron-positron droplets.* **Philippe Brechignac**, Universite Paris Sud, Orsay, France *Electronically excited states of* $(PAH)_n^+$*: Spectroscopic studies for naphthalene and coronene cluster cations.* **Fernand Spiegelman**, Universite Paul Sabatier, Toulouse, France *Simulating structural and dynamical properties of PAH-based complexes and clusters via density functional tight binding methods.*	*Morning session I-2: Ion, electron and photon cluster collisions* *Chair:* ***Eleanor Campbell*** *Location: the 6th floor* **Henrik Cederquist**, Stockholm University, Sweden *Ions and atoms interacting with PAHs, fullerenes, and clusters* **Uwe Becker**, Fritz-Haber-Institut, Berlin, Germany *Quantum optics phenomena in electron spectroscopy.* **Steven Manson**, Georgia State University Atlanta, Georgia, USA *Theoretical studies of the photoionization of free and endohedral fullerene molecules.*
$10^{00} - 10^{30}$	**Coffee break**	
$10^{30} - 12^{00}$	*Morning session II-1: Structure and dynamics of atomic clusters and nanoparticles* *Chair:* ***Philippe Brechignac*** *Location: the 5th floor* **Gerardo Delgado-Barrio,** Instituto de Física Fundamental , Madrid, Spain *Helium cluster doped by atoms or diatomic molecules.* **Dong-Sheng Yang**, University of Kentucky, USA *Spectroscopy and structures of small transition metal oxide clusters.* **Hao Gong**, National University of Singapore, Singapore *Synthesis and properties of semiconductor clusters.*	*Morning session II-2: Photon cluster collisions* *Chair:* ***Alfred Müller*** *Location: the 6th floor* **Eleanor Campbell**, The University of Edinburgh, UK *Femtosecond photoelectron spectroscopy of fullerenes.* **Alfred Z Msezane**, Clark Atlanta University, Atlanta, USA *Photoabsorption spectra of atoms encaged inside a fullerene.* **Alexey Verkhovtsev**, Frankfurt Institute for Advanced Studies, Frankfurt am Main, Germany *Quantum and classical phenomena in photoionization of atomic clusters.*
$12^{00} - 13^{00}$	**Lunch**	
$14^{00} - 17^{30}$	Three Gorges Dam sightseeing (by bus)	
$18^{00} -20^{00}$	**Captain Welcome Reception and Dinner**	
$20^{00} -22^{00}$	**Welcome Performance**	

Sunday, 21July 2013

7^{00} – 8^{30}	**Breakfast**	
8^{30} – 12^{30}	Shennong Stream sightseeing (by boat)	
13^{00} - 14^{00}	**Lunch**	
14^{30} - 16^{00}	*Afternoon session I-1: Cluster structure and dynamics on a surface* *Chair:* ***Eric Suraud*** *Location: the 5th floor* **Catherine Brechignac**, Academy of Sciences, CNRS, Paris, France *Silver oxidation : transition from clusters to nanoparticles* **Andrey Solov'yov**, Frankfurt Institute for Advanced Studies, Frankfurt am Main, Germany *MBN Explorer - a powerful, universal tool for simulating multiscale complex molecular structure and dynamics: case studies.* **Atsushi Nakajima,** Keio University, Yokohama, Japan *Electronic properties of soft-landed nanoclusters and nanocluster assemblies.*	*Afternoon session I-2: Structure and dynamics of atomic clusters and nanoparticles* *Chair:* ***Vadim Ivanov*** *Location: the 6th floor* **Vitaly Kresin**, University of Southern California, Los Angeles, USA *Delocalized dopants in fluid clusters - plasmons and dipoles.* **Bernd von Issendorf**, University of Frieburg, Germany *Thermodynamic properties of water clusters.* **Konstantin Hirsch**, Helmholtz-Zentrum Berlin fur Materialien und Energie GmbH, Berlin, Germany *Spin and orbital magnetic moments, magnetic-to-nonmagnetic transitions, and the Anderson impurity model in finite systems: XMCD studies on free size-selected clusters.*
16^{00} - 16^{30}	**Coffee break**	
16^{30} - 18^{00}	*Afternoon session II-1: Electron and photon cluster collisions* *Chair:* ***Karl-Heinz Meiwes-Broer*** *Location: the 5th floor* **Alfred Müller**, Giessen University, Germany *Confinement resonances in endohedral* $Xe@C_{60}^+$ *ions.* **Andrei Korol**, Frankfurt Institute for Advanced Studies, Frankfurt am Main, Germany *Collective electron excitations in photo- and electron impact ionization of fullerenes.* **Himadri Chakraborty**, Northwest Missouri State University, USA *Photoexcited resonances in fullerene materials and noble metal clusters: recent theoretical studies.*	*Afternoon session II-2: Cluster-molecule interactions, reactivity and nanocatalysis* *Chair:* ***Bernd Huber*** *Location: the 6th floor* **Alexander Kuleff**, Universität Heidelberg, Heidelberg, Germany *Recent advances in the study of interatomic Coulombic decay phenomena.* **André Fielicke**, Technical University Berlin, Germany *Vibrational spectroscopy of metal cluster complexes: investigating the chemistry on a small surface.* **Yongfeng Lu**, University of Nebraska Lincoln, USA *Laser resonant vibrational excitations of precursor molecules for promotion of energy efficiency in chemical vapor deposition.*
19^{00} - 20^{30}	**Dinner**	
20^{00} - 22^{00}	**Poster session** *Location: the 6th floor*	

Monday, 22 July 2013

7^{00} – 8^{30}	**Breakfast**	
9^{00} - 12^{00}	Fengdu Ghost Town sightseeing (walking)	
12^{00} - 13^{30}	**Lunch**	
14^{00} - 15^{30}	*Afternoon session I-1: Structure and dynamics of clusters and biomolecules* *Chair:* ***Henrik Cederquist*** *Location: the 5th floor* **Bernd Huber**, CIMAP-CEA, Caen, France *Chemical reactions in complex biomolecular systems* **Eric Suraud**, Université Paul Sabatier, Toulouse, France *Dynamics of irradiated clusters and molecules.* **Weijun Zheng**, Institute of Chemistry, Chinese Academy of Sciences, China *Microsolvation of monovalent salts in water: anion photoelectron spectroscopy and ab initio calculations.*	*Afternoon session I-2: Clusters and biomolecules in external fields* *Chair:* ***Thomas Möller*** *Location: the 6th floor* **Jörg Voigtsberger**, Goethe University, Frankfurt am Main, Germany *Imaging the structure of small He clusters.* **Julia Aysina**, UIBK Innsbruck, Austria *Mass spectrometric studies of water clusters.* **Shenggui He**, Institute of Chemistry, Chinese Academy of Sciences *Chemistry of oxygen-centered radicals: a cluster approach.*
15^{30} -16^{00}	**Coffee break**	
16^{00} - 17^{30}	*Afternoon session II-1: Cluster structure and dynamics on a surface* *Chair:* ***Catherine Brechignac*** *Location: the 5th floor* **Hisato Yasumatsu**, Cluster Research Laboratory, Toyota Technological Institute, Tokyo, Japan *Novel functions driven by subnano-space charge polarization created through cluster-substrate interaction.* **Gengyu Cao**, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences *Fullerenes on metal and metal oxide surfaces: molecular orientation, lattice ordering and interfacial structure.*	*Afternoon session II-2: Cluster research at Free Electron Lasers (FEL)* *Chair:* ***Bernd von Issendorf*** *Location: the 6th floor* **Karl-Heinz Meiwes-Broer**, University of Rostock, Germany *Controlling strong-field ionization dynamics in clusters.* **Kiyonobu Nagaya**, Kyoto University, Japan *Dynamics of nano-plasma of rare-gas cluster created by intense EUV-FEL pulses.* **Thomas Möller**, Technische Universität Berlin, Germany *Imaging clusters and their light induced dynamics with super intense X-ray pulses.*
18^{00}- 22^{00}	**Banquet**	

Tuesday, 23 July 2013

7^{00}- 8^{30}	**Breakfast**
	Departure after breakfast (in Chongqing)

Conference Chair

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Symposium's web page

More information and updates will be found in the ISACC2013 website:
http://isacc2013.csp.escience.cn

Symposium's e-mail

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Friday, July 19, 2013

ISACC 2013 Opening: 8:45-9:00 (WIPM)

Morning Session I: 9:00-10:30 (WIPM)

Lunch: 12:00-13:30

Evening Session I: 20:00-21:30 (the 5th floor)

Collaborative experiments between China and the UK on atoms in strong external fields

Jean-Patrick Connerade

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An account is given of collaborative experiments on atoms in strong externally applied static fields, involving Imperial College London, WIPM and ECUST in Shanghai. We stress unusual situations and unexpected orbital properties exhibited when the strength of the externally applied fields compares with the strength of fields internal to the atom. The collaboration has grown from an early exploratory series of experiments on atoms in externally applied crossed electric and magnetic fields, in which, for the first time, the two circular polarisations were separated successfully and the pure crossed field situation was explored, as originally advocated by Pauli. The resulting spectra revealed many interesting features, and were the subject of detailed calculations by the group of Professor Ken Taylor of the Queens University in Belfast. After this initial success, it was decided to upgrade the experimental system and, for a number of reasons, the second version of the apparatus was set up in Wuhan, with support from the CAS.

Under high field conditions, remarkable properties appear, which provide a ‘quantum laboratory’ to explore the following: (i) The breakdown of all quantum numbers (except z-symmetry), i.e. the fully interacting quantum system originally identified by Pauli as an important case – the simplest example of an atomic system exhibiting full breakdown of quantum numbers is the atom in strong, crossed electric and magnetic fields. A transition to Wigner statistics for a fully coupled system is expected and has indeed been observed. (ii) The quantum analogue of classically chaotic underlying dynamics for both strong purely magnetic fields and crossed fields (and the difference between the two). We have studied many such spectra, with different atomic cores and quantum defects, and developed models which account well for the observed behaviour (for completeness, parallel external electric and magnetic fields have also been included in our study) (iii) Issues concerning the symmetry of space, probed by considering the properties of ‘off centre’ states in crossed fields. It has been established theoretically by Professor Zhang Jian-Zu, in Shanghai, that such states have unique properties which, in principle, allow the x^+ x^- asymmetry of space (if it is present) to be searched for and detected experimentally. This test is important, because spatial asymmetry is a property which underpins many classes of string theories. Zhang has shown that, for appropriate potentials (which include those in our experiments) the effect does not depend on the ultra-small constants of string theory so that it becomes detectable on a conventional quantum scale. It still remains out of reach for the current generation of measurements (for reasons which will be given) but not necessarily so for the future. Studies are therefore under way theoretically, to determine what requirements will have to be satisfied for future attempts. described. As an offshoot of our work, a book entitled “Highly Excited Atoms” originally published by the Cambridge University Press has been translated into Chinese and published by the Chinese Academy of Sciences. The Chinese version is used for teaching in Shanghai.

Clustering in halo nuclei as probed by atomic spectroscopy: An overview

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Halo Nuclei provide an example of clustering at the interface between atomic physics and nuclear physics. As first discovered by Tanihata in 1985 [1], halo nuclei are characterized by a halo or cluster of excess planetary neutrons surrounding a tightly bound core. As a consequence, the matter radius is typically much larger than the charge radius. A study of these exotic loosely bound structures provides a sensitive probe of the forces holding them together. However, for many years there was no model-independent method of measuring the nuclear charge radius because of their low abundance and short lifetime. The situation has now changed with the advent of the techniques of single-atom spectroscopy on the one hand, and advances in high-precision atomic theory on the other [2]. Measurements of the isotope shift in atomic transition frequencies are sensitive to the nuclear charge radius, and so this can be used as a measurement tool, provided that other contributions to the isotope shift from atomic structure can be reliably calculated and subtracted. Accuracies at the level of ±10 kHz are required for both theory and experiment. Three broad series of measurements are now available for light nuclei, extending all the way from ^{3}He to the halo nuclei ^{6}He and ^{8}He, ^{6}Li to the halo nucleus ^{11}Li, and ^{7}Be to the single-neutron halo nucleus ^{11}Be [3]. The results are particularly significant because they are able to discriminate amongst various theoretical models for the effective interaction potential between nucleons. The principal theoretical challenges are (a) to obtain sufficient accuracy in the lowest order nonrelativistic and relativistic contributions to the isotope shift, and (b) to calculate the mass dependence of the higher-order QED contributions, such as the Lamb shift. The current status of theory will be reviewed, and compared with experiment, In view of the recently announced discrepancy in the proton radius, a comparison between muonic and electronic helium becomes particularly relevant and interesting.

References

[1] I. Tanihata *et al.*, *Phys. Rev. Lett.* **55**: 2676. (1985).
[2] G.W.F. Drake, W. Nörtershäuser, and Z.-C. Yan, *Can. J. Phys.* **83**: 311. (2005).
[3] W. Nörtershäuser *et al.*, *Phys. Rev. A*, **83**: 012516. (2012)

Novel Properties of Some Cluster-based Nanostructures By Low Energy Cluster Deposition

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Atomic clusters consist of a few to thousands of atoms and/or molecules, and attract a great attention in nanoscience and nanotechnology since they can be used as building blocks to assemble various kinds of nanostructures with novel properties. One of strategies for growing nanostructures with cluster beams consists in depositing low-energy particles. Ideally, by depositing the clusters with low kinetic energies, one would like to conserve the memory of the free-cluster phase to form thin films with their original properties. Since the kinetic energy is of the order of 10eV per cluster, i.e., a few meV per atom, which is negligible compared to the binding energy of an atom in the cluster, no fragmentation of the clusters is expected upon impact on the substrate [1]. In this talk we would like to present some of our work as examples to show how this can be realized.

1) **Quantization of surface modes of silicon clusters with soft landing**
2) **Long lifetime PL of Si cluster-assembled nanowires**
3) **Conductance Resonance of Au cluster-based nanostructures**
4) **Strong magnetoelectric effect in Tb-Fe/($Zr_{0.52}Ti_{0.48}$)O_3 heterostructures by low energy cluster beam deposition**
5) **Coupling enhancement of plasmons between Ag nanoclusters**

It demonstrated that production, manipulation and deposition of gas phase clusters is of primary importance for the synthesis of nanostructured materials and for the development of industrial processes based on nanotechnology[2].

References:

[1] P. Jensen, Review of Modern Physics 71(5), 1695 (1999).
[2] K. Wigner P. Piseri, H. Vakedi Tafreshi, P. Minani, J. Phys. D. Appl. Phys. 39, R439 (2006)

Probing the Structural and Electronic Properties of Atomic Clusters Using Photoelectron Spectroscopy

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Photoelectron spectroscopy in combination with quantum calculations over the past decade has become a powerful technique to probe the electronic and structural properties of size-selected atomic clusters. Using this technique, my group has investigated a variety of atomic clusters, including clusters of transition metals, metal oxides, metal carbides, and gold and boron most recently. In this talk, I will focus on our recent studies on boron clusters. We have found that boron clusters possess planar or quasi-planar structures [1-3], in contrast to that of bulk boron, which is dominated by three-dimensional cage-like building blocks. All planar or quasi-planar boron clusters are found to consist of a monocyclic circumference with one or more interior atoms. The propensity for planarity has been shown to be due to both σ and π electron delocalization over the molecular plane, giving rise to concepts of σ and π double aromaticity. Hydrogenation of the planar boron clusters has resulted in interesting ladder-like structures, which are analogous to polyenes [4]. We have found further that the central boron atoms in the planar clusters can be substituted by transition metal atoms to form a new class of aromatic compounds, which consist of a central metal atom and a monocyclic boron ring ($\mathrm{M©B}_n$). Eight-, nine-, and ten-membered rings of boron have been observed, giving rise to a family of novel borometallic compounds [5-8].

References:

[1] "Hydrocarbon Analogs of Boron Clusters: Planarity, Aromaticity, and Antiaromaticity" (H. J. Zhai, B. Kiran, J. Li, and L. S. Wang), *Nature Mater.* **2**, 827-833 (2003).

[2] "A Concentric Planar Doubly π Aromatic B_{19}^- Cluster", (W. Huang, A. P. Sergeeva, H. J. Zhai, B. B. Averkiev, L. S. Wang, and A. I. Boldyrev), *Nature Chem.* **2**, 202-206 (2010).

[3] "B_{22}^- and B_{23}^-: All-Boron Analogues of Anthracene and Phenanthrene" (A. P. Sergeeva, Z. A. Piazza, C. Romanescu, W. L. Li, A. I. Boldyrev, and L. S. Wang), *J. Am. Chem. Soc.* **134**, 18065-18073 (2012).

[4] "Elongation of Planar Boron Clusters by Hydrogenation: Boron Analogues of Polyenes" (W. L. Li, C. Romanescu, Tian Jian, and L. S. Wang), *J. Am. Chem. Soc.* **134**, 13228-13231 (2012).

[5] "Aromatic Metal-Centered Monocyclic Boron Rings: $\mathrm{Co©B}_9^-$ and $\mathrm{Ru©B}_9^-$" (C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev, and L. S. Wang), *Angew. Chem. Int. Ed.* **50**, 9334-9337 (2011).

[6] "Transition-Metal-Centered Nine-Membered Boron Rings: $\mathrm{M©B}_9$ and $\mathrm{M©B}_9^-$ (M = Rh, Ir)" (W. L. Li, C. Romanescu, T. R. Galeev, Z. A. Piazza, A. I. Boldyrev, and L. S. Wang), *J. Am. Chem. Soc.* **134**, 165-168 (2012).

[7] "Observation of the Highest Coordination Number in Planar Species: Decacoordinated $\mathrm{Ta©B}_{10}^-$ and $\mathrm{Nb©B}_{10}^-$ Anions" (T. R. Galeev, C. Romanescu, W. L. Li, L. S. Wang, and A. I. Boldyrev), *Angew. Chem. Int. Ed.* **51**, 2101-2105 (2012).

[8] "Transition-Metal-Centered Monocyclic Boron Wheel Clusters ($\mathrm{M©B}_n$): A New Class of Aromatic Borometallic Compounds" (C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev, and L. S. Wang), *Acc. Chem. Res.* **46**, 350-358 (2013).

State-to-State Spectroscopy and Dynamics by Vacuum Ultraviolet Laser Photoionization and Photoelectron Methods

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Abstract:

Recent experimental progress in the application of single-photon vacuum ultraviolet (VUV) laser and two-color infrared (IR)-VUV and VUV-VUV laser photoexcitation schemes for state-to-state photoionization, photoelectron, photodissociation, and ion-molecule collision studies will be presented.[1-5] By implementing a tunable VUV photoionization laser with a velocity-map-imaging (VMI) spectrometer, we have been able to perform VMI-threshold photoelectron (VMI-TPE) measurements, achieving an energy resolution comparable to that commonly observed in pulsed field ionization-photoelectron (PFI-PE) measurements. A newly developed VUV-VUV laser pump-probe VMI-photoion (VMI-PI) apparatus designed for state-to-state VUV photo-dissociation studies will be described. This apparatus consists of two independently tunable VUV lasers and thus allows state-selective photodissociation by the VUV photoexcitation laser and state-selective detection by the VUV photoionization laser. A novel VUV laser PFI-PI ion source has also been successfully developed for the preparation of rovibrationally selected PFI-PI ions for bimolecular collisional studies. By combining this novel VUV laser PFI-PI ion source with a guided ion beam mass spectrometer, we have been able to examine the kinetic, vibrational, rotational energy effects on chemical reactivity of molecular ions.

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Controllable fabrication of closely spaced nanoparticle arrays with low energy cluster beam deposition

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Nanostructures produced by depositing pre-formed clusters onto substrates have generated a great deal of interests. The size and interparticle spacing of the nanoclusters that constitute the nanostructures can have a dramatic effect on their properties. The electrical, optical as well as magnetic properties of cluster-based nanostructures can be seriously tuned by varying the particle–particle interactions. The most critical factor towards the realization of nanocluster-based technology is to develop effective ways for controllable fabrication of high density cluster films with defined size, density and functional structures in various dimensions. We will report on our recent researches on the formation of closely-spaced cluster-based nanostructures with gas phase cluster beam deposition. We demonstrate that with a large degree of control on the deposition parameters, such as the cluster beam kinetic energy, the mass distribution and intensity, the imping angle of the directed beam, the pre-formed substrate configurations, as well as the introduction of mask on the beam trajectory path, a variety of cluster-assembled structures and morphologies can be obtained. Heterogeneous patterning of clusters on microscales has also been realized, which offers extra dimension for functional nanostructure tailoring. Novel properties arose from the short-range electrical and optical coupling among the nanoclusters, such as the surface plasmon resonance and local field enhancement of the near-field coupled metal clusters, single electron transport and photoconductance through the closely-spaced cluster networks, have been investigated.

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Saturday, July 20, 2013

Morning session I-1: 8:30-10:00 (the 5th floor)

Morning session I-2: 8:30-10:00 (the 6th floor)

Coffee break: 10:00-10:30

Morning session II-1: 10:30-12:00 (the 5th floor)

Morning session II-2: 10:30-12:00 (the 6th floor)

Stability of Electron-Positron Droplets

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Recently a novel type of a matter-antimatter compound system, an electron-positron droplet (EPD), has been predicted [1]. This is a finite quantum object similar to an atomic cluster. It consists of an equal number of electrons and positrons coupled together due to strong Coulomb and mutual polarization forces. The current work is devoted to the further theoretical investigation of interparticle correlations responsible for the stability these exotic clusters.

The first calculations the EPD energies had been performed within the local density approximation (LDA) [1]. The negative value of the energy per an electron-positron pair obtained led to the conclusion that the bound state of the EPD can exist. The obtained absolute value of the energy per pair was lower than the same value for dipositronium molecule [2] (Fig.1). So, the stability of EPD against decay into the system of dipositroniums was under question. Up to date, the different attempts to improve the outcome have been taken. For example the Hartree-Fock approximation was used to take into account the exchange interaction in the most accurate way [3].

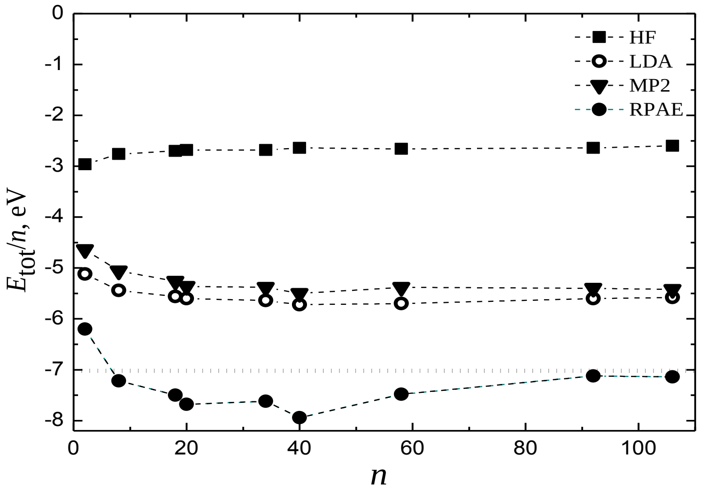

Figure 1: Total energy of the EPD per pair number *n* calculated within the different approaches. The dotted line is the same energy for dipositronium.

In the present work we take into account the many-particle correlations in the calculation of the total energy of EPD. Results obtained are presented on the Fig.1 [4]. The perturbation theory within the Møller-Plesset second order (MP2) approach predicts the values close to the LDA, but the Random Phase Approximation with Exchange (RPAE) approach provides the lowest values of the energy per electron-positron pair. So far, the crucial role of dynamical many-particle correlations for the EPD stability is manifested [4].

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Electronically excited states of $(PAH)_n^+$:

Spectroscopic studies for Naphthalene and Coronene cluster cations

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Since years, our teams are involved in the study of the properties of polycyclic aromatic hydrocarbons (PAHs) and PAH clusters, to investigate the formation and evolution of these species in interstellar conditions and the key role they play in the physical and chemical evolution of astronomical objects (cf. compilation of contributions in [1]). Their electronic properties, in particular, drive photo-dissociation and photo-ionization processes and provide the necessary fingerprints to identify PAHs and PAH clusters in astronomical environments.

Two experiments devoted to the study of the electronic properties of small PAH clusters will be described, and their results discussed:

- The spectra of the first two electronic transitions of the Naphthalene dimer cation $(C_{10}H_8)_n^+$ and its methylated analogue $(CH_3\text{-}C_{10}H_7)_n^+$ have been measured using the Ar-tagging method [2]). in a molecular beam – Time-Of-Flight set-up at ISMO (Orsay).
- Threshold Photoelectron spectra (TPES), as well as Total Ion Yeld (TIY) spectra of jet-cooled Coronene monomer and clusters $(C_{12}H_{24})_n$ have been obtained using the electron/ion coincidence velocity map imaging spectrometer, DELICIOUS II, available at the DESIRS beamline of the French Synchrotron facility SOLEIL [3]. The data concerning the monomer can be interpreted in the light of a time-dependent theoretical approach making use of DFT calculations. The results will be discussed in comparison to available photoelectron (PES) and optical absorption data. New autoionizing neutral states have also been observed and their relaxation to final cationic states characterized. The experimental data concerning clusters up to the pentamer n=5 will be presented and compared to theoretical predictions from the LCPQ group in Toulouse [4].

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Simulating structural and dynamical properties of PAH-based complexes and clusters via Density Functional Tight Binding methods.

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Density Functional Tight Binding (DFTB) is a computationally efficient scheme to approach ground state electronic properties of materials and large molecular systems, especially in the context of intensive molecular dynamics simulations. We will present extensions for the treatment of molecular complexes and clusters, namely the account of weak interactions (dispersion forces, hydrogen bonds), the development of a Density Functional Tight Binding +Valence Bond Configuration Interaction scheme (DFTB+VBCI) to describe resonnant charge transfer in ionized molecular clusters, and a DFTB-MM version to investigate the coupling with an inert environment. Benchmarks and applications will illustrate properties and dynamics of PAH-based (polycyclic aromatic hydrocarbons) complexes relevant in astrochemistry and atmospheric chemistry : (i) structural and temperature-induced conformational changes in water clusters interacting with PAHs, (ii) structure and stability of Van der Waals PAH clusters, (iii) charge localisation and excitations in ionized PAH clusters, (iv) structural and electronic properties of PAH -rare gas clusters.

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Ions and atoms interacting with PAHs, fullerenes, and clusters

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In this talk I will present experimental and theoretical results on the fragmentation of PAH molecules in collisions with alpha particles, He, and other gases.

I will present absolute fragmentation cross sections for 100 eV centre-of-mass collision energies and argue that non-statistical fragmentation processes dominate at these energies. For large PAHs the most prominent fragmentation channel is the one due to the loss of a single C-atom - or a CH-group although the lowest energy dissociation channels are H- and C_2H_2 loss. The latter are dominant in photo excitation processes. The present results show that interaction with heavy particles creates fragmentation products that are different from those from photo-absorption processes. This in turn, means that there will be other types of secondary reactions in for examples a molecular cluster following collisions with ions. The latter is demonstrated with clusters of fullerenes for which we show that alpha particles produces extremely reactive fragments like C_{59}^+ inside van der Waals clusters of fullerenes and that this leads to surprisingly efficient formation of dumb-bell C_{119}^+ molecules [1].

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Quantum optics phenomena in electron spectroscopy

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Electron spectroscopy and quantum optics are two fields with little overlap so far. This is due to the fact that in weak field ionization the phase between the emitted electron and the ionic core is lost. This is in contrast to strong field ionization were this phase is kept giving the opportunity to study phase dependent phenomena. However, employing inversion symmetric systems such as diatomic homonuclear molecules and fullerenes makes it possible to study such phenomena also for weak field ionization because a new phase due to symmetry considerations is introduced. This is in case of diatomic homonuclear molecules such as N_2 and O_2 the phase between the left and right emitter site in an electron emission process. This phase gives rise to the famous Cohen-Fano oscillations [1]. We will report on a new effect in the context of these oscillations, the change of the phase by $\pi/2$ in dependence of the de Broglie wavelengths. If it becomes shorter than the bond lengths the recoil momentum will be imposed either on the left or the right emitter site of the molecule and hence will provide information on the orientation of the molecule in space. This process transforms the originally random target into an oriented target with its phase shifted by $\pi/2$.

Another interesting phenomenon in this context is the role of the angular momentum regarding the Cohen-Fano oscillations. The angular distributions of photo- and Auger electrons are determined by their corresponding angular momentum components. Following the Cooper-Zare formula [2] of angular distributions there should be no Cohen-Fano oscillations in the angular distribution asymmetry parameter β. This is indeed true if only one partial wave is emitted. However, if there are more than one partial wave, as in most cases, one can show that if the (l+1) wave is emitted from the left site and the (l-1) wave from the right site and vice versa there will be an oscillation in β. We have observed these oscillations for the first time for N_2 and O_2, but also for the fullerenes C_{60} and C_{70}. The phase shift of these oscillations does not reflect the phase between the emitter sites, but the phase between the partial waves. This partial wave phase shift has been theoretically calculated and partly experimentally [3] determined to be $\pi/2$ for C and N and π for O. The predictions could be nicely reproduced. There are indeed several phases in electron emission processes, which could be employed for quantum optics purposes.

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Theoretical Studies of the Photoionization of Free and Endohedral Fullerene Molecules

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Studies of the photoionization of free fullerenes and endohedral fullerenes with an atoms trapped inside have been carried out using a variety of methodologies and models for the potential due to the fullerene. The methodologies employed include R-matrix (both nonrelativistic LS and relativistic Breit-Pauli) [1], random-phase approximation with exchange (RPAE) [2], relativistic random phase approximation (RRPA) [3], and time-dependent local-density approximation (TDLDA) [4]. Two potential models are used. The static model, in which a square-well (or a nearly square-well Woods-Saxon) potential which acts only upon the atomic electrons, is taken with the experimental width of the fullerene and a well-depth to reproduce the experimental electron affinity [2]. The dynamic model uses a similar potential except that this potential acts on both the atomic and the nonlocalized (valence) electrons of the fullerene molecule *and* the atomic electrons. In this potential, the depth is adjusted to reproduce the ionization energy of the free fullerene [5].

Examples will be presented to illustrate the utility of the various methodologies and models. Specifically, photoionization results shall be presented for Mg@C_{60} which show how R-matrix, RPAE, RRPA and TDLDA compare, for Xe@C_{60}, demonstrating the comparison of the R-matrix results with experiment, and for a number of smaller fullerenes, C_n (with $n < 60$), that have more-or-less spherical isomers, calculated at the TDLDA level, to illustrate the effect(s) of the size of the fullerene of the photoabsorption properties.

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Helium clusters doped with atoms and diatomic molecules

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Spectroscopic studies of simple molecules surrounded by He atoms show a drastic difference depending on the fermionic or bosonic character of the solvent atoms[1]. A quantum chemistry-like approach has been developed in our group to deal with He_N BC doped helium clusters, where the BC dopant is a conventional di-atomic molecule. The central idea is to consider the He atoms as electrons while the B and C atoms play the role of the nuclei in standard electronic structure calculations. The procedure provides spectral simulations and, hence, making feasible to do proper comparisons with current experiments[1]. However, due to the big difference of masses of He and electrons, and also to the replacement of Coulomb potentials by molecular interactions, it is worthy to asses at what extent the approximations involved (decoupling of orbital angular momenta of the He atoms from the BC rotation and adiabaticity of the BC stretch versus de He motions) lead to accurate results[2][3]. Here, we consider several atoms and diatomic molecules as dopants. The model provides the energy levels of the cluster and the intensities of the main lines of the spectrum at low temperatures [4][5][6].

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SPECTROSCOPY AND STRUCTURES OF SMALL TRANSITION METAL OXIDE CLUSTERS

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In spite of the extensive studies, the current knowledge about the electronic states and molecular structures of transition metal oxide clusters is largely derived from theoretical predictions. However, the reliable prediction of the electronic states and geometric structures is often complicated by the presence of many low-energy structural isomers and high density low-lying electronic states of each isomer. Therefore, a reliable identification of the molecular structures and electronic states for transition metal oxide clusters and their ions generally requires the confirmation by spectroscopic measurements, especially by high resolution spectroscopic techniques.

In this presentation, we will discuss the bonding and structures of group 3 metal oxide clusters probed by mass-analyzed threshold ionization spectroscopy in combination with quantum chemical calculations and spectral simulations [1-3]. We have identified the structural evolution from a planar M_2O_2 to a cage-like M_3O_4 (M = Sc, Y, and La) structure. The planar D_{2h} structure of M_2O_2 has alternating M-O-M bonds, and each M atom gives up two electrons in forming the cluster. The ground electronic states of the neutral clusters are ^1A_g for Sc_2O_2 and $^3B_{1u}$ for Y_2O_2 and La_2O_2. Ionization of the neutral states yields the ^2A_g ion states for all three clusters by removing a metal-based (n+1)s electron. The ionization energies of the clusters decrease from Sc to Y to La and are in the same trend as that of the metal atomic IEs. The frequencies of symmetric M-O stretching and M-O-M bending are measured for the three cluster ions. Because of the vibronic interaction, an antisymmetric M-O stretching mode is also observed for the La_2O_2 ion. The cage-like C_{3v} structure of M_3O_4 contains alternating M-O-M-O bonds and is formed by fusing three M_2O_2 fragments together, each sharing two M-O bonds with others. One of the four oxygen atoms is bonded to three metal atoms and the other three are bonded to two metals, whereas each metal atom forms at least three bonds with oxygen atoms. Molecular orbital analysis shows that the three metal atoms in the $^2A_1$ neutral ground state of M_3O_4 lose a total of eight electrons in forming the cluster and each metal has a +2.67 formal oxidation state. Ionization of the $^2A_1$ state yields the $^1A_1$ ion by removing a metal-based (n+1)*s* electron. For the $^1A_1$ ion sate, five vibrational modes were measured for all three clusters, and additional two modes were observed for Sc_3O_4.

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Synthesis and Properties of Semiconductor Clusters

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Semiconductors nanosized clusters show properties different from bulk counterparts. In this presentation, our focus will mainly be on semiconductors of very wide gaps, such as ZnO, SnS etc. We will talk about the synthesis of semiconductor clusters with different shapes: nanowires, nanoflowers, nanobranches, etc, see for example Figure 1. Magnetic core and semiconductor shell core-shell structure will also be presented. Furthermore, effects of metallic clusters on semiconductor properties (Figure 2) will be presented. The characterization and properties of the clusters will be discussed, especially upon photon collision and magnetic field interaction. Some applications of the semiconductor clusters will be given.

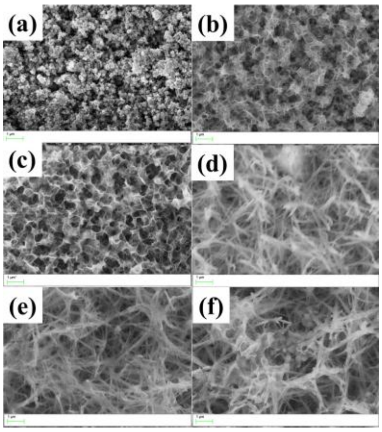

Figure 1

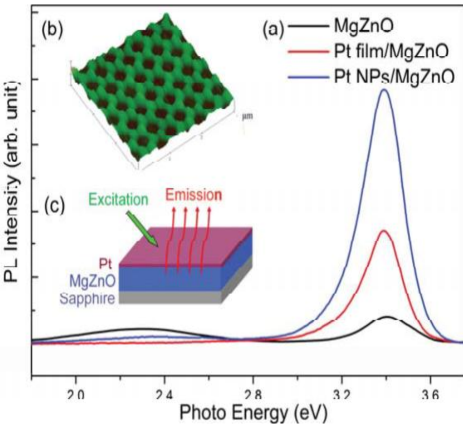

Figure 2

Figure 1 Different ZnO semiconductor clusters; Figure 2 PL spectra of ZnMgO semiconductor with metallic cluster coatings.

Femtosecond Photoelectron Spectroscopy of Fullerenes

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When ionised with fs lasers, fullerenes, and other conjugated molecules, show well-resolved peak structure in their photoelectron spectra that can be attributed to single photon ionisation of a large range of excited states, populated within the same laser pulse, thus providing a "fingerprint" of the molecule [1]. For fullerenes, strong peaks are observed that are attributed to the excitation of SAMO states (super-atom molecular orbitals), these are very simple hydrogenic-type orbitals that are centred on the fullerene core rather than on the carbon atoms. They are a consequence of the hollow nature of the molecule [2]. New studies that combine fs Rydberg fingerprint spectroscopy with angular-resolved photoelectron spectra obtained using velocity map imaging [3] and time-dependent density functional theory [4] are shedding new light on these states and the reason for their prominence in the photoelectron spectra. Angular-resolved photoelectron spectroscopy can also provide information on the timescale of electron emission [1] and provide evidence for the occurrence of thermal electron emission.

In this talk recent fullerene photoionisation studies will be described and their relevance for understanding the ionisation dynamics and mechanisms of large molecules will be discussed.

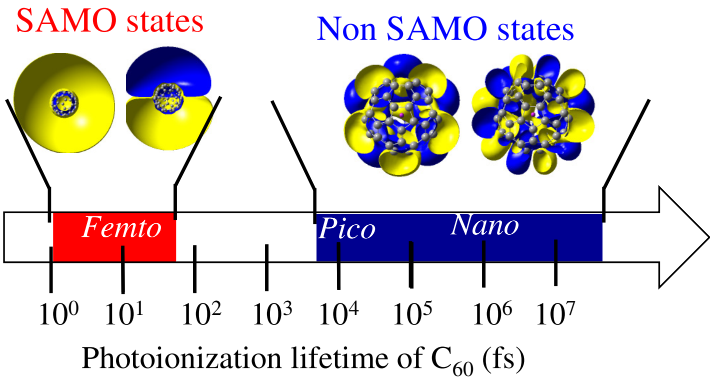

Fig. 1. Photoionisation lifetimes of excited states of C_{60} in an intense laser field (from [4]).

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Photoabsorption spectra of atoms encaged inside a fullerene

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Three important problems, confinement resonances, off-center effects, and the effect of the fullerene plasmon resonances, have been investigated in the photoabsorption spectra of atoms encapsulated inside a fullerene using the time-dependent-density-functional-theory [1].

The calculaton of the differential oscillator strengths (DOS's) for the photoabsorption of a Xe atom encaged inside a C_{60} demonstrates that the spectra is very sensitive to the position of the Xe atom, as indicated in Fig. 1. The main confinement resonances, peaks 2 and 4 result only if the Xe atom is located within a very small sphere around the center of the fullerene, with a radius of about 0.3 Å. Our study has identified that the peak 3 in Fig. 1 belongs to the original Xe 4d giant resonance. It is a shape resonance and is not a confinement resonance.

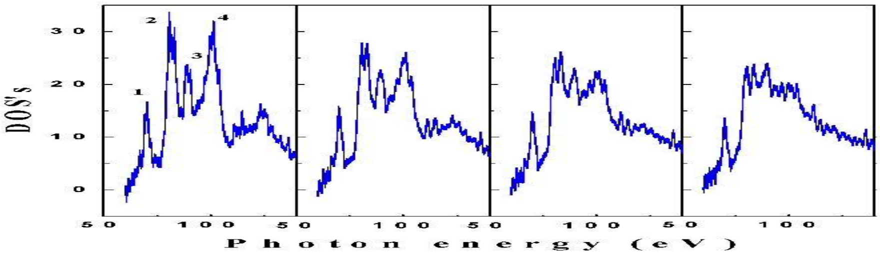

Figure 1: Photoabsorption spectra of the Xe atom encaged inside C_{60} (left to right) at the center, 0.2 Å, 0.3 Å and 0.4 Å away from center, respectively.

Our calculation also shows that when the Xe atom is far away from the center, such as at 2.0Å off the center, the photoabsorption spectrum is similar to that of the free Xe atom. Similarly the off-center effect has also been found in the Ce@C_{82} endohedral fullerene. The Ce atom was found at 1.85 Å off the center through the optimization process. The Photoabsorption spectra indicate that the Ce 4f autoionization process has been greatly suppressed. The calculation confirms the experimental data which observed no confinement resonance in the Ce@C_{82}^{+} photoionization measurement.

The DOS's for the photoabsorption of the Ne, and Ar atoms encapsulated in the C_{60} fullerene have also been evaluated [2] in the energy regions both inside and outside the C_{60} plasmon resonances. In the energy region of the C_{60} plasmon resonances the DOS's show strong oscillation and significant increase. This large enhancement cannot be explained through the confinement resonances but is due to the energy transfer from the C_{60} valence electrons to the photoelectron through the intershell coupling. The energy transfer occurs only when the photon energy is large enough to ionize the atom encapsulated in the C_{60}.

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Quantum and Classical Phenomena in Photoionization of Atomic Clusters

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Photoionization of atomic clusters and nanoparticles involves a number of prominent phenomena which have been studied by means of various theoretical methods. Being by its nature a quantum phenomenon, the photoionization process can be described in the framework of the quantum time-dependent density functional theory (TDDFT) [1]. However, it is well established that the photoionization of metallic clusters and nanoparticles as well as some of the nanocarbon systems, e.g. fullerenes, takes place through the collective excitations of delocalized valence electrons, called plasmons, induced by an external electric field. The plasmon excitations, corresponding to the collective oscillations of delocalized electrons with respect to the positively charged ions [2, 3], are well known in classical electrodynamics and are described in purely classical physics terms.

Considering the photoionization process of the C_{60} fullerene as a case study, we elucidate the contributions of various classical and quantum physics phenomena manifesting themselves in this process. By the comparison of the TDDFT results, obtained in [4, 5] and the present work, with those based on the plasmon resonance approximation ([2, 3, 6] and references therein), we map the well-resolved features of the photoionization spectrum to single-particle and collective excitations having the different physical nature [7]. We demonstrate that the peculiarities arising in the photoionization spectrum of C_{60} atop the dominating plasmon excitations have the quantum origin. In particular, we demonstrate that a series of individual peaks can be assigned to the particular single-electron transitions arising from the ionization of the inner molecular orbitals of the system.

A similar method, based on the comparative analysis of *ab initio* and model approaches, is utilized to study the photoionization spectra of other nanoscale systems, such as noble metal clusters and (polycyclic) aromatic hydrocarbons. The results of *ab initio* and model-based calculations are found to be in close agreement with each other and correspond well to the available experimental results on photoionization of atomic clusters and other nanoscale systems. The developed methodology is proved to be an efficient and reliable tool for the calculation and analysis of ionization spectra of complex molecular systems.

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Sunday, July 21, 2013

Afternoon session I-1: 14:30-16:00 (the 5th floor)

Afternoon session I-2: 14:30-16:00 (the 6th floor)

Coffee break: 16:00-16:30

Afternoon session II-1: 16:30-18:00 (the 5th floor)

Afternoon session II-2: 16:30-18:00 (the 6th floor)

Silver oxidation : transition from clusters to nanoparticles

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MBN Explorer - a powerful, universal tool for simulating multiscale complex molecular structure and dynamics: case studies

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MBN Explorer [1, 2] is a multi-purpose software package designed to study structure and dynamics of molecular systems of various degrees of complexity. A broad variety of interatomic potentials implemented in the MBN Explorer allows to simulate the structure and dynamics of different molecular systems, such as atomic clusters [3], fullerenes [4], nanotubes [5], metallic nanomaterials [6], proteins and DNA [7], crystals [8] composite bio-nano systems and nanofractals [9]. A distinct feature of the package, which makes it significantly different from other codes, is its universality, implemented multiscale features and applicability to a broad range of problems and complex molecular systems.

The talk will give an overview of the main capabilities of the package and its computational efficiency. The following case studies will be highlighted:

- Thermomechanical damage of DNA molecule in liquid water induced by ion irradiation
- Monte-Carlo simulation of atomic cluster deposition, nanofractal growth and post-growth evolution.

MBN Explorer is free of charge for academic institutions and can be downloaded from the website [2] upon the registration. Currently, there are more than 500 registered users of MBN Explorer. MBN Explorer is developed under the auspices of Virtual Institute on Nano Films. The reported case studied have been conducted at the Frankfurt Institute for Advanced Studies and the Beckman Institute for Advanced Science and Technology.

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Electronic Properties of Soft-landed Nanoclusters and Nanocluster Assemblies

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Self-assembled monolayers (SAMs) of organic molecules formed on metal and semiconductor surfaces are excellent deposition target for the soft-landing because the long-chain alkanethiolate SAM effectively dissipates the translational energy of the projectiles, and the organometallic complexes are embedded in the SAM, as a results of their soft-landing at hyperthermal collision energy of ~20 eV [1]. Furthermore, chemical modification of organic molecules forming SAM matrices can produce a wide variety of adsorption regime and/or supporting system of gas-phase species soft-landed on the SAM substrate [2, 3]. Recently, we have developed a new method to fix the organometallic complexes on a surface with the separation of the binding and functional d-π sites of the complexes to achieve the preservation of the organometallics' properties above room temperatures. Together with terminal modification of the SAM surface from methyl to carboxyl group, aromatic ligands of the organometallic complex are chemically modified; a Cr_1(aniline)$_2$ complex, were deposited onto COOH-SAM [4]. In the landing processes, the incoming charged clusters are neutralized at the surface through tunneling current, and it is important to characterize the electron dynamics at the SAM. In fact, the SAM plays an important role for the charge separation at the surface/interface, and charge separation dynamics relevant to an electron transfer have been revealed by time- and angle-resolved two-photon photoemission spectroscopy for the CH_3-SAM on Au(111) surface fabricated by a chemical process [5]. The electron was photo-excited into an image potential state, and the electron dynamics was observed. Furthermore, the electronic properties of alkanethiol self-assembled monolayers (alkanethiolate SAMs) associated with their molecular-scale geometry are investigated using scanning tunneling microscopy and spectroscopy (STM/STS) [6]. Electronic states originating from rigid covalent bonds between the thiol group and substrate surface are observed near EF in the standing-up and lying-down phases but not in the lattice-gas phase. A new development of surface modification with nanoclusters generated by magnetron sputtering will be also discussed as well as nanocluster assemblies.

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Delocalized dopants in fluid clusters - plasmons and dipoles

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This presentation will describe two experiments probing the electromagnetic response of dopants embedded into fluid clusters.

The first series of experiment [1,2] studied the photoabsorption profiles of silver and copper clusters, Ag_N and Cu_N, grown in superfluid helium droplets by sequential pick-up of metal atoms. It was possible to obtain assemblies of up to thousands of atoms in size. For N below $\sim 10^3$, the spectra are characteristic of individual metallic particles (for example, displaying the expected surface plasmon resonances), but in larger clusters a strong, broad absorption feature appears in the near-infrared region. This suggests a transition from single- to multi-center condensation: as the arrival frequency of metal atoms exceeds their transport time within the helium matrix, they nucleate into small individual agglomerates, and the latter collect into a non-compact, possibly fractal or percolative, assembly. Furthermore, the data offers a signature of coexistence of localized and delocalized electronic excitations in the composite clusters. The helium droplet technique thus allows the formation of contaminant-free cluster-cluster aggregates with unusual optical properties.

The second experiment to be described [3] applies the electrostatic deflection technique [4] to water clusters $(H_2O)_n$ embedding a DCl acid molecule. The dipole moment of such a complex should be sensitive to the process of acid dissociation, due to the appearance of a separated ion pair. By monitoring the cluster beam deflection as a function of n, one should then be able to identify the minimum water cluster size needed to trigger dissociation of the acid molecule, a question that has attracted a lot of interest in the study of solvation. Indeed, the evolution of the electric susceptibilities of $DCl(H_2O)_{n=2\text{-}10}$ turns out to be quite distinctive. The mixed clusters deflect much stronger than neat water clusters, reflecting the contribution of the highly polar dopant. Furthermore, the susceptibility shows a noticeable jump at $n=7$, suggesting that ionization of the solvated acid molecule takes place in this size range and that the critical size for complete dissociation may actually be larger than suggested by previous spectroscopic studies.

This research is supported by the U.S. National Science Foundation.

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Thermodynamic properties of water clusters

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Water exhibits many unusual properties, which mirror the complexity of its hydrogen network structure. It is therefore not surprising that water clusters and nanoparticles are special in many aspects as well. We have recently shown that negatively charged water clusters exhibit a melting-like transition at surprisingly low temperatures (at about 120 K for $H_20_{118}^-$) [1]. This transition has now been studied for a broad range of water cluster anions, as well as for water clusters doped with different impurities (oxygen, aniline). Further experiments on protonated water clusters have been performed in Orsay [2], and on deprotonated ones in Toulouse [3]. All data indicate that the transition does not extrapolate to the melting transition of normal ice, but rather to the glass transition of amorphous ice, which occurs at about 136 K. This can be rationalized by the fact that water clusters with few hundred molecules do not form a crystalline network like bulk ice, but exhibit structures much closer to that of the amorphous forms of solid water.

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Spin and orbital magnetic moments, magnetic-to-nonmagnetic transitions, and the Anderson impurity model in finite systems: XMCD studies on free size-selected clusters

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X-ray magnetic circular dichroism (XMCD) spectroscopy is a local and element specific technique to study spin and orbital magnetization. By applying XMCD spectroscopy to size-selected free clusters, we are able to resolve spin and orbit contributions to the magnetization in particles without any interaction with a support or matrix. This experimental technique allows us to study magnetic coupling in pure transition metal clusters and follow the quenching of the orbital angular momentum [1]. Recently we are also able to investigate a single magnetic impurity embedded in a finite host. Therefore we can reveal that the magnetic to non-magnetic transition in doped silicon clusters is driven by coordination [2]. The influence of the discretized nature of the host density of states in chromium-doped gold clusters on the impurity's magnetic moment is interpreted within the Anderson impurity model [3, 4].

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Confinement Resonances in Endohedral Xe@C_{60}^{+} Ions

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Single-molecule photoelectron-interferometry is possible by photoionizing an atom located at the center of a spherical fullerene shell. Multi-path interference of photoelectron waves arising from the encaged atom and transmitted or reflected by the carbon cage results in confinement resonances. A first experimental hint to such interference was found by Kilcoyne *et al* [1] in a merged-beam study on photoionization of endohedral Xe@C_{60}^{+} fullerene ions at the Advanced Light Source (ALS) in Berkeley. This proof-of-principle experiment has been much improved by employing optimized implantation schemes for sample production using isotopically pure ^{136}Xe atoms. In the investigated 60 - 150 eV photon energy range ionization of a $4d$ electron in the Xe atom is the predominant process and the resulting Xe^{+} ion with its $4d$ vacancy favors relaxation by Auger decay. The total oscillator strength f of the ten $4d$ electrons is concentrated in $4d \rightarrow \epsilon f$ transitions leading to a broad maximum in the cross section of the free Xe atom. This 'giant resonance' is most prominent in the net double ionization of the Xe atom and the cross section is known to be associated with roughly two thirds of the total $4d$ oscillator strength (f=10). When the Xe atom is encapsulated in a C_{60} shell the giant resonance is substantially distorted and instead of a smooth peak the cross section shows the effect of confinement resonances. New experimental and theoretical results are displayed in figure 1.

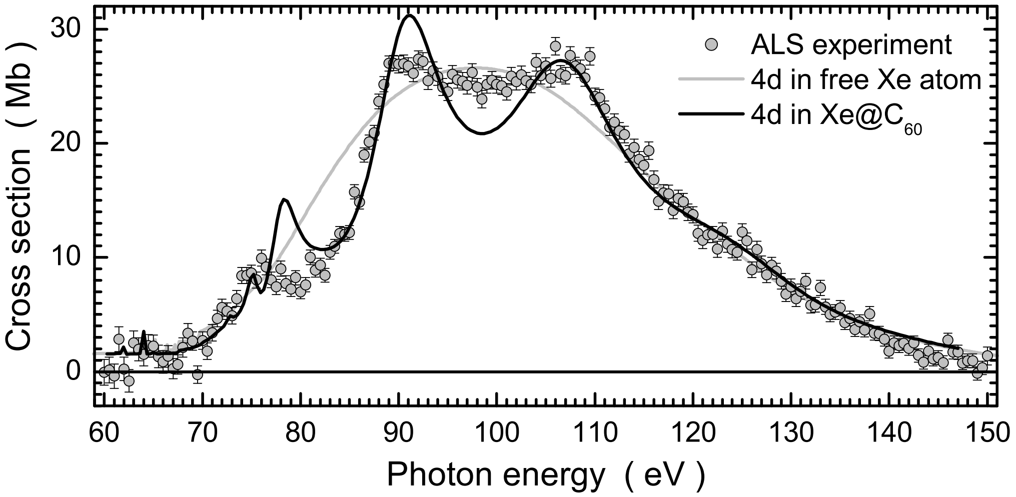

Figure 1: Experimentally inferred net Xe-4d contribution to photoabsorption by ^{136}Xe@C_{60}^{+} ions along with preliminary results of Dirac R-matrix calculations for free Xe atoms and for Xe atoms encapsulated inside a C_{60} cage [2].

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Collective Electron Excitations in Photo- and Electron Impact Ionization of Fullerenes

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We present the results of investigation of collective electron excitations (plasmons) in the C_{60} fullerene in the processes of photoionization and electron inelastic scattering. By means of a recently developed theoretical model [1] we study the formation of plasmons which manifest themselves as prominent resonances in the spectra. We show that the model is in good agreement with experimental data on photo- [2] and electron impact ionization [3, 4].

In the photoionization process, the uniform field of an electromagnetic wave excites the surface plasmon, which has two coupled modes, the symmetric and antisymmetric ones [5] (Fig. 1, left). In the process of inelastic scattering of electrons on fullerenes, the action of a non-uniform external field of the charged projectile leads to the formation of three collective excitations, namely the two modes of the surface plasmon and the volume plasmon as well (Fig. 1, right). By means of the model calculations we show that the electron energy loss spectra (EELS) of fullerenes are described by the contribution of the three resonant peaks. At small angles EELSs are determined mostly by the symmetric mode of the surface plasmon, while at larger angles the antisymmetric surface and the volume plasmons become more prominent [3, 4]. Usually, *ab initio* calculations of electron energy loss spectra on complex molecular targets require rather significant computational resources, therefore the developed theoretical approach, called plasmon resonance approximation, accounting primerely for the essential plasmon excitations turns out to be a useful alternative. The latter is used to elucidate the dominating role of the plasmon excitations in the formation of the cross sections of the studied processes.

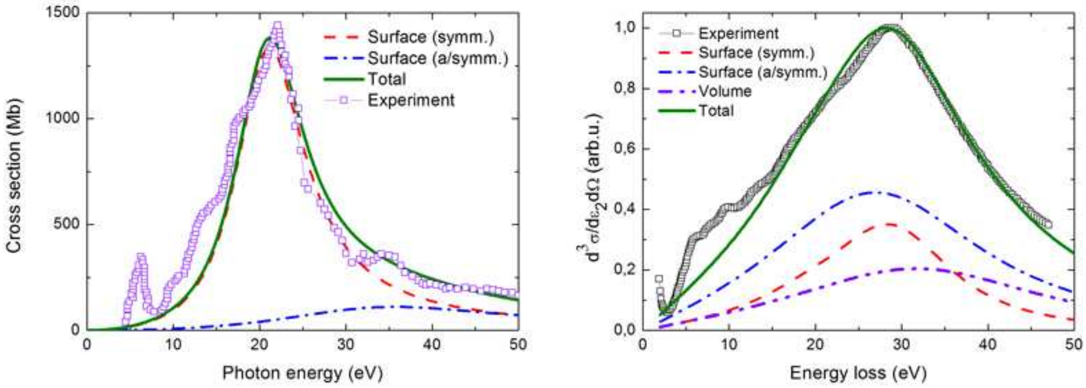

Figure 1: Plasmon resonances in photo- (a) and electron impact ionization (b). EELS in (b) correspond to the scattering angle $\Theta = 5°$ [3, 4].

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Photoexcited resonances in fullerene materials and noble metal clusters: Recent studies

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A time dependent local density approximation scheme is employed to examine various resonant processes in the photoresponse of carbon and noble metal clusters:

First, we find an abundance of atom-fullerene *cross-link* Auger processes in the photoionization of a fullerene molecule with an atom endohedrally confined in it. For instance, autoionizing decays of atomic core-excitations through the fullerene continuum and, reciprocally, fullerene core-excitations through the atomic continuum – the two-way resonant inter-coulombic decays – are detected. Further, electron-transfer excitations from the fullerene to the atom, and vice versa, are found to decay concurrently *via* either continuum. These processes result in a wealth of special resonances in the spectra which can be accessed by the photoelectron spectroscopy [1].

Second, considering the photoionization of a two-layer fullerene-onion system, $C_{60}@C_{240}$, strong plasmonic couplings between the nested fullerenes are demonstrated. The resulting hybridization produces four cross-over resonances generated from the bonding and antibonding mixing of excited charge clouds of individual fullerenes. The result suggests the possibility of designing buckyonions exhibiting plasmon resonances with specified properties [2].

Third, experiments in noble-metal nanoclusters and nanofilms routinely show a higher energy peak besides the regular plasmon resonance. It is generally assumed that the $s \rightarrow d$ interband transition directly induces this effect which, however, cannot be correct, since the $s \rightarrow d$ transitions in noble-metals occur at energies lower than the onset of this feature. Our recent calculations suggest that it is more likely that the interband transitions damp the plasmon resonance which then revives at higher energies when this damping weakens. Hence the interband effect is more likely to induce a plasmon-suppression followed by a plasmon-resurrection at higher energies for noble metal clusters [3].

The work was supported partly by the US National Science Foundation and Department of Energy.

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Recent advances in the study of interatomic Coulombic decay phenomena

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When embedded in a suitable environment, excited or ionized atoms and molecules can hand over their excess energy to their neighbors extremely efficiently via the interatomic (intermolecular) Coulombic decay (ICD) mechanisms. The ICD was predicted theoretically in the late 90's [1] and later found its full confirmation in a series of spectacular experiments [2, 3, 4] (for a full list of theoretical and experimental works on ICD see the ICD bibliography at [5]). The theoretical and experimental work on ICD performed until now and the progress achieved established the generality of the phenomenon and open new horizons for the ICD research. Here, the recent advances in the theoretical description of the ICD phenomena will be presented and some newly predicted ICD related processes [6, 7, 8] will be discussed.

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

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Transition metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of surface reactions. In many cases, however, there is a lack of information on their structures and the relationship between structure and chemical behaviour. Present developments of computational electronic structure methods often still have difficulties with a reliable prediction of cluster structures, and their properties, from first principles. This holds in particular for metals with only partially filled d (transition metals) or f (lanthanides, actinides) shells or for heavy elements, like gold, where relativistic effects become more pronounced. Experimental data can help for testing the validity of these predictions and in motivating methodological developments. We investigate the clusters and their complexes with small molecules size-selectively in the gas phase. Infrared spectra are obtained by IR multiple photon dissociation spectroscopy using the Free Electron Laser for Infrared eXperiments (FELIX). The spectra give access to the internal vibrational modes of the metal clusters in the far-IR as well as the characteristic vibrational modes of cluster-bound ligands in the mid-IR.

Here I will focus on discussing the structural characterization of small platinum clusters[1] and their chemistry. We have recently studied two reactions occurring on small Pt_n^+ cluster cations: (i) the CO oxidation with O_2 and (ii) C–H bond activation in methane. Under thermalized conditions (25 °C) the co-adsorbate $Pt_n(CO)O_2^+$ can be formed and an IR band characteristic for molecular CO is observed. However, excitation of this band can induce reaction of the CO with an O-species and release of CO_2.[2] Methane activation by gas-phase Pt clusters has been a research topic of several groups, but so far only methane decomposition products have been identified. Using ligand exchange on Ar covered Pt clusters by CH_4 we recently succeeded in forming $Pt_nCH_4Ar^+$ complexes, which turn out to contain highly activated molecular CH_4 units.[3] The observation of such intermediates and their subsequent reactions provide an opportunity for more in-detail experimental studies on the reaction mechanism

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Laser Resonant Vibrational Excitations of Precursor Molecules for Promotion of Energy Efficiency in Chemical Vapor Deposition

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In this study, we explored laser resonant vibrational excitations for promotion of energy efficiency in chemical reactions, for enhancement of diamond deposition, and for control of chemical reactions. The research mainly focused on resonant vibrational excitations of precursor molecules using lasers in combustion flame deposition of diamond, which led to: 1) promotion of chemical reactions; 2) enhancement of diamond growth with higher growth rate and better crystallizations; 3) steering of chemical reactions which lead to preferential growth of {100}-oriented diamond films and crystals; and 4) mode-selective excitations of precursor molecules toward bond-selective control of chemical reactions.

Diamond films and crystals were deposited in open air by combustion flame deposition through resonant vibrational excitations of precursor molecules, including ethylene (C_2H_4) and propylene (C_3H_6) (Fig. 1). A kilowatt wavelength-tunable CO_2 laser with spectral range from 9.2 to 10.9 μm was tuned to match vibrational modes of the precursor molecules. Resonant vibrational excitations of these molecules were achieved with high energy efficiency as compared with excitations using a common CO_2 laser (fixed wavelength at 10.591μm). With resonant vibrational excitations, the diamond growth rate was increased; diamond quality was promoted; diamond crystals with lengths up to 5 mm were deposited in open air; preferential growth of {100}-oriented diamond films and single crystals was achieved; mode-selective excitations of precursor molecules were investigated toward control of chemical reactions.

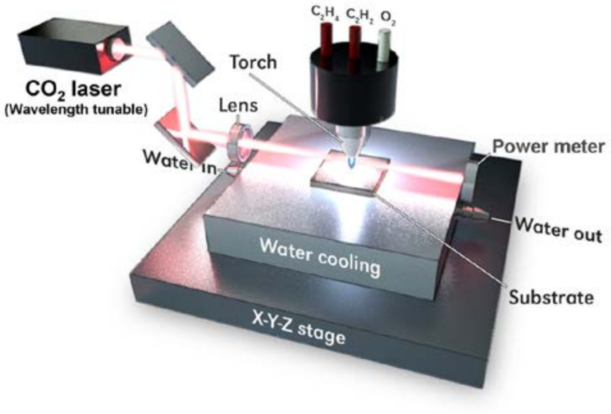

Figure 1: Schematic experimental setup for the laser-assisted synthesis of diamond.

Monday, July 22, 2013

Afternoon session I-1: 14:00-15:30 (the 5th floor)

Afternoon session I-2: 14:00-15:30 (the 6th floor)

Coffee break: 15:30-16:00

Afternoon session II-1: 16:00-17:30 (the 5th floor)

Afternoon session II-2: 16:00-17:30 (the 6th floor)

Chemical reactions in complex biomolecular systems

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Different processes which occur when ions collide with molecules and clusters of biological interest will be discussed, in particular focusing on the underlying reaction mechanisms. Due to the transfer of charge and energy chemical reactions between target constituents can be induced. Gas phase experiments do have the advantage that high mass resolution can be obtained yielding detailed information on final reaction states, reaction paths and branching between them [1,2]. However, the main disadvantage of these studies is the absence of any natural environment which may play an important role concerning the radiation damage of biological systems. Therefore, recently first experiments have been performed with nanosolvated systems in the gas phase [3,4]. Here, the molecules of biological interest are surrounded either by a certain number of water molecules or they are embedded in a cluster of similar or different molecules. It has been shown that new reaction channels - compared to the isolated biomolecules - show up due to modified binding conditions in the complex or that intermolecular reactions may occur between cluster constituents as for example protonation processes.

We will describe results for some of these processes occurring in collisions of multiply charged ions at collision energies of several keV up to 500 keV and for projectile charge states between 1 and 25. The biological target systems will include nucleobases like adenine or amino acids (glycine, GABA), isolated in the gas phase as well as nanosolvated in a cluster system or water complexes.

Acknowledgments: This work has been performed at the ARIBE facility on the site of GANIL. We acknowledge the support by the COST Action MP1002 (Nano-Scale Insight into Ion Beam Cancer Therapy), as well as by the French ANR project PIBALE (*Platform for irradiation of biomolecules at low energies*), the European I3 project ITSLEIF (Ion Technology and Spectrometry at Low Energy Ion Beam Facilities) and the Conseil Régional de Basse-Normandie.

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Dynamics of irradiated clusters and molecules

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We discuss the non adiabatic dynamical response to laser irradiation of clusters and small organic molecules, possibly in contact with an environment (insulating substrate or matrix). The electronic degrees of freedom are treated at a microscopic quantum level through Density Functional Theory (DFT) in the time domain. A proper account of electronic emisson requires some dedicated treatment, especially when ionization is to be explicitly followed in time. We have thus included elaborate theoretical methods to treat the well known hindrance constituted by the Self Interaction Problem in the simple and robust Local Density Approximation of DFT. The description of electrons is complemented by a classical Molecular Dynamics treatment of ions. Environment is, when necessary, included via a dynamical hierachical modelling in the spirit of Quantum Mechanical/Molecular Mechanical approaches of quantum chemistry.

A major focus of these studies concerns the properties of ionized electrons. We discuss in particular photoelectron spectra (PES) and photoelelectron angular distributions (PAD) in relation to recent experimental results. Experimental results provide here a challenging environment for theoretical modelling. But such observables are easily attainable within the formalism we have developed and calculations lead to encouraging results. We also consider the impact of variations of laser parameters, discussing several dynamical regimes from the one to the multi photon regimes. We finally explore short time scales at the attosecond level in direct relation to ongoing experiments.

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Microsolvation of monovalent salts in water: Anion photoelectron spectroscopy and *ab initio* calculations

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In order to understand the microsolvation of monovalent salt in water and provide information about the dependence of solvation processes on different ions, we investigated a series of salt-water clusters, such as $LiI(H_2O)_n^-$, $CsI(H_2O)_n^-$, and $NaCl(H_2O)_n^-$, using photoelectron spectroscopy. The structures of these clusters and their corresponding neutrals were investigated with *ab initio* calculations and confirmed by comparing with the photoelectron spectroscopy experiments. Our studies show that the SSIP type of structures start to appear at n=3 in $LiI(H_2O)_n^-$ cluster anions and at n=5 in neutral $LiI(H_2O)_n$. However, the separation of the Cs^+-I^- ion pair by water is insignificant in $CsI(H_2O)_n$ clusters. In $NaCl^-(H_2O)_n$ clusters, the Na-Cl distance increases abruptly at n=2, then decreases slightly and remains at about 4.0Å for n=3-6; while the Na-Cl distance in $NaCl(H_2O)_n$ neutral increases slightly from n=0 to n=3, reaches a maximum at n = 3 and then stays at about 2.75 Å for n=4-6. The neutral $NaCl(H_2O)_n$ clusters have CIP type of structures for cluster size up to n=6. The M-X distance in $MX(H_2O)_n^-$ is longer than that in neutral $MX(H_2O)_n$ and it is easier to separate the M and X atoms in $MX(H_2O)_n^-$ than those in neutral $MX(H_2O)_n$, because the excess electron weakens the Coulomb attraction of the M^+-X^- ion pair. The effect of water-water interactions starts to show up when the number of water molecules increases to five. These results indicate that the structural variation and microsolvation in $MX(H_2O)_n$ clusters are determined by the delicate balance between ion-ion, ion-water, and water-water interactions, which may have significant implications for the general understanding of salt effects in water solutions.

Imaging the structure of small helium clusters

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Predicted in 1928 by Slater [1], the helium dimer was experimentally first observed more than 60 years later, by Schöllkopf [2] and Luo [3], independently. Before its discovery and even afterwards many theories were published giving strongly varying values for the binding energy and with it the bond length.

Being bound only by van-der-Waals forces the He dimer is the largest diatomic groundstate molecule in the universe: with a binding energy of only about 100 neV helium dimers are very difficult to produce and only stable at low temperatures. So far Grisenti et al. [4] were able to determine the mean internuclear distance to be 52 Å. Havermeier et al. [5] ionized single helium dimers with synchrotron radiation. Being limited by statistics, these measurements yielded bond lengths of only up to 10 Å.

Separating different clusters, formed in a supersonic gas expansion, with a nano transmission diffraction grating, we were now able to measure the square of the complete vibrational wavefunction using the COLTRIMS technique yielding internuclear distances of up to 450 a.u..

In addition we investigated $^4He_3$ and $^4He_2{}^3He$ trimers. Both systems have the same potential and only differ in mass. Furthermore $^4He_3$ is also believed to have a vibrationally excited state with Efimov characteristics [6]. In our experiment the binding energies and the shape of the trimers are measured, clearly revealing the “floppy” character of these systems and their difference in shape and binding energy due to the different masses.

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Mass Spectrometric Studies of Water Clusters

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In recent years there has been a significant interest in the understanding of damage processes of DNA, specially induced by low energy electrons. It has been suggested that ionizing radiation releases a large number of secondary electrons in cells with kinetic energies in the range of up to few of tens of eV [1, 2]. The study by Sanche and co-workers [3, 4] demonstrated that these low energy electrons can induce single and double strand breaks in a film of plasmid DNA upon dissociative electron attachment (DEA). A large number of studies on electron attachment to various simple biomolecules (e.g. DNA bases, sugars, amino acids) in the gas phase have been carried out [5, 6]. However, for applications in radiotherapy it is highly important to understand how DEA process to biomolecules is modified by surrounding environment. It was shown lately that electron attachment to nucleobases embedded in helium droplets indicates significant changes in molecular fragmentation pattern upon solvation and thus the environment may cause strong modification of the DEA process [7, 8].

Therefore, it is beneficial to use clusters of water (the main component of living cells) as a realistic environment to study electron interaction with a biomolecule when the attaching biomolecule is placed in a water cluster environment. In order to understand the influence of a water matrix on DEA to a biomolecule we recently developed a new cluster source. Details on development, implementation and testing together with mass-spectrometric studies of pure water clusters will be presented. We also plan to investigate simple biomolecules, such as nucleobases and amino acids, embedded in water droplets.

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Chemistry of Oxygen-Centered Radicals: A Cluster Approach

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Oxygen-centered radicals ($O^{-\bullet}$) are one of the most important reactive species in many processes, such as in combustion reactions, atmosphere chemistry, biochemistry, and catalytic chemistry. Due to its high reactivity, short life-time and insufficient concentration, it is hard to investigate the chemistry of $O^{-\bullet}$ in condensed phase studies. Therefore, it is quite useful and necessary to adopt alternative ways, such as using clusters as the model systems, in order to obtain the nature of $O^{-\bullet}$. It is noticeable that methane activation and low-temperature CO oxidation are topics full of challenges, and the reactions involved with the $O^{-\bullet}$ radicals can be essential in these processes.

The reactivity of transition metal oxide clusters containing $O^{-\bullet}$ toward CO and methane are investigated by using time-of-flight mass spectrometry combined with density functional theory calculations[1,2]. It has been proposed that $M_xO_y^q$ clusters with $O^{-\bullet}$ centers satisfy a general equation: $\Delta \equiv 2y - nx + q = 1$, in which n is the number of metal valence electrons[3]. This statement is also applicable to heteronuclear oxide clusters. In addition, distributions of the unpaired spins and charges within the clusters are two important factors that can dramatically influence the reactivity of the $O^{-\bullet}$-containing clusters[1]. The doping of Au atom into oxide clusters such as $AuNbO_3^+$ can promote triple C–H bonds abstraction from one butane molecule and the unique stability of 6s orbital in Au atom facilitate this novel reactivity[4]. In addition to the studies of the small and medium sized clusters, the reactivities of nanosized clusters toward CO and hydrocarbon molecules are also investigated. The size and metal dependent reactivity is observed and the mechanism of low-temperature oxidation of CO in related condensed phase systems can be proposed[5].

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Novel functions driven by subnano-space charge polarization created through cluster-substrate interaction

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We have successfully created charge accumulation/polarization in a subnano-space [1,2] according to the Schottky barrier junction by binding a metal subnano-cluster onto a semiconductor surface [3,4]. The STM/STS measurements [1] and the theoretical calculation [2] have shown the spatial distributions of the accumulated charges.

Consequently, we aim to educe specific functions driven by the subnano-space charges in catalysis and photo-electric action with controlling the charge through the size and the atomic composition of the clusters [5,6], taking advantages of their large charge-transfer efficiency and photoabsorption cross section.

As a representative function, we have found a low-temperature catalytic activity in CO oxidation for Pt_{30} monatomic-layered disks constructed on the (111) surface of a silicon substrate by means of ultrahigh-sensitive mass-spectroscopic detection of the reaction products [7], possessing an anti-poisoning characteristic and thermal stability at a temperature as high as 673 K [8]. These novel and high-performance characteristics lead to a large advantage in practical use as a real catalysis.

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Fullerenes on metal and metal oxide surfaces: molecular orientation, lattice ordering and interfacial structure

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In this talk I shall report the molecular orientation, lattice ordering of C_{60} and Gd@C_{82} deposited on Pt(111), Cu(111) and FeO ultra-thin layer studied by scanning tunneling moscroscope (STM) and DFT computation. The surface-adsorbates interaction, the intra-molecular interaction and the temperature (annealing) will affect the molecuar orientation and the lattice ordering. The interfacial structure between the topmost surface and the fullerence molecules (layer) is also discussed.

Controlling strong-field ionization dynamics in clusters

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Atomic clusters in intense laser fields are a nice playground to study the non-linear coupling of electromagnetic radiation into matter. The availability of intense ultrashort laser pulses has been key to study exceptional light-matter phenomena in the strong-field regime, ranging from the generation of coherent attosecond pulses from gaseous targets to the production of monoenergetic ion beams from structured thin foils. Exposed to strong laser fields, atomic clusters transform into a transient nanoplasma at near solid density [1], providing a unique system for studying nonlinear laser-matter interactions in finite systems free of dark reaction channels [2,3]. It is the plasmonic field enhancement in clusters under strong fields which leads to anisotropic emission of ions and electrons. For ions emitted parallel to the laser polarization axis, both the maximum energies [4] and the mean charge states [5] are increased over the result for perpendicular emission for laser pulse durations above 50 fs. Electrons exhibit strong anisotropies for rare gas as well as for metal clusters, with peak energies substantially exceeding the ponderomotive potential of a free electron in the laser field [6, 7].

In this contribution we report on experimental studies on controlling the strong-field ionization dynamics in clusters. Several means are taken to steer the electron emission: among those are the laser polarization, the delay between dual fs pulses, optimized pulse shapes, and the phase control in ω/2ω and few cycle excitation. The experimental results will be compared to those from current theoretical approaches. The example depicted in Fig. 1 demonstrates the strong angular dependence of the electron emission once the system is resonantly excited [8]. Both the experimental and theotetical spectra show an alignment along the laser polarization, which is horizontal in this case.

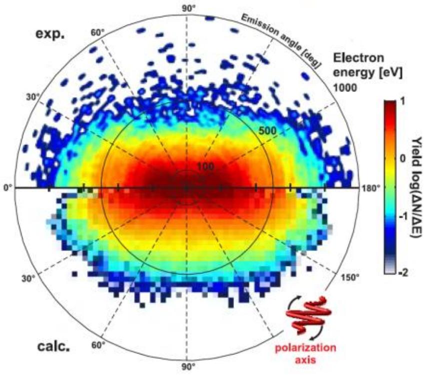

Figure 1: Angular-resolved electron spectra from silver clusters, excited with dual fs pulses at a delay of 1.2 ps. Top: experiment, bottom: calculated spectra as extracted from MD simulations [8].

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Dynamics of nano-plasma of rare-gas cluster created by intense EUV-FEL pulses.

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Recent developments of the free electron laser (FEL) light sources based on self-amplified spontaneous-emission (SASE) invoke the new research fields on the response of matters to intense laser pulses in the short wavelength region. We report here some latest experimental results at the SPring-8 compact SASE source (SCSS) test facility, which delivers intense FEL pulses in the Extreme Ultra Violet (EUV) spectral region (λ=51~ 61nm) . We investigate the multiple photoionization processes of rare-gas clusters induced by intense EUV-FEL pulses by using electron spectroscopy and pump-probe measurements.

(1) Electron emission spectra: Multiple ionization and nano-plasma formation
The electron spectra of rare-gas clusters have been measured as a function of FEL intensity by using a Velocity Map Imaging (VMI) spectrometer. Electron energy spectra of Xe cluster (N~5,000) measured at $h\nu$ = 51 nm show the explicit plateau at the low-energy side of photo-line that is consistent with the multistep ionization model suggested by Bostedt [1]. In addition, the exponential tail around low energy (0 - 5 eV), which suggests the formation of nano-plasma, has been observed.

(2) Time evolution of nano-plasma investigated by pump-probe measurements

We investigate the dynamics of nano-plasma by using the enhanced energy absorption due to surface plasmon resonance [2]. The ion time-of-flight (TOF) spectra of xenon clusters (N~5,000) have measured as a function of delay time between EUV-FEL (λ=51nm) and IR laser (800nm). Notable enhancement of highly charged ions (up to ~Xe^{14+}) have been observed when the EUV-FEL pulses made temporal overlap with NIR laser, that indicates the enhanced ionization of the xenon cluster. We discuss the FEL-induced dynamics of xenon cluster based on experimental data.

We are grateful to SCSS Test Accelerator Operation Group at RIKEN for continuous support in the course of the studies. This study was supported by the X-ray Free Electron Utilization Research Project of the MEXT of Japan, by JSPS.

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Imaging clusters and their light induced dynamics with super intense X-ray pulses

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The understanding of the interaction of high intensity, short-wavelength, short-pulse radiation with matter is essential for virtually all experiments with new superintense X-ray sources, in particular for flash imaging of nm sized particles. Clusters as a form of matter intermediate between atoms and bulk solids are ideal samples to study fundamental light – matter interaction processes. They are finite systems with the density of bulk solids allowing the investigation of inner- and interatomic phenomena.[1,2,3] Very recently, initial experiments have shown that nm-sized gas phase particles can be imaged by single shot scattering.[4,5 6, 7] Upcoming X-ray lasers will allow improving the resolution and going to smaller particles. This will open new fields in cluster and nanometer-scale science. Ultrafast electron and ion dynamics can be studied with nm spatial resolution by means of time-resolved scattering using pump-probe techniques as well as time of flight spectroscopy. The talk will give an overview of recent results obtained at the FLASH facility in Hamburg and the LCLS in Stanford.

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Poster session

Sunday, July 21, 2013: 20:00-22:00 (the 6th floor)

Enhanced quantum coherence in graphene by Pd cluster absorption and its Golubev-Zaikin zero-temperature saturation

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KEYWORDS： Graphene Palladium Clusters Zero-temperature saturation Quantum Coherence

ABSTRACT： We report the increase of the dephasing lengths of the graphene sheet after the deposition of Pdnanoclusters, as demonstrated by the measurement of weak localizations. The dephasing lengths are found to reach some saturated values with the decreasing temperatures, essentially the zero-temperature decoherence. Detailed analysis is carried out on the temperature-dependent and saturated decoherence periods. Our data agree well with the predication of Golubev and Zaikin, where such zero-temperature decoherence is mainly induced by local fluctuations of the electrical fields near disorders. The competition between the surface scattering and electrical field screening leads to the final improvement of quantum coherence.

Photoelectron Spectroscopy Study on the $TiAl_n^-$ (n=6~14) Clusters

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In the gas phase, Al_{13}^- is well known to be an icosahedral cluster with high geometric stability and a closed electronic shell as well.[1] Doping aluminum clusters with other impurity atoms (C, Ge, Sn, Pb, Li, Cu, and Au)[2, 3] provide an additional degree of freedom to fabricate mixed clusters with unique and tunable electronic and chemical properties. However, transition metal doped aluminum clusters have been less studied over the past decade.

In the work, the photoelectron spectra of $TiAl_n^-$ (n=6~14) anionic clusters generated by laser ablation were obtained by 266 nm laser, as shown in Figure 1. It was found that the vertical detachment energies (VDEs) of $TiAl_n^-$ (n=9~11) anionic clusters are higher than the ones of other clusters, which showed that their structures have exceptional stability A further theoretical study on the structures for these clusters will be carried out to explore their stability.

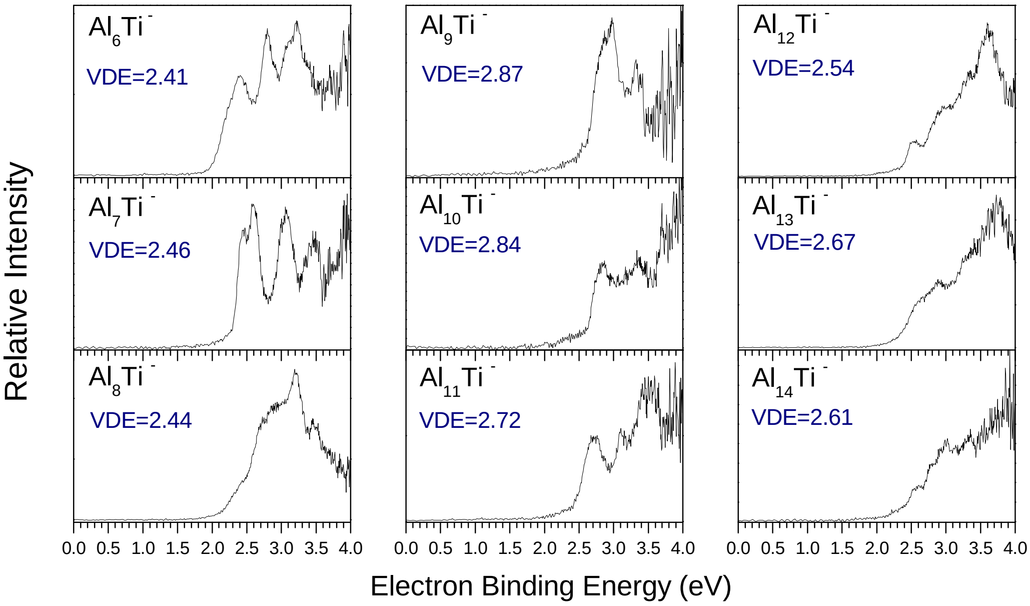

Figure 1: Photoelectron spectra of $TiAl_n^-$ (n=6~14) cluster anions recorded with 266 nm laser.

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Molecular Structure of Rhodium Oxide Ion Clusters by Infrared Photodissociation Spectroscopy

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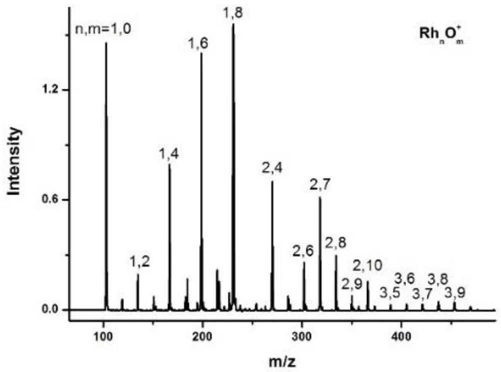
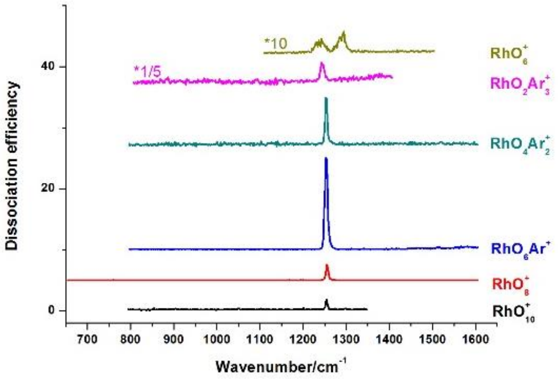
Rhodium-oxygen ion clusters, $Rh_nO_m^+$(n=1~3, m=0~10), were generated by using a home-made laser vaporization cluster source. RhO_8^+ was found with the most intensity in mass spectra (Figure 1), indicating that it has the highest stable molecular structure. Based on the $4d^8$ electron configuration of Rh^+, a square planar structure can be predicted for RhO_8^+ ion where four oxygen molecules symmetrically connected to the central Rh^+. Through applying a “mass gate” to select a target rhodium oxide ion, RhO_x^+, its infrared photodissociation spectrum was recorded in Figure 2 by detecting the corresponding fragment ion. Only an IR vibronic band at 1254 cm^{-1} was observed in the wavelength range of 800 ~ 1600 cm^{-1}. Subsequently, a density functional theory calculation also confirms a stable D_{4h} structure of $Rh(O_2)_4^+$ as we expected, which is consistent with the present IR spectra. In addition, two IR active bands were observed in the IR dissociation spectrum of RhO_6^+ ion, implying that the original structural symmetry of four coordination geometry is broken due to dissociation of an O_2 moiety.

Keywords: IR dissociation spectroscopy, Rhodium-oxygen cluster, electron configuration





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Reactivity of Atomic Oxygen Radical Anions Bound to Titania and Zirconia Nano-Particles in the Gas Phase: Low-Temperature Oxidation of Carbon Monoxide

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Titanium and zirconium oxide cluster anions with dimensions up to a nano-size are prepared by laser ablation and reacted with carbon monoxide in a fast low reactor [1]. The cluster reactions are characterized by time-of-flight mass spectrometry and density functional theory calculations. The oxygen atom transfers from $(TiO_2)_nO^-$ (n = 3−25) to CO and formations of $(TiO_2)_n^-$ are observed whereas the reactions of $(ZrO_2)_nO^-$ (n = 3−25) with CO generate the CO addition products $(ZrO_2)_nOCO^-$ which lose CO_2 upon the collisions (studied for n = 3−9) with a crossed helium beam. The computational study indicates that the $(MO_2)_nO^-$ (M = Ti, Zr; n = 3−8) clusters are atomic radical anion (O^-) bonded systems and the energetics for CO oxidation by the O^- radicals to form CO_2 is strongly dependent on the metals as well as the cluster size for titanium system. Atomic oxygen radical anions are important reactive intermediates while it is difficult to capture and characterize them for condensed phase systems. The reactivity pattern of the O^- bonded $(TiO_2)_nO^-$ and $(ZrO_2)_nO^-$ correlates very well with different behaviors of titania and zirconia supports in the low-temperature catalytic CO oxidation [2,3].

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Experimental and Theoretical Study of the Reactions between MO_2^- (M = Fe, Co, Ni, Cu, and Zn) Cluster Anions and Hydrogen Sulfide

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Removal of poisonous H_2S from natural gas and petroleum refinery gases is of great importance.[1] Many transition metal oxide catalysts are commonly used to recover elemental sulfur in the selective oxidation of H_2S: $H_2S + 1/2O_2 \rightarrow 1/n\ (S_n) + H_2O$.[2] However, molecular level reaction mechanisms are still unclear, especially for the details of dehydration at the gas-solid interface: $M_xO_y + H_2S \rightarrow M_xO_{y-1}S + H_2O$.[3] In order to disclose the reaction mechanisms involved, we have studied the reactions of $M_mO_n^-$ (M = Fe, Co, Ni, Cu, and Zn) with H_2S by time-of-flight mass spectrometry and density functional theory (DFT). The experiments reveal a suite of O/S exchange and O/SH exchange reactions which were also identified in our recent study of clusters $V_mO_n^+$ and $Mn_mO_n^-$ with H_2S. [4-5] The O/S exchange reaction to release water was evidenced for all of the MO_2^- clusters: $MO_2^- + H_2S \rightarrow MOS^- + H_2O$, while the O/SH exchange reaction to derive OH radical was only observed for reactions of NiO_2^-, CuO_2^-, and ZnO_2^-. As is shown in Figure 1, for FeO_2^-, CoO_2^-, and NiO_2^- with H_2S, the O/S exchange reaction is more favorable than O/SH exchange reaction; while the O/S exchange reaction is less favorable than O/SH exchange reaction for CuO_2^- and ZnO_2^-. DFT calculations were performed for $MO_2^- + H_2S$ and the results are in good agreement with the experimental observations. This gas-phase study provides an insight into the metal dependent reactivity and selectivity in the removal of H_2S over metal oxides.

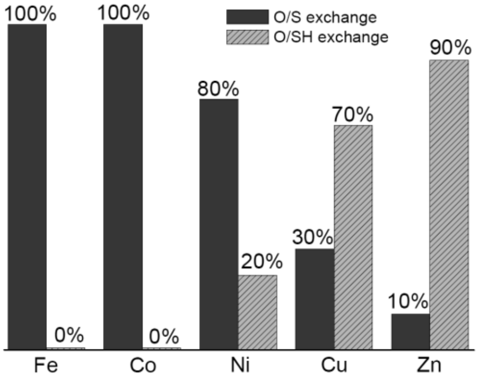

Figure 1: Branching ratios of O/S and O/SH exchange channels in the reactions of MO_2^- (M = Fe, Co, Ni, Cu, and Zn) with H_2S.

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Size-dependent C-H bond activation of *n*-butane over vanadium oxide cluster anions

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Carbon-hydrogen (C-H) bond activation of alkane molecules is currently a subject of considerable interest for the transformation of inexpensive hydrocarbon compounds into valuable products [1], and oxide clusters are good model to investigate the reaction mechanism of C-H bond activation [2-4]. However, most of these oxide clusters studied are small, typically with three to five metal atoms, and for larger clusters, the structures and properties have not been well established. Herein, vanadium oxide cluster anions are produced by laser ablation and reacted with *n*-butane in a fast flow reactor. A reflectron time-of-flight mass spectrometer is used to detect the cluster distribution before and after the reactions. Hydrogen atom abstraction (HAA) reaction is observed upon the interaction between clusters $(V_2O_5)_nO^-$ with *n*-butane. The rate constants exhibit sharp increase from $(V_2O_5)O^-$ to $(V_2O_5)_6O^-$, then, it is less perturbed with the further increase of cluster size when $n \geq 8$. Furthermore, clusters $(V_2O_5)_nO_2^-$ ($n \geq 6$, with dimension up to nanosize) can also react with *n*-butane through HAA. Theoretical calculations indicate that the reactivity of clusters $(V_2O_5)_nO_2^-$ may result from the excited quartet states.

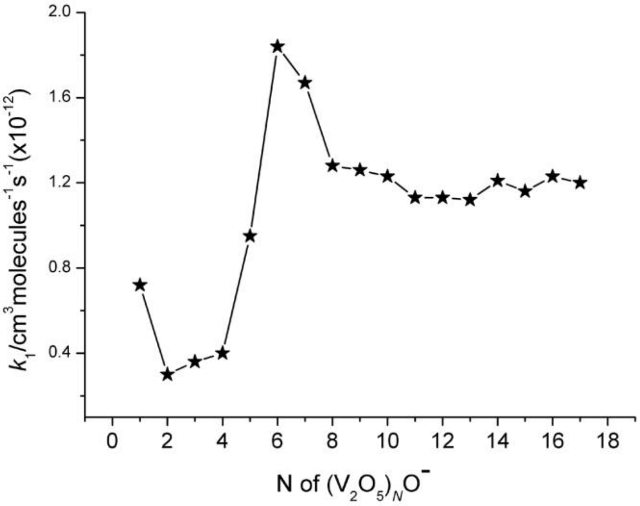

Figure 1: Experimentally determined rate constants (k_1) for the reactions of $(V_2O_5)_nO^-$ with *n*-butane.

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Collision-Induced Dissociation and Infrared Photodissociation Studies of Methane Adsorption on $V_5O_{12}^+$ and $V_5O_{13}^+$ Clusters

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The collision induced dissociation (CID) and infrared photodissociation (IRPD) methods paired with quantum chemistry can provide reliable structural information for neutral and charged species in the gas phase[1-3]. In this work, CID and IRPD methods are used to characterize the CH_4 adsorption on the cationic clusters of $V_5O_{12}^+$ and $V_5O_{13}^+$. $V_5O_{12}CH_4^+$ and $V_5O_{13}CH_4^+$ clusters are generated from the interaction of pregenerated $V_5O_{12}^+$ and $V_5O_{13}^+$ with CH_4 in a fast flow reactor, respectively. The two adsorption complexes are then characterized by CID and IRPD methods. The CID studies indicate that CH_4 is molecularly adsorbed on $V_5O_{12}^+$ and $V_5O_{13}^+$. Each of the IRPD spectra of $V_5O_{12}CH_4^+$ and $V_5O_{13}CH_4^+$ has a broad red band located around 2770 cm^{-1} and a narrow blue band located around 2990 cm^{-1}. The red and blue bands have large and small red-shifts with respect to the symmetric and antisymmetric C-H stretch vibrations of free CH_4, respectively. Density functional theory calculations are carried out for the structures and vibrational frequencies of $V_5O_{12}^+$ and $V_5O_{12}CH_4^+$. The computed results suggest that the anharmonicity including Fermi resonance should be taken into account to interpret the observed IRPD spectrum. In $V_5O_{12}CH_4^+$, the CH_4 unit adsorbs on the three-fold coordinated V^{5+} site with an η^2 configuration. The stretch of the two C-H bonds close to the V^{5+} ion is associated with the red band and the stretch of the other two C-H bonds is associated with the blue band. This study may shed light on the nature of methane adsorption onto vanadium pentoxide surfaces.

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Experimental and theoretical studies of the reaction between VC^+ cluster and methane

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The activation of CH_4 and its conversion to higher hydrocarbons remains an important challenge posing significant thermodynamic and kinetic hurdles. The catalytic conversion of methane to aromatics via non-oxidative routes has attracted significant attention since the initial report of the selective formation of benzene on Mo/H-ZSM5.[1] Subsequently, many catalysts consisting of transition metal ions, such as Mo, W, V, Fe and Cr, exchanged into or load onto various zeolites have been examined for this reaction and exhibited similar catalytic performance. The transition metal carbide (TMC) clusters have been proposed to perform the dehydrogenation and coupling of methane to ethylene.[2] The structures and stability of TMC clusters have been extensively investigated while their reactivity studies are very limited. In order to understand molecular level mechanisms involved with activation and transformation of stable molecules including methane by TMC catalysts under oxygen-free conditions, we propose to study reactions between some typical TMC clusters and small molecules including hydrocarbons. In this work, the VC^+ cluster is generated with laser ablation and reacted with methane in a fast flow reactor. The high resolution mass spectrometry is used to characterize the reactions. The experimental results indicate that VC^+ can react with CH_4 to produce $VC_2H_2^+$ and H_2. The isotopic labeling experiment with $^{13}CH_4$ confirms that one carbon atom in $VC_2H_2^+$ comes from $^{13}CH_4$. The DFT calculations have been performed on the reaction between VC^+ and CH_4. It is noteworthy that there are two reaction channels between VC^+ and CH_4 and both channels are thermodynamically and kinetically favorable.

$$VC^+ + CH_4 \rightarrow VC_2H_2^+ + H_2 \quad (\Delta H_{0K}/\Delta G_{298K} = -3.15/-3.11\ \text{eV});$$

$$VC^+ + CH_4 \rightarrow V^+ + C_2H_4 \quad (\Delta H_{0K}/\Delta G_{298K} = -1.02/-0.99\ \text{eV})$$

It should be pointed out that the channel to produce V^+ ion and ethylene is not observed in the experiment due to the overlap. The homemade quadrupole mass filter and the hexapole reaction cell will be used to characterize the complete reaction channel of VC^+ with CH_4 later.

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Thermal Methane Activation by $La_6O_{10}^-$ Anionic Clusters

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Various cationic oxide clusters can activate methane under thermal collision conditions,[1,2] while there may be a big disparity for them to simulate active sites on surfaces because the electron affinities (EA) of them are generally larger than the work functions of surfaces. Thus, it is of great importance to investigate the structures and reactivity of anionic oxide clusters. Here, we present that $La_6O_{10}^-$ cluster can abstract one hydrogen atom from methane combined experimental and computational studies. The vertical electron detachment energy (VDE) of $La_6O_{10}^-$ cluster which has C_{4v} symmetry is 4.07 eV, and a terminal oxygen-centered radical ($O_t^{\bullet}$) constitutes the active site. Proton coupled electron transfer (PCET) mechanism is conducted in this gas phase reaction. This work enriches the chemistry of methane activation at ambient conditions, and may shed light on understanding the mechanisms of methane C–H activation on surfaces.

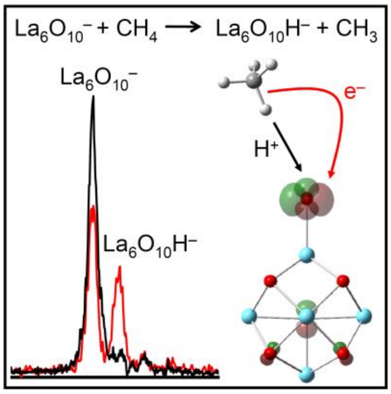

Figure 1: PCET mechanism in thermal methane activation by $La_6O_{10}^-$

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Hydrated Sodium Chloride Clusters: Implications for NaCl Solvation in Water

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Solvation of NaCl in water is a fundamental process and is of great importance ranging from our daily life to chemistry and biology. However, its solvation mechanism at molecular level is still unclear. In this work, we investigated the initial solvation process of NaCl in water by employing negative ion photoelectron spectroscopic study on $NaCl^{-}(H_2O)_n$ (n = 0-6) clusters. The structures of these clusters and their neutrals were determined by comparing the ab initio calculations with the experiments. The observed spectral changes are well correlated with the structural evolutions obtained from the theory. It is found that the Na—Cl distance in $NaCl^{-}(H_2O)_n$ has an abrupt increase at n = 2, while the Na—Cl distance in the neutrals increases slightly and reaches a maximum at n = 3 and then stays almost unchanged with the water molecules increasing up to 6. Our studies show that the transition of CIP to SSIP structures happens at n = 2 for $NaCl^{-}(H_2O)_n$ clusters, while in the neutrals three water molecules are already enough to influence the $Na^{+}Cl^{-}$ ionic bond significantly, but, quite surprisingly, even six water molecules can not break the bond and completely separate the Na^{+}—Cl^{-} contact ion pair. This can be attributed to the strong Na^{+}—Cl^{-} interaction in the neutrals. We also compared the structural parameters of the large clusters with those of the NaCl solutions obtained from X-ray diffraction and theoretical simulations, and found good correlations. These results may be helpful to further our understanding on the solvation of NaCl in water at molecular level and to investigate the hydration structures and the forms of ions in aqueous NaCl solutions.

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Adsorption behavior and electronic properties of Pd_n ($n \leq 10$) clusters on silicon carbide nanotubes: A first principles study

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Abstract

First-principles calculations have been carried out to investigate the adsorption of Pd_n ($n \leq 10$) clusters on the single-walled (8, 0) and (5, 5) SiC nanotubes (SiCNTs). We find that the Pd_n clusters can be stably adsorbed on the outer surfaces of both SiCNTs through an exothermic adsorption process. The adsorption energies of the Pd_n clusters on the (8, 0) SiCNT are generally larger than those of Pd_n on the (5, 5) SiCNT. The bond number between the Pd_n clusters and the SiCNTs increases with increasing cluster size. The Pd atoms adjacent to the SiCNTs prefer to adsorb on the bridge sites over an axial Si-C bond. The adsorption leads to elongation of the Pd-Pd bond lengths and structural reconstruction for the Pd_n clusters. Moreover, the adsorbed Pd_n clusters show two-layered structures as the cluster size $n \geq 4$. We also find that the adsorbed Pd_n clusters induce some impurity states within the band gap of the pristine SiCNTs and the strong pd-hybridization near the Fermi level, thereby reducing the band gap. The charge transfer occurring from the SiCNTs to the Pd atoms is observed for all the systems considered. Due to the strong interactions between the Pd_n clusters and the SiCNTs, most adsorbed Pd_n clusters exhibit zero magnetic moment.

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RRK-based model for molecular clusters formation in a supercooled gas

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In a supercooled gas, as the one obtained in a supersonic adiabatic expansion, molecules join each other, forming Van der Waals bonds and creating small clusters. The classical nucleation theory, valid for describing the formation of large aggregates, is not appropriate in this regime, mainly because it is based on macroscopic parameters. It is therefore necessary to develop new models to explain the kinetics of small molecular clusters formation using equations and parameters that are proper of the microscopic system.

A few years ago, authors like Okada et al. [1] and Veenstra et al. [2] implemented a model based on RRK theory [3]. This semiclassical theory introduces a number of approximations that allow to simplify the energy-transfer involved in cluster formation, and successfully model the kinetics of their dissociation.

In the presented work this model is analyzed and modified by introducing statistical distributions for magnitudes inherent to the system, such as the particles kinetic-energy and clusters internal-energy distributions. The model is then numerically implemented to obtain the evolution of cluster concentrations under different conditions of pressure and temperature. As an example, it has been applied to describe the cluster formation kinetics in a supercooled molecular beam of sulfur hexafluoride (SF_6) diluted 4% in argon (figure 1).

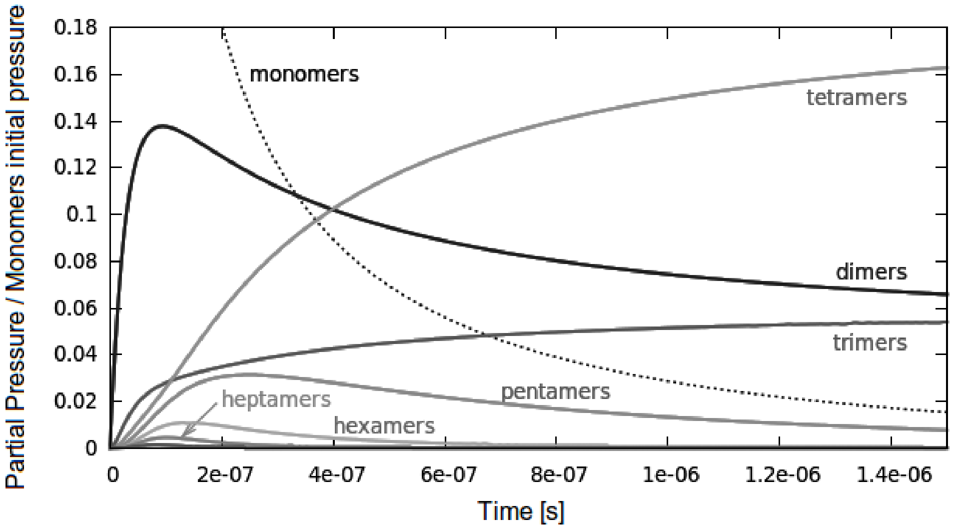

Figure 1: Growth simulation of different cluster sizes in a supercooled SF_6 gas.

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Ultrafast Carrier Dynamics of Carbon Nanodot

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Carbon nanodot(CND) have attracted increasing attention in several fields because of their unique advantages such as biocompatibility,low toxicity, chemical stability ,strong fluorescence .But the luminescence mechanisms of CND are not fully understood. The luminescence has been proposed to arise from excitons, emissive traps, quantum confinement effects of aromatic structure , free zizag sites and edge defects.[1]Herein we report the ultrafast carrier dynamics in the CND by transient absorption(Figure 1).

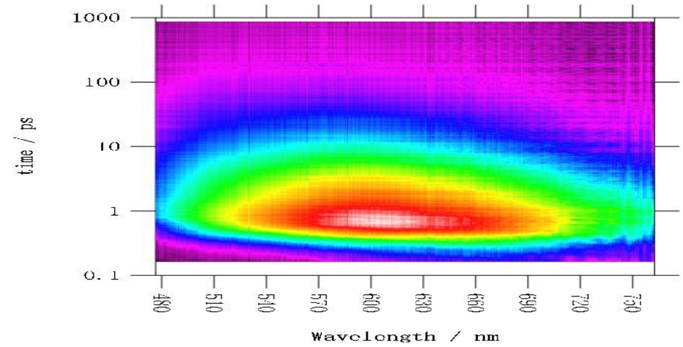

Figure 1: Contour plot of the femtosecond broad band transient absorption spectra of CND at the pump 400nm (energy 0.5 μ J)

Wen X. demonstrated the ultrafast carrier dynamics of the CND with femtosecond resolved up-conversion technique, they assign the fast process to excited electron in the nano domain trapped by the surface state [2]. At the shorter wavelength ,significant contribution is from the intrinsic state, which mainly arises from the quantum confinement of π electron. The functional group of oxygen in the CND can lead to accelerate the decay of trapped electron in the longer wavelength. A few picoseconds process can be attributed to the phonon induced relaxation, which was observed in some carbon based nano-materials. The longer decay time was found in nanosecond scale. According to semiconductor quantum dot, we can ascribe this to carrier recombination.

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Photoelectron Spectroscopy and Density Functional Calculations of VGe_n^- (n = 3-12) Clusters

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It has been suggested that the transition metal (TM) dopants can stabilize germanium clusters, and they can be used as building blocks of nanotubes.[1,2] Some TM-doped germanium clusters reveal novel structures and many interesting properties such as large HOMO-LUMO gaps, unique magnetic moments and so on.[3,4] We investigated the structural and electronic properties of VGe_n^- (n = 3-12) clusters using anion photoelectron spectroscopy in combination with density functional theory calculations, and those of VSi_n^- (n = 7-10) clusters were investigated for comparison. The results display that the dominate geometries of VGe_n^- are exohedral structures when the number of Ge atom less than 8, then the endohedral structure emerges at n = 8, and V atom is encapsulated completely at n = 10. Furthermore, VGe_{12}^- has an endohedral structure with the V atom centered at the Ge_{12} hexagonal double-chair framework. In addition, the charges transfer from Ge_n framework to V atom for VGe_n^- clusters, indicating that V atom play an important role in saturating dangle bonds in Ge atoms. As for VSi_n^-, the endohedral structure emerges at n = 10, and the charges transfer from V atom to Si_n framework, which is different from VGe_n^- clusters.

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Multistage Transformation and Charge Effect during Fragmentation Phase Transition in Atomic Cluster

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In a series of theoretical works from Gross's group [1, 2], the caloric curve for a cluster system was found to be divided into four parts, after an initially rising a plateau and a backbending are present before the curve rises again. The results indicate a multistage Fragmentation Phase Transition (FPT) related to a stepwise appearance of typical fragmentation phenomena from No Fragmentation (NF) through Asymmetrical Dissociation (AD) and Multi-Fragmentation (MF) to Complete Fragmentation (CF). Furthermore, charging the cluster shifts the transition to lower excitation energies and forces the transition region to narrow or even disappear. These features were considered as signatures of charge effect on the FPT. Here, taking charge-selected $C_{60}^{3,4+}$ as model systems, we experimentally explore the FPT using a CIDEC technique [3, 4]. The multistage transformation was obtained by analyzing the population distributions of fragmentation phenomena as a function of excitation energy for each model system (as shown in figure 1). The charge effect was demonstrated by a comparison between the two model systems with different initial charges.

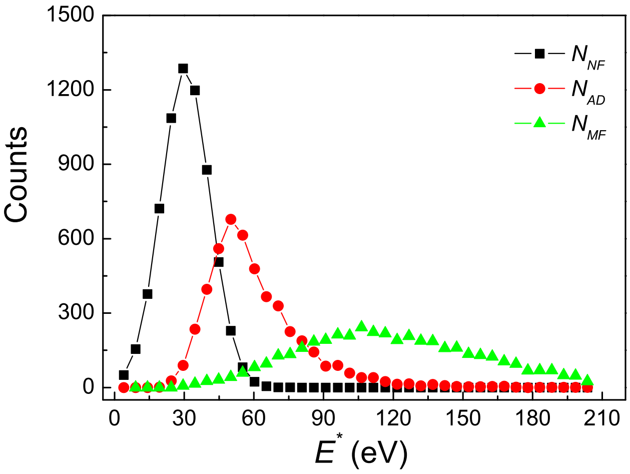

Figure 1: Population distributions of fragmentation phenomena associated to C_{60}^{4+*} model system as a function of excitation energy.

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Photoelectron Spectroscopy and Density Functional Investigation of $V_2Si_{20}^-$: An Endohedral Dodecahedron Structure

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Transition metal-doped caged silicon (M@Si_n) clusters have attracted great attention because of their novel structural features and potential technical applications. Anion photoelectron spectroscopy experiments were conducted to investigate the vanadium-doped silicon cluster, $V_2Si_{20}^-$. Extensive DFT calculations were performed to identify low-lying isomers of $V_2Si_{20}^-$ cluster. The most stable structure of $V_2Si_{20}^-$ is an elongated dodecahedron cage structure with a V_2 encapsulated inside the silicon cage. The Si_{20} cage is composed of twelve pentagonal faces. The V-V distance in the dodecahedron V_2@Si_{20} is about 2.31 Å, which is longer than that of the V_2 dimer (1.77 Å) but shorter than that in metallic vanadium (2.62 Å). The calculated ADE and VDE of this structure are about 3.47 eV and 3.52 eV, in reasonable agreement with the experimental measurements (3.5 eV and 3.7 eV). The constant electronic charge density of dodecahedron structure shows that Si atoms sp^3 hybridization leads to the formation of Si-Si σ bonds, and the electron density between two V atoms is higher. The strong bonding between two V atoms in dodecahedron $V_2Si_{20}^-$ cluster is consistent with those of small size V-Si clusters. We further investigated the geometric and electronic properties of one-dimensional nanowires assembled by a series of endohedral dodecahedron V_2@Si_{20}, (V_2@Si_{20})$_n$ (n=2-4). It can be seen that the V_2@Si_{20} units can be connected to form pearl-chain structures with two Si-Si bonds between each pair of neighboring V_2@Si_{20} units. We also found that electrical conductivity of one-dimensional nanowires mainly takes place via *s* and *p* electrons. These make the endohedral dodecahedron V_2@Si_{20} cluster a promising building block of self-assembly materials.

The Proton Transfer and Dissociation Dynamics of Water Cluster Ions: $H_5O_2^+$, $D_5O_2^+$, and $H_3D_2O_2^+$

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Water cluster ions are of great interest since they are involved in aqueous proton transfer which plays important roles in many chemical and biological processes. We investigated the proton transfer and dissociation dynamics of water cluster ions, $H_5O_2^+$, $D_5O_2^+$, and $H_3D_2O_2^+$, based on the harmonic and anharmonic oscillator models using micro-cannonical and canonical transition state theory. These results show that the anharmonic Rice-Ramsperger-Kassel-Marcus (RRKM) theory can provide a reasonably good understanding for the dissociation and proton transfer processes. The calculation method can be extended to other molecules with large anharmonicity, e.g. the complex of DNA molecule and water cluster. Furthermore, a theoretical model to demonstrate the principle of vibrational pre-dissociation spectroscopy (VPS) is established from the viewpoint of RRKM theory and applied in determining the experimental condition and understanding the role of the dissociation rate constant *k(E)* played in the VPS experiment using $(H_2O)_2H^+$ and $(D_2O)_2D^+$ as examples.

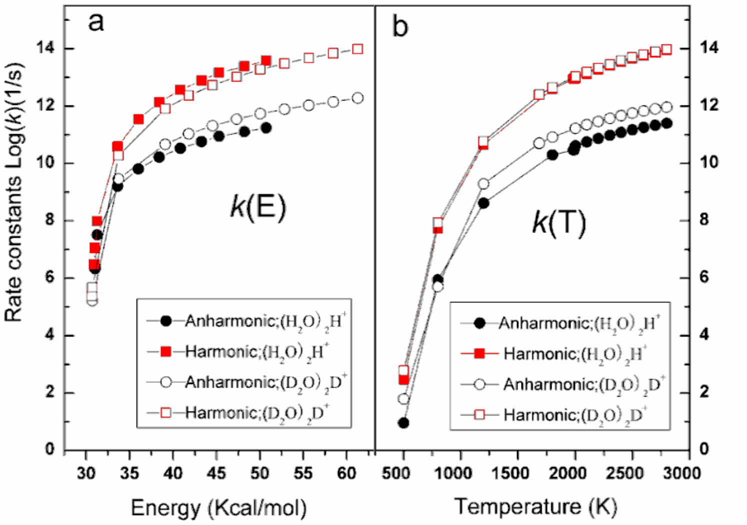

Figure 1. Dissociation rate constants of $(H_2O)_2H^+$ and $(D_2O)_2D^+$ in the (a) microcanonical case and (b) canonical case. The solidsquares and circles represent harmonic and anharmonic rate constants for $(H_2O)_2H^+$, respectively. The hollow squares and circles shows the harmonic and anharmonic rate constants for the $(D_2O)_2D^+$, respectively.

Photoelectron Spectroscopy and Theoretical Study of $LiBO_2^-(H_2O)_n$ Clusters

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Salt dissolution in water is a fundamental physicochemical process and its microsolvation process can be investigated through the study of salt-water clusters. There are two kinds of configurations for the salt ions when they interact with water molecules, i.e., contact ion pair (CIP) and solvent-separated ion pair (SSIP). It's interesting to know how many water molecules are needed to separate a specific salt CIP. We studied the change of the electronic state of $LiBO_2^-$ with increasing number of water molecules by employing negative ion photoelectron spectroscopy. By comparing quantum chemical calculations with experiments, the structures of these clusters and their corresponding neutrals were assigned, and their structural evolutions were revealed. It is found that $LiBO_2^-$ is linear and the ion pair structures vary when the number of water molecule changes; at n=3, the anion cluster shows a ring-type SSIP configuration and the transition of CIP to SSIP structures starts; at n=4, the cluster presents a linear-type SSIP structure. However, in $LiBO_2(H_2O)_{1\text{-}5}$ neutrals, the Li^+-BO_2^- ion pair always retains the CIP structure. This study may provide information on the initial solvation process of $LiBO_2$ in water.

Polyhedral Cage Structures of Stoichiometric $(V_2O_5)_N$ Clusters

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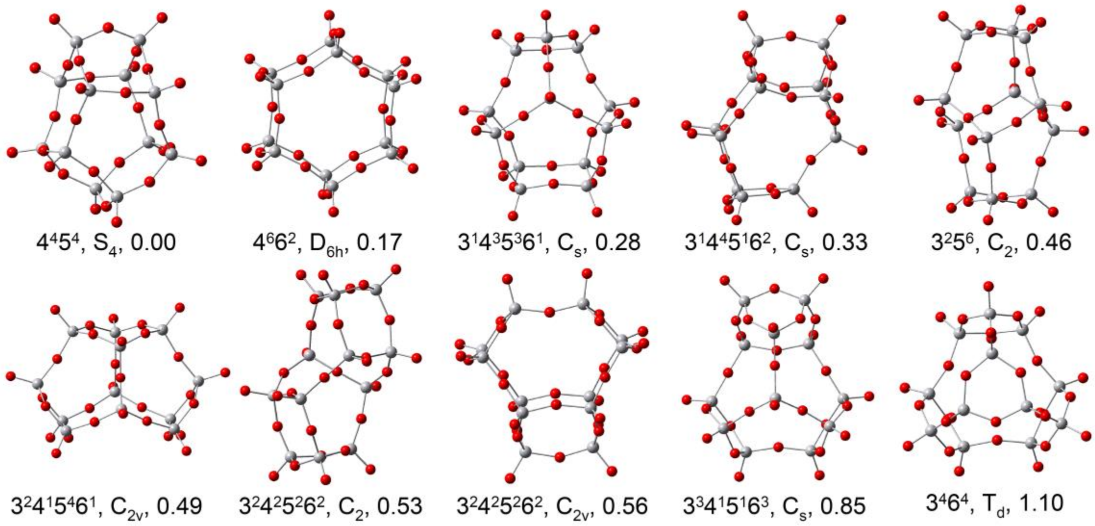
It is important to study the structures of V oxide clusters which is the starting point to investigate the reactiviy and catalytic mechanisms of nanozised or bulk V oxide based materials.[1] Interesting polyhedral cage structures were suggested by Vyboishchikov and Sauer for stoichiometric $(V_2O_5)_N$ (N=2−5, 8, 10, and 12) clusters.[2] However, only a few selected structures had been tested in their work.

In this work, we systematically studied all possible polyhedral cage structures for each of $(V_2O_5)_N$ (N=2−6) clusters. In these structures each V is coordinated with three bridgingly-bonded O atoms (denoted as O_b) and one terminally-bonded O atom (O_t). So the topological structure constructed of V and O_b atoms (ignoring the O_t atoms) is a three-dimensional 3-regular graph (each vertex has 3 neighbours). A modified code of CaGe[3] is used to generate such polyhedron structures. When the faces of polyhedron are restricted to be 3 to 6-edge polygons, 1, 1, 2, 5, and 10 isomeric structures are obtained for N = 2−6 clusters, respectively. The number of isomeric structures increases quickly as N increases. Structural properties of studied clusters may serve as useful guidance for studying N>6 clusters. For example, structures containing triangle surfaces are found to have high relative energy (Fig. 1), thus they can be safely excluded when studying large clusters.



$4^4 5^4$, S_4, 0.00
$4^6 6^2$, D_{6h}, 0.17
$3^1 4^3 5^3 6^1$, C_s, 0.28
$3^1 4^4 5^1 6^2$, C_s, 0.33
$3^2 5^6$, C_2, 0.46
$3^2 4^1 5^4 6^1$, C_{2v}, 0.49
$3^2 4^2 5^2 6^2$, C_2, 0.53
$3^2 4^2 5^2 6^2$, C_{2v}, 0.56
$3^3 4^1 5^1 6^3$, C_s, 0.85
$3^4 6^4$, T_d, 1.10

Fig. 1 Structure, symmetry and relative energy of each isomeric structure of $V_{12}O_{30}$. Structure symbol g^k indicates that the polyhedron has k of g-edge polygons as the surfaces.

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Reactions of $V_4O_{10}^+$ cluster ions with simple inorganic and organic molecules

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Vanadium oxide clusters are being actively studied [1,2] in order to discover molecular level mechanisms for chemical processes over the surfaces of vanadium oxide based catalysts that are widely used in laboratory and industry. [3,4] Vanadium oxide cluster ions are prepared by laser ablation and the $V_4O_{10}^+$ clusters are selected by a quadrupole mass filter and interacted with simple inorganic and organic molecules (H_2, CO, CH_4, C_2H_2, C_2H_4, and C_2H_6) in a hexapole reaction cell. The reactant and product ions are detected by a reflectron time-of-flight mass spectrometer. Hydrogen and oxygen atom transfer reactions are observed （$V_4O_{10}^+ + CO \rightarrow V_4O_9^+ + CO_2$; $V_4O_{10}^+ + CH4 \rightarrow V_4O_{10}H^+ + CH_3$). Density functional theory calculations are carried out for the reaction mechanism of $V_4O_{10}^+ + H_2$. The oxygen atom transfer (OAT) channel $V_4O_{10}^+ + H_2 \rightarrow V_4O_9^+ + H_2O$ is much more exothermic than the hydrogen atom transfer (HAT) channel $V_4O_{10}^+ + H_2 \rightarrow V_4O_{10}H^+ + H$ whereas the former is less favorable than the later in terms of the reaction barriers. The computational result is in good agreement with the experiment that the HAT (H_2 splitting) rather than the OAT (water formation) is observed for $V_4O_{10}^+ + H_2$.

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Photoelectron Spectroscopy and Density Functional Study of Nucleobase-Ag Complexes

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Understanding the interactions between silver and nucleobases is important in nanotechnology because it can provide useful information for the design of special DNA templates for silver nanoparticle assembling. In addition, it can also provide useful information regarding the biological safety of coinage metal nanomaterials. In this work, we investigated nucleobase-Ag complexes with anion photoelectron spectroscopy and density functional calculations. The experiments were conducted on a home-built apparatus consisting of a linear time-of-flight mass spectrometer and a magnetic-bottle photoelectron spectrometer. The VDEs of Ag-Uracil, Ag-Cytosine, Ag-Thymine, Ag-Adenine and Ag-Guanine complexes were estimate to be 2.18, 2.05, 2.11, 2.18 and 2.20 eV, respectively according to their photoelectron spectra. The structures of the nucleobase-Ag complexes were determined by comparison between the theoretical calculations with experiments. The results show that the silver anion interacts with the nucleobase mainly via N-H ⋯Ag and O-H ⋯Ag hydrogen bonds in the complexes.

Microsolvation of Sodium Acetate in Water: Anion Photoelectron Spectroscopy and Density Functional Calculations

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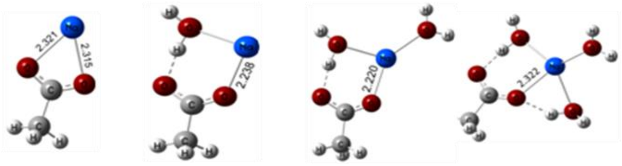
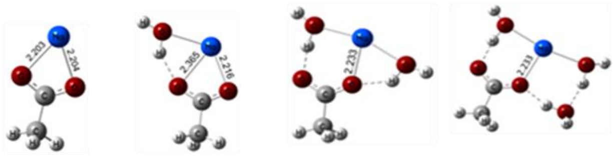
In order to study the microsolvation of sodium acetate (NaAc) in water, we investigated $NaAc^-(H_2O)_n$ (n = 0-3) clusters by conducting photoelectron spectroscopy and density functional calculations. $NaAc^-(H_2O)_n$ (n = 0-3) cluster anions were produced in a supersonic laser vaporization source and mass-analyzed with a time-of-flight mass spectrometer. The $NaAc^-(H_2O)_n$ (n = 0-3) cluster anions were each mass-selected and decelerated before being photodetached with 1064 and 532nm photons. The vertical detachment energies (VDEs) of $NaAc^-(H_2O)_n$ (n = 0-3) cluster anions were estimated to be 0.44 ±0.04, 0.42 ±0.08, 0.45 ±0.08, 0.34 ± 0.08 eV, respectively, based on their photoelectron spectra. The structures of these clusters and their corresponding neutrals were optimized by density functional calculations. By comparing the theoretical results with the photoelectron spectroscopy experiments, the most probable structures of $NaAc^{-/0}(H_2O)_n$ (n = 0-3) were determined. The most stable structures of these clusters are presented in Figure 1. Our study shows that water molecule can insert between one of the Na—O bonds of sodium acetate to form six-membered ring structures. The water molecules can interact with the sodium atom through its O atom and with the oxygen atoms of acetate by forming hydrogen bonds.



$NaAc^-(H_2O)_n$ (n = 0-3)



$NaAc(H_2O)_n$ (n = 0-3)

Figure 1: The most stable structures of $NaAc^{-/0}(H_2O)_n$ (n = 1-3) clusters obtained by density functional calculations at LC-wPBE/6-311++G(d, p) level of theory.

Adsorption of CO on Au_n^+ (n = 1 - 10): Extensive Theoretical Studies

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The unusual catalytic property of gold clusters in the reactions of CO oxidation, water-gas shift process etc. attracted great interests. Numerous studies have suggested that this property can be attributed to the interplay among various factors. In this work, we explored the adsorption of CO on Au_n^+ (n = 1 - 10) using Basin-Hopping strategy and DFT calculations. All structures within the energy range of 1.0 eV from the global minimum point for each $[Au_n(CO)]^+$ were analyzed. In the structures with CO bonding on one Au atom, the CO stretching frequencies are slightly larger than that of free CO and seem independent on the coordination numbers of the adsorption sites. In the structures with CO bridging on two Au atoms, the CO stretching frequencies are 100-300 cm^{-1} smaller than that of the free CO, and the CO bridging on the 3D structures of Au_n^+ has smaller frequencies than those on the 2D ones. Since the energies of some structures containing bridging CO are very close to the global minima of $[Au_n(CO)]^+$, they could present in experiments and contribute to the catalytic processes.

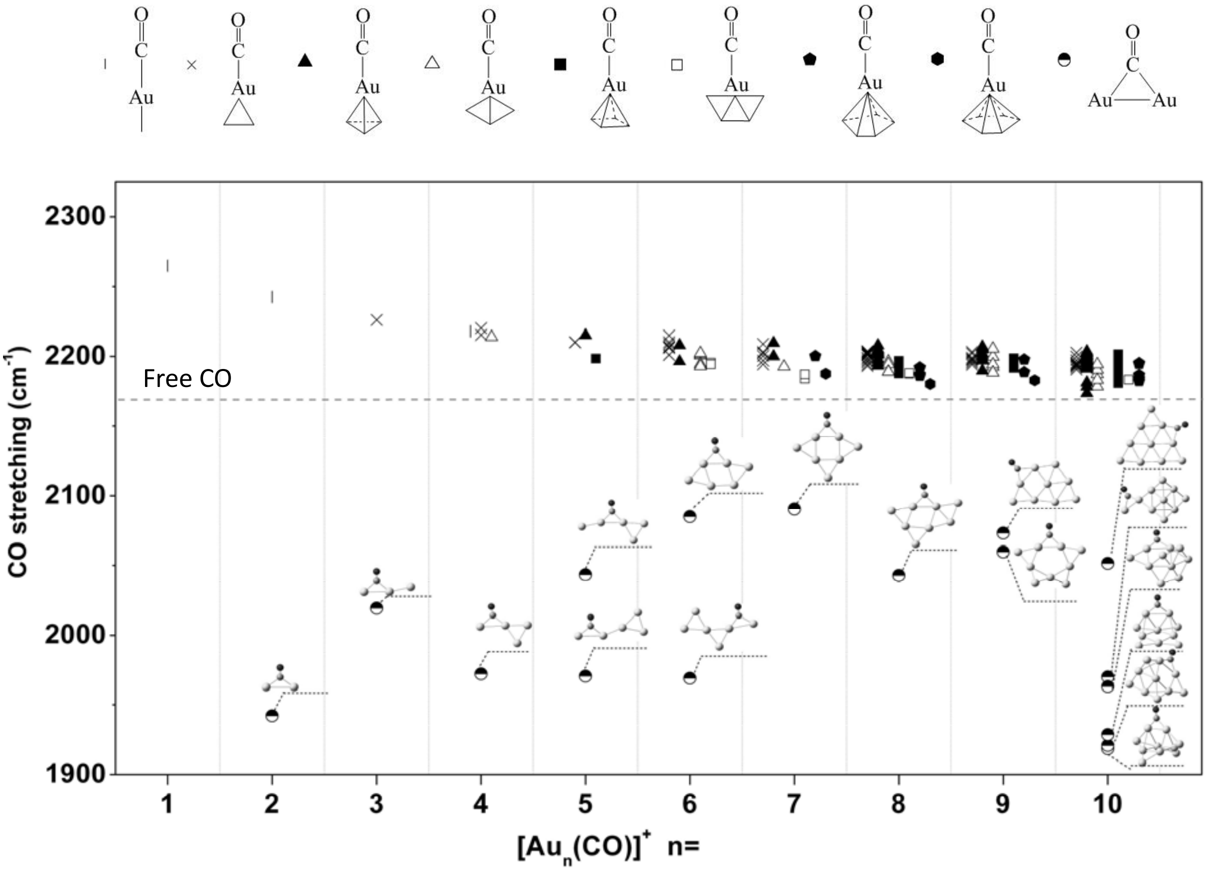

Figure 1: The theoretical frequencies of the CO stretching mode in the predicted structures of $[Au_n(CO)]^+$ (n=1-10), in which CO bond on different sites.

The solidification feature of liquid metal studied by viscosity measurement

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Temperature dependence of viscosities of liquid melts has been studied by a torsional oscillation viscometer. During the measurement process, a deviation from the Arrhenius behavior is found when the temperature is higher than the melting point. The abnormal increasing of the viscosity and the activation energy indicates the changes of the elementary melt structure during cooling towards the melting point. The deviation region from Arrhenius viscosity is defined as the transition state. The differential scanning calorimeter experiments also show the existence of the critical transition state in liquid metals near the melting point. The drastic increase of the viscosity in the transition state can be regarded as continuum transition and be presented well by the amended Arrhenius equation which is based on the critical phenomenon.

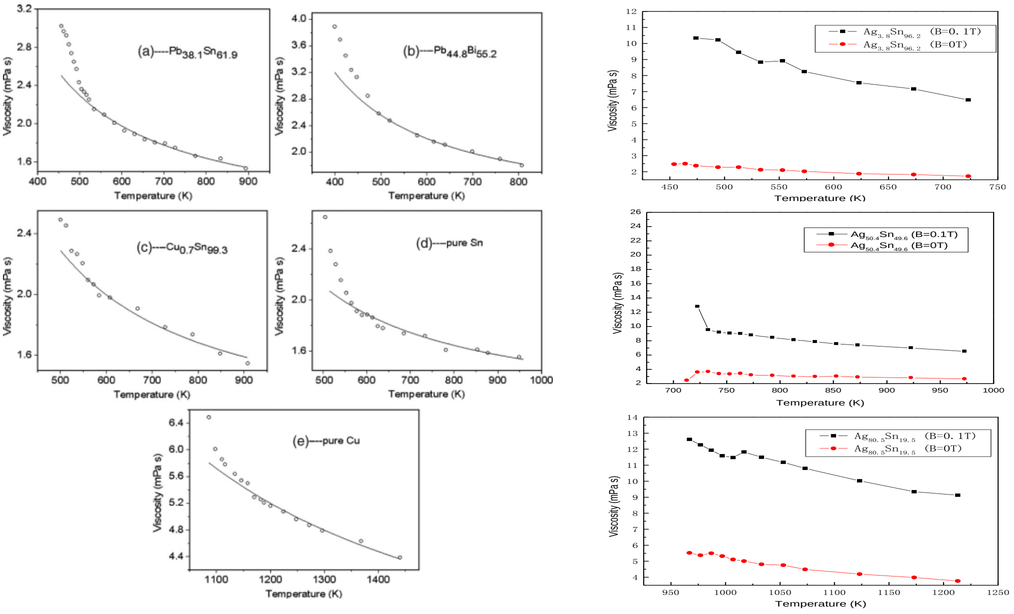

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Fig. 1. （1）Temperature dependence of viscosities of liquid Sn, Cu, $Pb_{38.1}Sn_{61.9}$, $Pb_{44.8}Bi_{55.2}$ and $Cu_{0.7}Sn_{99.3}$ metals from the highest temperature to the melting point. The solid lines are the Arrhenius plots. （2）The relationship between temperature and the viscosity of Ag3.5Sn96.5, Ag50.4Sn49.6, and Ag80.5Sn19.5 alloy both under the magnetic field or not.

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First-principles Study on Small Palladium Clusters on NiAl(110) Alloy Surface

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Abstract

Theoretical calculations focused on the geometry, stability, electronic and magnetic properties of small palladium clusters Pd_n(n=1-5) adsorbed on the NiAl(110) alloy surface were carried out within the framework of density functional theory (DFT). In agreement with the experimental observations [1], both Ni-bridge and Al-bridge sites are preferential for the adsorption of single palladium atom, with an adsorption energy difference of 0.04eV. Among the possible structures considered for Pd_n (n=1-5) clusters adsorbed on NiAl(110) surface, Pd atoms tend to form one-dimensional (1D) chain structure at low coverage (from Pd_1 to Pd_3) and two-dimensional (2D) structures are more stable than three-dimensional (3D) structures for Pd_4 and Pd_5. Furthermore, metal-substrate bonding prevails over metal–metal bonding for Pd cluster adsorbed on NiAl(110) surface. The density of states for Pd atoms of Pd/NiAl(110) system are strongly affected by their chemical environment. The magnetic feature emerged upon the adsorption of Pd clusters on NiAl(110) surface was due to the charge transfer between Pd atoms and the substrate. These findings may shade light on the understanding of the growth of Pd metal clusters on alloy surface and the construction of nanoscale devices.

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Molecular clusters based on weak hydrogen bond networks: a rotational study of the tetramer of difluoromethane

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Molecular clusters forming a net of relatively strong OH··O hydrogen bonds (such as $(H_2O)_6$), have been well characterized by rotational spectroscopy. However, only a few examples are available on the clusters of relatively large asymmetric rotors, with the subunits held together by weak hydrogen bonds (WHBs). Following the rotational studies on the dimer[1] and the trimer[2] of difluoromethane (CH_2F_2), we assigned the rotational spectrum of one conformer of the tetramer $(CH_2F_2)_4$ with the indications from high level *ab initio* calculations.

The observed rhomboid form is stabilized by a net of ca. 16 WHBs, with hydrogen bond lengths in the range 2.54-3.55 Å, as shown in Figure 1. This can be compared to the 9 WHBs net found in the trimer with hydrogen bond lengths in the range 2.48-3.25 Å.[2]

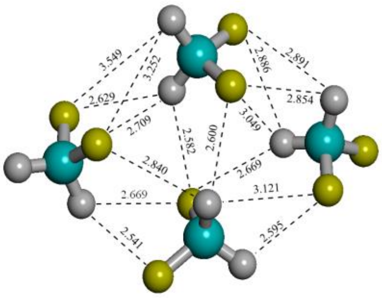

Figure 1: The WHBs network underlying the observed configuration of $(CH_2F_2)_4$.

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Photodissociation dynamics of $\mathrm{H_2 \rightarrow H(1s)+H(2s/2p)}$ at 14.7-14.8 eV studying by XUV laser pump and UV laser probe method

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The photodissociation of H_2 in the energy region above the threshold for the production of H(2s/2p) is a benchmark example about the nonadiabatic interaction in molecular dynamics. It is well established that the dissociation occurs mainly via the predissociation of $H_2(3p\pi, D^1\Pi_u)$ interacting with the vibrational continuum of $H_2(3p\sigma, B'^1\Sigma_u^+)$. The product branching ratios between H(2s)/H(2p) and angular distributions of the fragments reflect the relative strength of the noadiabatic interaction between the two states. Therefore, these two parameters are essential to study the photodissociation dynamic. Both experimental measurements and theoretical calculations have been done to obtain the branching ratios. However, they are not consistent and further there is also no measurement reported for the angular distribution of the photofragments. In this work we measured the product branching ratios between H(2s)/H(2p) and also the angular distribution of the photofragments by a combination of XUV-laser and UV –probe method and ion velocity map imaging technique. Furthermore, a new independent way to extract the branch ratio of H(2s)/H(2p) is proposed, which makes use of the fact that the photoionization cross sections of hydrogen atom are accurately known by theoretical calculations. More specifically, the total intensities of the probe signal can be expressed as,

$$S(I,\omega) = A\left[R(1-e^{-\sigma_{2s}(\omega)\cdot C\cdot I}) + (1-R)(1-e^{-\sigma_{2p}(\omega)\cdot C\cdot I})\right],$$

where the R is the branch ratios and A, C are constants related with the experimental condition. Using the different measurements with different sets of intensities I and frequencies w, the branch ratio R can be determined. Our measured branch ratios (0.88) are larger than those previously measured value (0.57). The angular distribution of the fragments showed that most of the dissociation occurred via the parallel transition.

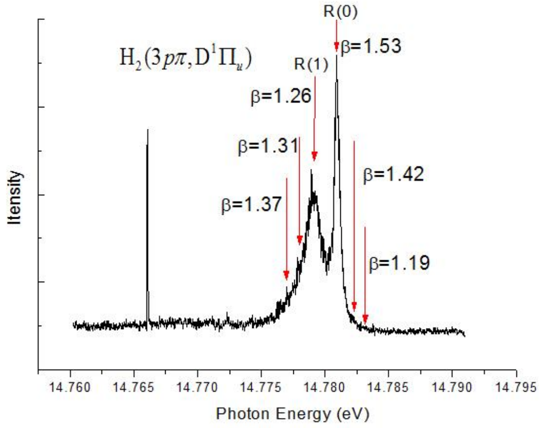

Figure 1. The signal intensities of H(2s/2p) as a function of excitation photon energies. β is anisotropy parameter. The angular distribution of the fragments are described by $f(\theta) = \frac{1}{4\pi}\left(1+\beta P_2(\cos\theta)\right)$, where θ is the angle between the fragment recoil direction and excitation laser polarization angle.

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Tunnel ionization: enabling population inversion in molecular ions

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Recently, amplification of harmonic-seeded radiation generated through femtosecond laser filamentation in air has been observed, giving rise to coherent emissions at wavelengths corresponding to transitions between different vibrational levels of the electronic $B^2\Sigma_u^+$ and $X^2\Sigma_g^+$ states of molecular nitrogen ions [Phys. Rev. A 84, 051802(R)(2011)]. This unusual phenomenon seems to be universal as it has also been observed in other molecules such as carbon dioxide and water. It is extremely interesting that the lasing signal carries all the information of rotational wavepacket of the molecules, making it possible to retrieve the rotational states distribution from the lasing spectra. Here, we present the experimental and theoretical results and discuss the likely physical mechanism behind the population inversion.

Novel dye molecular clusters for nonlinear optical imaging

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We discuss producing molecular clusters that have unique nonlinear responses to linear light excitation for superresolution bioimaging applications. Two examples will be provided in this presentation. In the first example, two kinds of molecules are co-doped in a transparent nanoparticle, which could be fabricated using either silica or polymer materials. The small size of nanoparticles can confine the dyes in a very compact space, forcing energy exchange to occur between the molecular dyes. We show that such a fluorescent nanoparticle can exhibit exotic fluorescence behavior under the linear light excitation. In the second example, we show that similar fluorescent probes can be synthesized using chemical approaches. We present theoretical analysis on the fluorescence behavior of such nonlinear fluorescent probes.

The solvent-dependent dynamics of trans-4-DEAAB studied by femtosecond transient absorption spectroscopy

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Abstract: As we known, the excited state dynamics of molecules can be affected a lot by the solvent, such as DNA, stilbene, etc.[1,2] In order to avoiding ptotodamage, excess vibrational energy of ground state in DNA is transferred to the environment extremely rapid by H-bonding forming easily in protic solvent. In addition, new insights have been made into the role of solute/solvent friction by researching the isomerization dynamics of stilbene. The viscosity of the solvent can affect rotation relaxation rate along the reaction coordinate, because of the friction between solvent and solute. These solvation effects have considerable use in understanding the photoisomerization reactions of azobenzene and its derivatives. The solvent-dependent photoisomerization dynamics of a substituted trans-azobenzene, trans-4-diethylaminoazobenzene (trans-4-DEAAB) was studied in different polarity and viscosity solvents.

Combining with quantum computation, we determined that the time scale of internal conversion from the S_2 state to the S_1 state is faster in polar solvent than that in nonpolar solvent. It indicates that the energy gap at the crossing region between these two lowest excited states is smaller. What's more, the time scale of trans-cis photoisomerization of trans-4-DEAAB occurring on the S_1 state potential energy surface is similar in different viscosity solvents. It indicates that photoisomerization from the S_1 state occurs by an inversion mechanism, because the friction between high viscosity solvent and solute will result in much slower time scale of photoisomerization in the torsion mechanism. After photoisomerization to the hot S_0 state of cis-4-DEAAB, the time scale of the hot S_0 vibrational cooling is faster in protic solvent because hydrogen bond forming easily in protic solvent promotes energy transfer between solutes and solvents. The results suggest that the molecular environment affects the photoisomerization dynamics of the trans-4-DEAAB.

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The mechanisms of the relaxation of singlet excited state and formation of triplet states of polythiophenes

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Polythiophenes (nT, the number of monomers) have been extensively studied theoretically and experimentally, both for applications such as light-emitting diodes and for a better understanding of physical properties. Oligothiophenes are suit to study properties of the transition from monomer to polymer for their well-defined structures. When oligothiophenes interacts with light it becomes good singlet oxygen sensitizers and bio photosensitizers. In such interaction processes the singlet-to-triplet transition represents a key process in the phototoxic action.

Ultrafast broadband absorption measurements were performed based on the Ti:sapphire femtosecond laser system. The second harmonic pulse 400nm was used as the pump laser to excite the molecules. The white light continuum was generated by focusing a portion of 800nm laser pulse on a 1 mm thick sapphire crystal plate and used as the probe laser. The two laser beams were focused in the sample solution which flowed in a quartz cell with optical length of 1 mm. The angle between polarizations of the pump and the probe beam were set to the magic angle. Optical intensities of the probe and the reference light were detected by a CCD camera equipped with a spectrometer and the difference of the optical density was evaluated.

The fluorescence quantum yields are determined: ~0.01, ~0.04, ~0.20 and ~0.36 for 2T, 3T, 4T and 5T, respectively. The triplet quantum yield has the highest value 0.99 of 2T, and decreases from 0.95 of 3T to 0.59 of 5T. Combining with the quantum chemical calculations, we discussed the intersystem crossing and triplet transition processes of nT. We discussed the probable formation mechanism for intersystem crossing. It is interesting that the vibrational relaxation and coherence decay processes in 4T are observed due to very efficient coherence transfer between vibration levels.

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Role of the electron correlation in sequential double ionization

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Double ionization of atoms in strong field is one simple and fundamental process that reveals the electron correlation and has been of great interests over the past several decades. Nevertheless, due to the electron correlation, the underlying dynamics of double ionization is more complicated than single ionization and have not been fully understood. It is generally recognized that in the high intensity regime two electrons are independently ionized in a sequential way, which is called sequential double ionization (SDI). But the role of electron correlation in SDI is a long-standing question and has not be clarified.

In a very recent experiment, Pfeiffer et al.[1] demonstrated that the ionization time of Ar in the SDI regime is in good agreement with the prediction of single ionization formula for the first electron, but is much earlier than the theoretical prediction for the second electron. Such a finding doubts the previous idea of independent-electron approximation in the SDI regime and has attracted significant interests immediately. Zhou et al[2] and Eberly et al [3] have simulated the ionization time of Ar with a classical model by including or excluding the electron correlation, respectively. However, contradictions still exist between Zhou and Eberly et al. Moreover, the role of electron correlation is still not clear.

In our work, we investigate the SDI of Ar in an elliptically polarized field by using a quantum model. The experimental observations, such as the four-peak momentum distribution and the ionization time of the first and second electrons, are investigated and well reproduced with the quantum model. It is shown that the electron correlation indeed shifts the ionization time of the second electron. However, the accurate ionization time also depends on the focal volume geometry. Therefore, due to the experimental uncertainties, ionization times are not suited to reveal the role of electron correlation. However, based on the comparison of experiment and simulation, we show that the inclusion of electron correlation is necessary to reproduce the momentum distribution of electrons, clearly demonstrating the influence of electron correlation in the SDI regime.

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Control of Nuclear Motion and Electron Localization in Molecular Dissociation Using a Two-Color Laser Field

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The nuclear and electronic motions inside molecules are of fundamental importance in determining the formation and fracture of chemical bonds. The first realization of direct light-field control of a chemical reaction via the steering of electronic motion was achieved by Kling *et al.* in their experiment [1], where the electron localization in the dissociative ionization of D2 was controlled with a carrier-envelope phase (CEP) stabilized few-cycle pulse. This has stimulated continuous interest to study the strong-filed molecular dissociation and many methods have been proposed to control the nuclear motion and the electron localization in dissociating molecules [2–5].

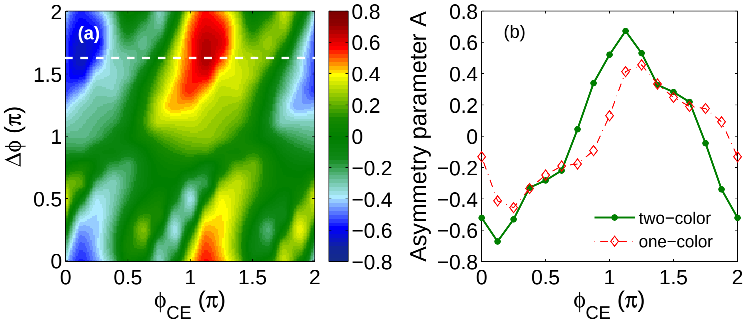

Figure 1: Average minimum (hollow) and maximum (solid) temperatures in Wuhan, Yichang and Chongqing.

Aiming at further enhancement of the control over electron localization, we have studied the nuclear motion and electron localization in H_2^+ dissociation by using a two-color laser field. In our scheme, the first pulse is used to drive a strong nuclear vibration with low ionization so that more electronic wave packets can be localized on the dissociating nuclei. To this end, we have chosen the 1600-nm midinfrared pulse with an intensity of 4×10^14 W/cm^2. The second weak pulse with a proper time delay of Δt can steer the electron by directly manipulating the electronic transfers in the one-photon coupling region with minor influence on the nuclear motion. Then the individual manipulations of nuclear vibration and electronic transfers can be efficiently achieved by changing the relative phase between the two laser pulses. As shown in Fig.1, the nuclear and electronic dynamics will reach a best balance at $\Delta\phi \approx 0.16\pi$ (indicated by the dashed line), and the degree of control over electron localization in the two-color scheme is significantly higher than that in a single midinfrared CEP-controlled field.

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Molecular orbital imaging with femtosecond laser pulses

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The femtosecond laser pulses have extremely short pulse duaration and extremely strong peak power. The apperence of femtosecond laser provides an unprecedented detection tool to investigate the material structure and ultrafast dynamics in extreme conditions, bringing the significant breakthrough and rapid development of strong-field physics. The recent investigation has demonstrated that, by initiating the ultrafast strong filed processes of the molecule with an femtosecond laser pulse, the emitted photonic and electronic signal carries abundant structural information about the molecular orbital of the detected molecule [1, 2]. Therefore, the imaging or structure detection of the molecular orbital can be achieved by analyzing the photonic and electronic signal. Since the molecular orbital carries the most important information reflecting the nature of the molecule, investigations on the imaging or structure detection of the molecular orbital will benefit people to realize the physical essence of the physical processes and chemical reactions in the microscopic world more directly and clearly. This will improve the development of not only physics but also many other disciplines such as chemistry, materials science and life science.

There are mainly two ways to realize the imaging or structure detection of a molecular orbital with femtosecond laser pulses. One is the ultrafast laser scanning method via strong-field ionization of molecules [3], and the other one is the molecular orbital tomography via high-order harmonic generation [4]. However, base on these two mechanisms, there are still many problems waiting to be solved. The symmetry of the molecular orbitals that can be imagined is restricted in previous works. To overcome this problem, we propose several methods to extend the range of application of molecular orbital imaging by using the nonlinearly polarized or two-color laser pulses or by applying new reconstruction algorithm [5, 6, 7]. Moreover, these methods may also eliminate the distortion and decrease the error in the recontested picture, or simplifying the experimental scheme and reducing the experimental difficulty.

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Friday, July 19	
08:45	Opening Ceremony *at WIPM*
Morning Session I *at WIPM* *Chair: Andrey V. Solov'yov*	
09:00	Jean-Patrick Connerade
09:30	Gordon W. F. Drake
10:00	Guanghou Wang
Evening session I *at the 5th floor* *Chair: Jean-Patrick Conneradе*	
20:00	Lai-Sheng Wang
20:30	Cheuk-Yiu Ng
21:00	Min Han

Saturday, July 20		
Morning Session I		
	I-1 *at the 5th floor* *Chair: Gerardo Delgado-Barrio*	I-2 *at the 6th floor* *Chair: Eleanor Campbell*
08:30	Vadim Ivanov	Henrik Cederquist
09:00	Philippe Brechignac	Uwe Becker
09:30	Fernand Spiegelman	Steven Manson
10:00	Coffee break	
Morning Session II		
	II-1 *at the 5th floor* *Chair: Philippe Brechignac*	II-2 *at the 6th floor* *Chair: Alfred Müller*
10:30	Gerardo Delgado-Barrio	Eleanor Campbell
11:00	Dong-Sheng Yang	Alfred Z Msezane
11:30	Hao Gong	Alexey Verkhovtsev

Sunday, July 21		
Afternonn Session I		
	I-1 *at the 5th floor* *Chair: Eric Suraud*	I-2 *at the 6th floor* *Chair: Vadim Ivanov*
14:30	Catherine Brechignac	Vitaly Kresin
15:00	Andrey Solov'yov	Bernd von Issendorf
15:30	Atsushi Nakajima	Konstantin Hirsch
16:00	Coffee break	
Afternonn Session II		
	II-1 *at the 5th floor* *Chair:Karl-Heinz Meiwes-Broer*	II-2 *at the 6th floor* *Chair: Bernd Huber*
16:30	Alfred Müller	Alexander Kuleff
17:00	Andrei Korol	André Fielicke
17:30	Himadri Chakraborty	Yongfeng Lu
20:00	Poster session *at the 6th floor*	

Monday, July 22		
Afternonn Session I		
	I-1 *at the 5th floor* *Chair: Henrik Cederquist*	I-2 *at the 6th floor* *Chair: Thomas Möller*
14:00	Bernd Huber	Jörg Voigtsberger
14:30	Eric Suraud	Julia Aysina
15:00	Weijun Zheng	Shenggui He
15:30	Coffee break	
Afternonn Session II		
	II-1 *at the 5th floor* *Chair:Catherine Brechignac*	II-2 *at the 6th floor* *Chair: Bernd von Issendorf*
16:00	Histao Yasumatsu	Karl-Heinz Meiwes-Broer
16:30	Gengyu Cao	Kiyonobu Nagaya
17:00		Thomas Möller