

# INTERNATIONAL SYMPOSIUM ON ATOMIC CLUSTER COLLISSIONS

October 2<sup>nd</sup> - October 6<sup>th</sup> 2017

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- 24.- Prof. Andrey V. Solov'yov (*Frankfurt*, Germany) Exploration of irradiation/collision induced processes in Meso-Bio-Nano (MBN) systems by means of MBN Explorer and MBN Studio
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Capture of heliophilic atoms by quantized vortices in  $^4\text{He}$  nanodroplets

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Particles with similar LET values generate DNA breaks of different complexity and reparability: a high-resolution microscopy analysis of  $\gamma\text{H2AX/53BP1}$  foci

30.- Prof. Llinersy Uranga-Piña (Havana, Cuba)

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31.- Prof. Aliezer Martinez-Mesa (Havana, Cuba)

Mechanisms of energy redistribution in laser-driven dynamics in interconnected quantum dot - metal nanoparticle systems

## **Adventures in Anion Photoelectron Spectroscopy**

**Kit H. Bowen**

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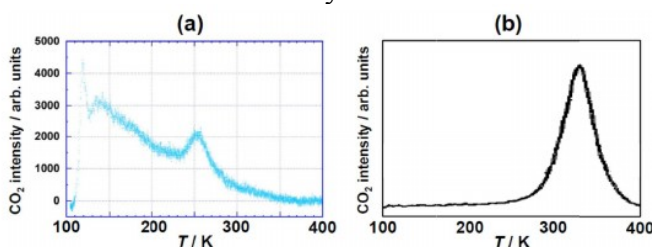
Negative ion photoelectron spectroscopy is a powerful technique for studying atomic, molecular, and cluster anions. Its fruits include electron affinities, electronic and vibrational splittings, geometrical structures, and thermochemical values. Anion photoelectron spectroscopy is a rather general technique; it has been used to study many topics in chemistry as well as several in biophysics, materials science, and condensed matter physics. Today's talk will sample some of the topics we have studied recently using this technique. These include electron-promoted activation of molecules, solvent-induced stabilization of otherwise unstable molecular anions, electron-induced proton transfer, ligation of metal clusters, cluster catalysis, and/or the characterization of highly diffuse electron states, such as dipole bound, quadrupole bound, and double Rydberg anions. The study of several of these systems was only possible because of the development of unique ion sources, some of which will also be discussed.

## Low-temperature catalytic activity of CO oxidation and NO reduction driven by uni-sized Pt clusters bound to Si substrate

Hisato Yasumatsu<sup>†1</sup> and Nobuyuki Fukui<sup>§2</sup>

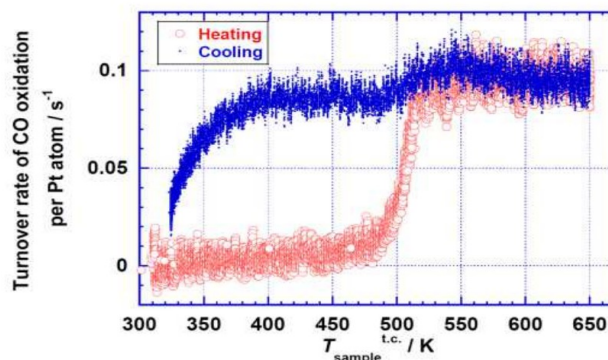
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As exhaust gas from fuel-efficient engines is cooler than that from conventional ones due to high thermal efficiency, lower-temperature catalytic converters are required for sustainable society still for decades. We are tackling this crucial issue with new materials, i.e. Pt cluster disks chemically bound to a Si substrate, Pt<sub>N</sub>/Si ( $N=5-60$ ) [1]. We have found that CO oxidation on the Pt<sub>30</sub>/Si disks starts at 130 K by atomically-adsorbed O [2], which is lower by 200 K than that on the Pt(111) single-crystal surface [3] (see Figure 1). Furthermore, NO reduction proceeds at lower temperature by 100 K than supported Pt nano-particles. In this talk, the prominent low-temperature catalytic activity is unveiled on a basis of surface-chemistry measurements.



**Figure 1.** Temperature-programmed reaction/desorption spectra of CO oxidation by atomically-adsorbed O on (a) Pt<sub>30</sub>/Si disks and (b) a Pt(111) single-crystal surface.

This particularity was observed also in turnover rates (TOR) under a more practical condition of continuous supply of CO and O<sub>2</sub> [4]. Figure 2 shows quasi-stead-state TOR of the CO oxidation on the Pt<sub>30</sub>/Si disks. Hysteresis is discernible in the heating and subsequent cooling periods due to the bistability switching between O- and CO-rich regimes of Pt<sub>30</sub>/Si, while no hysteresis for Pd nanoparticles on an MgO substrate [5]. Furthermore, the CO oxidation proceeds at as cool as 330 K in the cooling period.



**Figure 2.** CO-oxidation TOR on Pt<sub>30</sub>/Si disks at O<sub>2</sub> and CO pressures of  $1.3 \times 10^{-4}$  and  $2 \times 10^{-5}$  Pa, respectively.

Considering a report that a small reaction rate compared to the adsorption rates damps the hysteresis of nano-reactors [6], the atomic O species produced by Pt<sub>N</sub>/Si are highly reactive to maintain the hysteresis. This is also true in the NO reduction, in which reactive atomic N species recombine into N<sub>2</sub> at lower temperatures. It is probable that the low-temperature and highly-efficient catalytic activities of Pt<sub>N</sub>/Si derive from electron accumulation at the sub-nano interface between the Pt cluster and the Si surface [1].

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## Substrate and solvent effects studied in mixed molecular clusters

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Molecular clusters are unique model species enabling studies of bulk and surface processes by vacuum restricted methods. This is of particular importance for the reactions of low-energy electrons, which have extremely short penetration depth in bulk environments. This contribution overviews our recent experiments with low-energy electrons and clusters prepared by different techniques.

First, the deposition of molecules on argon nanoparticles enables the studies of electron induced chemistry of iron pentacarbonyl on the surface [1]. These studies are relevant for the focused electron beam induced deposition - FEBID technique. In this technique, high energy electron beam is used to create 3D metal nanostructures from organometallic precursors. The precursor molecules such as iron pentacarbonyl are known to be easily decomposed by low energy electrons created as a secondary species in the vicinity of the primary electron track. Already at electron energies near 0 eV, dissociative electron attachment leads to an effective loss of one organic ligand from the isolated compound. However, this reaction channel has not been observed in the surface experiments [2]. That was explained by trapping of the DEA reaction products inside the substrate. In our studies substrate is Ar cluster. In the case, the product ions are trapped in the substrate, we can detect the whole mixed cluster in our experiments. We clearly show that this is not the case. Therefore, the interaction with low energy electrons do not occur at all. We discuss the possible reasons in our recent publication [3].

Second, using the gas humidification method, we have been able to prepare single microhydrated molecules of uracil and its analogues that mimic biological conditions. It is believed that dissociative electron attachment to the nucleic acid bases can be the key process in the synergistic action of radiation with halogenated uracils in the concomitant chemoradiation therapy of cancer. Typically, electron attachment to halogen uracils leads to the formation of transient negative ion that dissociates to form Uyl radical or Uyl radical anion, which are highly reactive. Most of the studies so far therefore focus on the stability of the halouracil transient anions. In our recent study [4] we showed that the water environment is very effective in the stabilization of the transient anions and the dissociation is not effective. However, such stabilization results in the effective energy transfer to the solvent. We will show, how electron attachment spectroscopy of sequentially microhydrated halogen uracils can be used for estimation of the energy transferred to the solvent [5].

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## Energetics and Structure of Cluster Ions Inferred from Abundance Distributions

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If cluster ions are formed with excess energy and allowed to cool by evaporation, anomalies in the ensuing abundance distributions  $I_n$  often reveal corresponding anomalies in the evaporation (or dissociation) energies  $D_n$ . Anomalies in  $D_n$ , in turn, often provide a clue to the geometric structure. The correlation between  $I_n$  and independently computed  $D_n$  can be quite compelling.

This talk will focus on  $\text{Cs}^+$  or coronene clusters  $(\text{C}_{24}\text{H}_{12})_m^+ = \text{Cor}_m^+$  solvated in hydrogen. The corresponding neutral precursors are formed by passing He nanodroplets through a pickup cell containing Cs or coronene vapor and another cell containing  $\text{H}_2$ . The doped droplets are ionized by electron impact and extracted into a mass spectrometer.

Fig. 1 displays the abundance distribution of  $(\text{H}_2)_n\text{Cs}^+$  [1]. Abrupt drops in the abundance are observed at  $n = 8, 12, 32, 44,$  and  $52$ . Three of these,  $12, 32,$  and  $44$ , are identical to anomalies in the distribution of  $\text{He}_n\text{Ar}^+$  which had been assigned [2] to three solid-like nested solvation shells of icosahedral symmetry (an icosahedral shell inside a dodecahedral shell inside an icosahedral shell). That conjecture has been corroborated by a path-integral Monte Carlo study [3]. The origin of anomalies at  $n = 8$  and  $52$  remains to be explained.

The abundance of  $\text{Cor}^+$  solvated in hydrogen (Fig. 2a) features an abrupt drop at  $n = 38$  which likely corresponds to a structure in which all molecules occupy commensurate sites, i.e. 2 c-sites,  $2 \cdot 6$  i-sites, and  $2 \cdot 12$  o-sites with an overall  $D_{6h}$  symmetry. Additional anomalies at  $n = 32$  and  $36$  indicate that formation of vacancies in the crowded solvation shell can reduce stress.

For the coronene dimer ion the drop in the abundance shifts to  $n \approx 51$ . It shifts by about another 11 units for the coronene trimer, and another 10 for the tetramer. We assign these shifts to a columnar structure in which adjacent coronenes are parallel displaced, forming terraces that offer additional strong adsorption sites. The cartoon in Fig. 2b illustrates the dimer structure. The experimental value for the number of adsorption sites per terrace, approximately six, barely depends on the number of coronene molecules. The displacement estimated from this number (6)

exceeds the value reported in several theoretical studies of the bare, neutral coronene dimer.

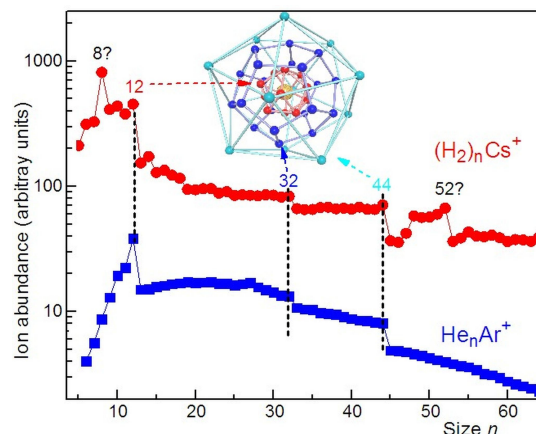


Fig. 1. Abundance of ions solvated in  $\text{H}_2$  and  $\text{He}$  [1,2].

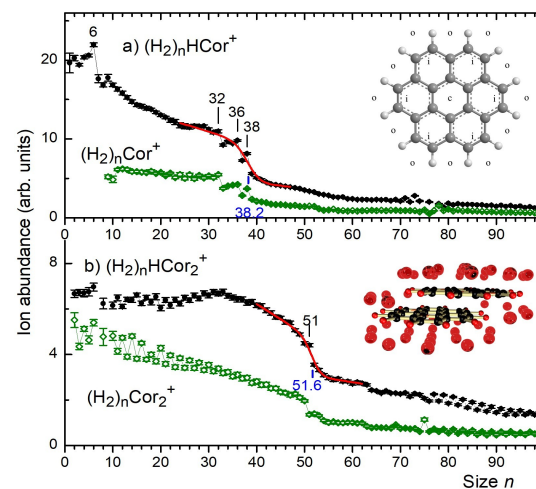


Fig. 2. Abundance of coronene monomer and dimer ions solvated in hydrogen [4].

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## Spin states of transition metal atoms in free clusters and organometallic complexes studied by x-ray magnetic circular dichroism spectroscopy

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While transition metals typically form high-spin states as free atoms, they might adopt high-spin or low-spin states when embedded into a host material, depending on the details of the interaction. The electronic ground states of endohedral transition-metal-doped silicon clusters have recently been discussed controversially, in particular with respect to high-spin [1] or low-spin ground states, [2] or to the presence of open-shell singlet states [3] with a local high-spin configuration on the transition metal atom that is counterbalanced by opposite spins in the silicon shell.

To resolve this controversy, we have studied a variety of size-selected transition metal atom doped silicon cluster ions by x-ray magnetic circular dichroism spectroscopy in a dedicated ion trap setup at the Berlin synchrotron radiation source BESSY II, [4–6] where we find a qualitatively similar behaviour of different transition metals. For a broader view, we have extended the range of samples to organometallic sandwich complexes of 3d transition metals with well-characterized ground states as simple model systems for spin states of endohedral clusters.

This talk will briefly summarize the spectroscopic technique of x-ray magnetic circular dichroism in cryogenic ion traps that has recently even been able to demonstrate ion temperatures as low as  $7.4 \pm 0.2$  K of a cloud of approx.  $10^7$  ions in the space charge limit. [7] General findings on

the interdependency of electronic and geometric structure of transition metal doped silicon and organometallic clusters will be discussed from the spectroscopic point of view.

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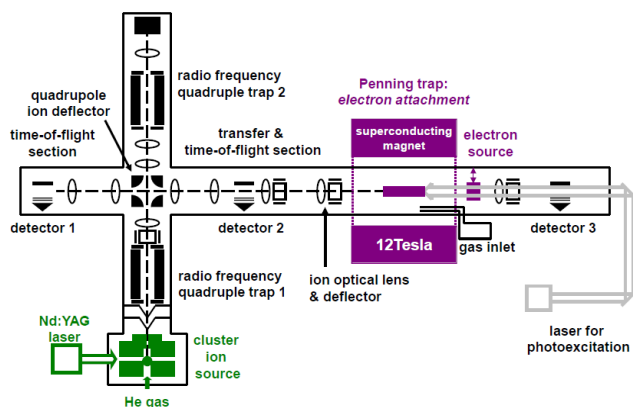


## Polyanionic metal clusters: How to make ‘em and to break ‘em

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Clusters of a few up to a few hundred atoms bridge the gap between single atoms and the bulk phases of matter. Their properties are governed by their geometric and electronic structure. There is a competition between both aspects and depending on the material one or the other dominates. Insight can be gained by varying both the cluster size, i.e. the number of constituents and thus their spatial arrangements, as well as their charge state and thus the occupation of the electronic levels.

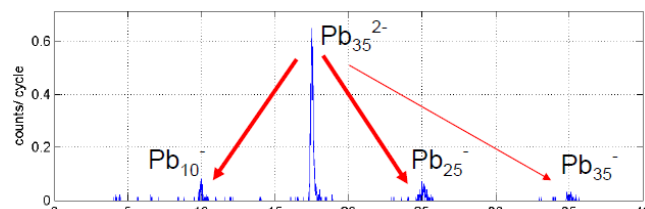


**Figure 1.** Schematic overview of ClusterTrap setup.

While there is a long tradition of the investigation of multiply charged cationic systems, the production of multiply negatively charged clusters, i.e. the attachment of further excess electron, is more challenging. A successful approach was found at ClusterTrap [1] (Fig. 1) by subjecting mono-anionic clusters to an electron bath in a Penning trap [2,3]. Gold clusters, e.g., of charge states up to  $z = -6$ , i.e. with six excess electrons [1] and, recently, aluminum clusters even up to  $z = -10$  have been observed. The corresponding appearance sizes, were studied in detail [4].

In addition, polyanionic clusters have been probed with respect to their stability and decay processes upon excitation, e.g. by laser irradiation. The decay pathways include electron emission and evaporation of neutral atoms. They depend on the cluster sizes under investigation [5]. Recently, new decay pathways were found, where

larger fragments (either neutral or charged) break off (Fig. 2).



**Figure 2.** Cluster abundance spectrum after photoexcitation of size-selected dianionic lead clusters.

On the technical side, the production of polyanionic clusters by attachment of further excess electrons has been extended to Paul traps, i.e. rf traps that operate without a field of a superconducting magnet. To this end, a “3-state digital ion trap” has been developed [6] for the electron-beam irradiation of stored clusters in the field-free time windows of the guiding field [1].

Furthermore, the upcoming investigations of polyanionic metal clusters will include time-resolved measurements of delayed photodissociation, which have already proven very valuable in the case of mono-cations [7,8]. And, last but not least, the first photoelectron spectra of polyanionic metal clusters have been recorded recently.

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## Size-dependent reactivity of transition-metal-doped silver clusters: A study of electronic and geometric structures

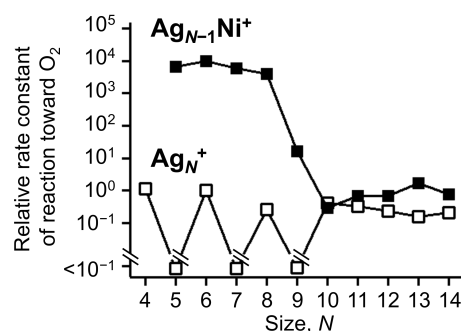
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Transition-metal-doped coinage metal clusters provide us with a model system for investigating s-d electron interaction in the finite-size regime, which is known as the Kondo effect in the bulk. The first cluster experiment was performed by photofragmentation of positively charged Au [1] or Ag [2] cluster cations doped with a series of open 3d transition-metal atom, where highly abundant magic sizes were observed in the fragment mass spectra. These sizes were explained to have enhanced stability due to a closed electronic shell with 18 valence electrons formed by delocalized 3d electrons along with s electrons of the dopant and the host atoms. These studies pointed out that the clusters tend to promote delocalization of 3d electrons when a closed electronic shell can be formed. Recently X-ray spectroscopy has been performed to discuss s-d electron interaction [3,4]. Size-dependent change in the electronic structures has been investigated also by a computational study [5]. In this context, corresponding anionic clusters have been studied as well by photoelectron spectroscopy [6-8], although it is limited only to several systems. Studies of anions are important to examine influence of the number of electrons in the system compared with cations.

To extend these studies in a systematic way, the present study employs chemical reaction to probe electronic structures both for cations and for anions; reactivity is expected to be reduced upon electronic-shell closure. We have carried out reactivity measurement of 3d-transition-metal (M) doped silver cluster cations ( $\text{Ag}_N\text{M}^+$ ) and anions ( $\text{Ag}_N\text{M}^-$ ) toward oxygen. Figure 1 shows the result obtained for  $\text{Ag}_{N-1}\text{Ni}^+$  along with that of bare  $\text{Ag}_N^+$ ; the value of  $N$  is shifted by one so as to compare clusters with the same number of constituent atoms. A dramatic drop in the

reactivity was observed for  $\text{Ag}_{N-1}\text{Ni}^+$  at  $N = 9$ ; the reactivity at  $N > 9$  is at the same level as those of  $\text{Ag}_N^+$ . This behavior is explained by encapsulation of the Ni atom at larger sizes, i.e., screening the active site. A reactivity minimum was observed at  $N = 10$ , which is attributable to an 18-electron closed shell, suggesting delocalized Ni 3d electrons [9]. We will report our results obtained for a series of dopant atoms ( $M = \text{Sc-Ni}$ ) for cations and several preliminary results for anions.



**Figure 1.** Relative reaction-rate constants of  $\text{Ag}_{N-1}\text{Ni}^+$  and  $\text{Ag}_N^+$  toward an  $\text{O}_2$  molecule

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## The Complex Nonmetal-to-Metal Transition in Zinc Clusters

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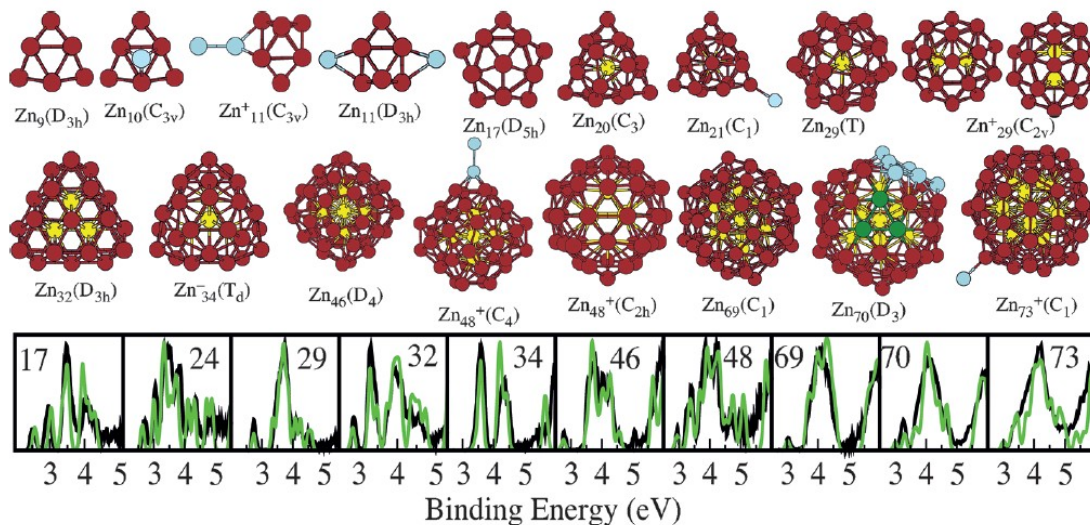
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Divalent metal clusters are known to exhibit a nonmetal-to-metal transition as a function of size. Small clusters exhibit a pronounced band-gap, which can be well observed by photoelectron spectroscopy on cluster anions [1-3]. With increasing size this gap shrinks until it vanishes at a material dependent size, which has been interpreted as the onset of metallicity. In a combined experimental/theoretical study on zinc clusters we could now show that the situation is much more complex: for some seemingly metallic particles metallic and insulating phases exist within the same particle; furthermore most of the particles exhibit a core-shell structure with a very weak interaction between the core and the shell, which can even lead to different symmetry properties of both regions[4].

The results demonstrate that there is no well-defined and abrupt transition from an insulator to a simple metal, but rather a large transition region where the clusters exhibit properties very unusual both for insulating and metallic systems.

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**Figure 1:** Putative ground state structures of different zinc clusters and comparison of measured photoelectron spectra with calculated density of states. Blue spheres indicate weakly bound atoms; yellow spheres core regions uncoupled from the shell region (red spheres). From [4].

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## Fragmentation of doubly and triply charged mercury clusters

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As a mercury atom has an electronically closed shell structure, the van der Waals dispersion force dominates in the binding of small mercury clusters. As the cluster size increases, the metallic property appears [1]. Sato and coworkers observed fragmentation of doubly and triply charged mercury clusters [2]. Parent clusters are produced by ion bombardments on amalgam surface. Fragment size distribution in the decay of doubly charged clusters was observed. The appearance size, the minimum size that a multiply charged cluster is stable, is measured for doubly and triply charged clusters.

We make an analysis on this experiment to reveal the mechanism of fragmentation. In the upper panel of Fig. 1, we show the measured fragment size distribution in the fission  $\text{Hg}_n^{2+} \rightarrow \text{Hg}_m^+ + \text{Hg}_{n-m}^+$  for parent size  $n = 11$  as a function of fragment size  $m (> 2/n)$ . As shown the figure, nearly symmetric fission ( $m = 6$  and  $7$ ) are predominantly observed. In the lower panel, we show the energy barrier  $E_b$  in this fission calculated with a liquid drop model proposed by Echt et al.[3]. The energy barrier is lower for nearly symmetric fission and is higher for strongly asymmetric fission. The calculation well explains the experiment. It means that small mercury clusters behave as van der Waals clusters.

In table 1, we show two types of critical sizes,  $n_{c1}$  and  $n_{c2}$  calculated with this model. The former corresponds to the size where all the fragmentation path has a finite energy barrier while the latter the size where the fission barrier exceeds the monomer evaporation energy. The measured appearance sizes are found to be close to  $n_{c2}$ . This fact means that clusters are internally so excited that fission and evaporation takes place competitively.

Table 1. Appearance sizes for  $\text{Hg}_n^{z+}$ , calculated and measured values.

$z$	$n_{c1}$	$n_{c2}$	experiment [2]
2	14	22	20
3	27	41	46

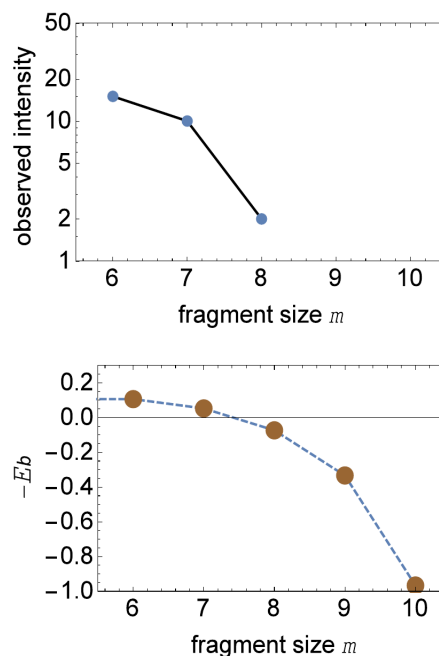


Figure 1. The upper panel is logarithmic plot for product size distribution in  $\text{Hg}_{11}^{2+} \rightarrow \text{Hg}_m^+ + \text{Hg}_{11-m}^+$  [2] and the lower panel shows the energy barrier  $E_b$  as a function of fragment size  $m$ .

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## Electron attachment to molecules in a cluster environment: suppression and enhancement effects

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Cluster and surface environments can strongly influence dissociative electron attachment (DEA) processes. These effects are important in many applications, particularly for surface chemistry, radiation damage, and atmospheric physics. The effects can vary depending on physical mechanisms involved in the process. If the DEA is controlled by a vibrational Feshbach resonance (VFR) due to long-range electron-molecule interaction, surface or cluster environment screens this interaction resulting in the VFR suppression. A remarkable example is DEA to the CH<sub>3</sub>I molecule [1]. Very pronounced VFR is observed in DEA to this molecule below the first threshold for excitation of the symmetric stretch C-I vibrations in the gas phase. In addition, there is a very strong enhancement of DEA cross sections at low energies due to the weakly-bound anion state (that is actually a virtual state at the equilibrium geometry due to rotational effects). However, both effects were not observed [2] in DEA to CH<sub>3</sub>I on a surface of rare-gas films at cryogenic temperatures.

On the other hand, the surface and cluster environments can cause not only suppression, but also a strong enhancement of DEA cross sections. In many chloro- and chlorofluorocarbons the effect is mostly caused by the downward shift of the anion potential energy curves due to the polarization interaction between the anion in the resonance state and the medium. To describe these effects for clusters, a multiple-scattering theory combined with the nonlocal complex potential theory has been developed [3]. The scattering matrix and the wavefunction for electron scattering in the cluster environment is constructed using the scattering matrix for each individual molecule. Then this wavefunction is used to modify the electron capture amplitude in the presence of a cluster environment [3]. In addition the resonance negative-ion curve is shifted to represent the long-range interaction between the attaching molecule and the cluster

molecules. In small-size cluster the dipolar interaction becomes important, and as a result, depending on the orientation of molecules in the cluster, the shift can be both negative and positive [4]. However, for large-size clusters the polarization interaction takes over, and the shift is dominantly negative.

The results of DEA to molecules in a water cluster environment [3,5] show a new interesting feature: the width of the low-energy shape resonance decreases resulting in a higher surviving probability of the resonance negative ion state and enhancement of the cross section. This phenomenon can be explained by the trapping effects: after autodetachment electron can

be rescattered and recaptured by the attaching molecule. However, the present theory does not trace the fate of the survival anion which can be destroyed due to caging effect and/or other reaction processes. Indeed, in recent experiments [6] with microsolvated uracil and thymine the DEA channels were suppressed, and only intact molecular and hydrated anions were detected.

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## **The photo electron cutoff for ionization with intense few cycle pulses: From atoms over clusters and nanoplasmas to liquids**

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High order above threshold ionization leads in atoms to a well known cutoff for the photo electron energy of  $10.007 U_p$ , where  $U_p$  is the ponderomotive energy. Does a similar cutoff exist in extended targets and if so, how does it evolve from the atomic limit ?

We will show that this is indeed the case where for finite systems the cutoff is larger than the atomic one for two reasons (i) photo electrons can re-scatter from a different atom since (in contrast to high harmonic generation) the process is incoherent, (ii) they impact the atom at recollision with a higher momentum since they are accelerated by a positive background potential (of the cluster or nanoplasma).

A very simple description gives a universal maximal cutoff energy as a function of the radius of the extended target  $R$  scaled to the quiver amplitude and the depth  $V$  of the background potential.

Comparison with new experimental data on clusters and results from molecular dynamics simulations for different parameters of cluster size (a few 10 to a few 10000 atoms) pulse intensity, pulse length (in the 10 fs range) and photon wavelength (from 2 microns to 400 nm) show good agreement with the simple prediction and underscore its universal character.

## Quantum Chemistry-like and Path Integral Calculations on Doped Helium Clusters

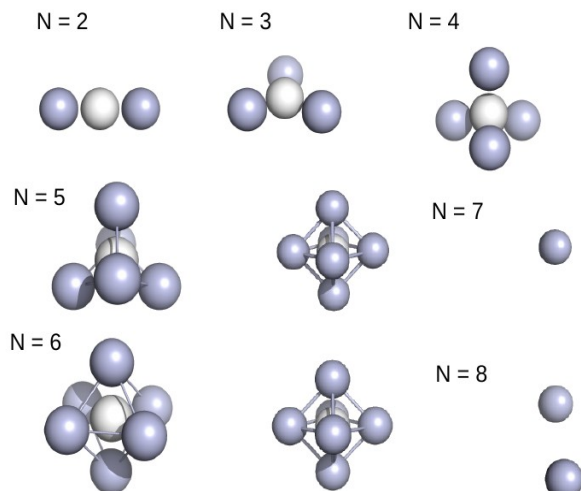
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**Synopsis** For molecular species immersed in or attached to helium clusters, quantum chemistry-like and Path Integral calculations are presented and discussed.

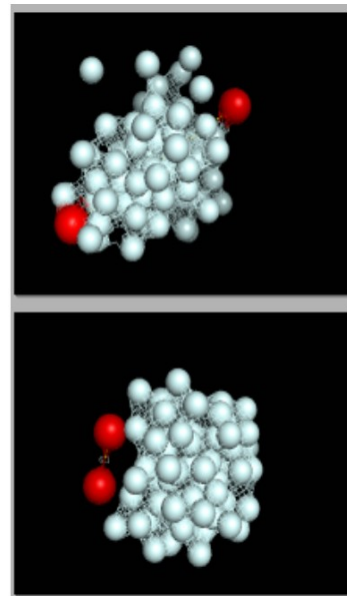
We review some theoretical studies carried out in our group involving molecular species immersed in (or attached to) He clusters at very low temperatures. Using a quantum chemistry-like methodology, superfluidity of boson  $^4\text{He}$  (in contrast with fermion  $^3\text{He}$ ) clusters is demonstrated for dopants residing inside the droplet by spectroscopic IR or Raman simulations depending on their polar or non-polar nature [1, 2, 3, 4]. Also, Path Integral Monte Carlo (PIMC) calculations are used to determine the energy and structure for different atomic, molecular and ionic species sometimes placed at the surface of boson He droplets [5, 6, 7, 8]. Fig 1 displays initial configurations obtained through an evolutive algorithm for further PIMC simulations of small  $^4\text{He}_N$  clusters doped with an  $^4\text{He}^{*-}$  anion [7, 8].

In turn, Fig 2 displays the formation of a rubidium dimer on a  $^4\text{He}_{70}$  cluster obtained using a coloured thermostat in a Path Integral Molecular Dynamics (PIMD) simulation with the i-PI package [9]. The approaching of rubidium atoms evolves inside the helium aggregate and eventually the  $\text{Rb}_2$  emerges towards the surface of the cluster.



**Figure 1.** Initial configurations of  $^4\text{He}_N$ - $^4\text{He}^{*-}$ anionic clusters.

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**Figure 2.**  $^{87}\text{Rb}_2(^3\Sigma_u^+)$ - $^4\text{He}_{70}$  complex: Initial configuration (upper panel) and final one (lower panel) after a PIMD simulation at  $T=2$  K.

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## Negative ions formation in fullerenes and heavy complex atoms

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**Synopsis** Our robust Regge pole methodology is used to explore negative ion formation in low-energy electron elastic scattering from  $C_n$  ( $n=20$  to  $240$ ) and selected heavy atoms through the total cross sections (TCSs) calculation. All the TCSs are found to be characterized by dramatically sharp resonances manifesting stable anionic formation during the collisions. The energy positions of the anionic ground states resonances are compared with the measured electron affinities

Recently, a theoretical breakthrough was achieved in low-energy electron scattering from fullerenes through our robust Regge pole methodology [1], where-in is fully embedded the electron-electron correlations and the vital core-polarization interaction. Entirely new in the field of cluster/fullerene collisions, the Regge pole methodology was benchmarked on the measured electron affinities (EAs) of  $C_{60}$  and  $C_{70}$  fullerenes [2, 3].

The unprecedented accomplishments of the Regge pole methodology in low-energy electron elastic scattering are demonstrated in the following:

**Ground state fullerene negative ion formation:** The Regge pole methodology has been used to calculate ground state TCSs for selected fullerenes, from  $C_{54}$  through  $C_{240}$ . Our energy positions of the very sharp anionic resonances in the TCSs and the measured EAs [2-4] matched excellently.

**Long-lived metastable anions in fullerene molecules  $C_{60}$  to  $C_{92}$ :** A strong motivation for the exploration is the availability of high quality measured EAs for the fullerenes from  $C_{60}$  through  $C_{92}$  [2-4] and the experimental observation that electron scattering cross sections from fullerenes are characterized by long lived metastable anionic formation [5]. Indeed, the TCSs are characterized by sharp resonances manifesting both ground and metastable anionic formation. Importantly, the metastable anionic states could be mistaken for the ground state anions and the impact of the size is drastic as the fullerene size changes from  $C_{76}$  through  $C_{82}$  to  $C_{92}$ ; it induces additional metastable resonances in TCSs.

**New insights in low-energy electron-fullerene interactions:** Additional to producing first time anions in  $C_n$  ( $n=20, 24, 26, 28, 44, 70, 92$  and  $112$ ) through low-energy electron scattering TCSs, here we also investigated the size-effect through the induced metastable resonances as the fullerene size varied from  $C_{20}$  through  $C_{112}$ . The  $C_{20}$  TCSs exhibit atomic behavior consistent with the view [6] while the  $C_{112}$  TCSs demonstrate strong departure from atomic behavior due to the size effect. Surprisingly, the small  $C_{24}$  has the largest EA, 3.79 eV among the investigated fullerenes. It is therefore suitable for use in organic solar cells to counter the rate of irreversible polymer photobleaching in blend films (polymer: fullerene) and to resist fullerene degradation by the photo-oxidation mechanism [7]. The large fullerenes  $C_{92}$  and  $C_{112}$  and the small fullerene

$C_{24}$  could be used to catalyze the oxidation of water to peroxide through their first metastable anions as well as serve as an inexpensive single nanocatalyst for water purification in the developing world [8].

**Conundrum in measured electron affinities of heavy atoms:** Recently, the EA of atomic Eu was measured to be  $0.116 \pm 0.013$  eV [9]. This value is in outstanding agreement with the values of the Regge pole [10] and MCDF-RCI [11] methods. Previously, the EA of Eu was measured to be  $1.053 \pm 0.025$  eV [12], which agrees excellently with the Regge pole value of 1.085 eV. Here we have a conundrum because an atom can have only a single EA. Also, a recent experiment [13] measured the EA of Nb and obtained generally good agreement with existing theoretical EAs, including ours which corresponds to the BE of an excited state. Our  $Nb^-$  ground state BE is 2.48 eV. The quandary requires that the measured EAs above, including those for Gd, Tb and Tm be reinterpreted.

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## **Attosecond control of electron acceleration in cluster Coulomb explosions**

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Strong field driven electron recollision is the key to conduct high-harmonic spectroscopy experiments, laser-induced electron diffraction, and allows to generate attosecond pulses. In atoms, molecules, and surfaces elastic backscattering produces the most energetic electrons and enables for an precise spectral, directional, and temporal control of the acceleration process through the sub-cycle waveform of the driving laser field. With metal clusters we reveal a so far unexplored route for waveform controlled electron acceleration emerging from the extreme enhancement of forward rescattering in plasmonic systems [1]. In the experiments we studied the plasmon-

enhanced photoemission from silver clusters and find that the directional electron acceleration can be controlled up to keV energies through the relative phase of a two-color laser light field.

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## Attosecond Molecular Dynamics

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Attosecond light pulses allow one to probe the inner workings of atoms, molecules and surfaces on the timescale of the electronic motion. For example, in molecules, sudden ionization by an attosecond pulse is followed by charge redistribution on a time scale from a few-femtoseconds down to hundreds attoseconds, which is usually followed by fragmentation of the remaining molecular cation. Such complex dynamics arises from the coherent superposition of electronic states covered by the broadband attosecond pulse and from rearrangements in the electronic structure of the molecular cation due to electron correlation. To investigate these ultrafast processes, attosecond pump-probe and transient absorption spectroscopies have been shown to be very valuable tools [1-10]. In this talk I will present the results of molecular attosecond pump-probe experiments and theoretical simulations in which several molecules, from the simplest H<sub>2</sub> one to the aminoacids phenylalanine and tryptophan, are ionized with a single attosecond pulse (or a train of attosecond pulses) and are subsequently probed by one or several infrared or xuv few-cycle pulses. In all cases, the evolution of the electronic and nuclear densities in the photo-excited molecule or remaining molecular ions can be inferred from the measured (or calculated) ionization or fragmentation yields with attosecond time-resolution, and can be visualized by varying the delay between the pump and probe pulses. The results of these pioneering works will certainly serve as a guide of future experimental efforts in more complicated molecules and may open the door to the control of charge transfer in biologically relevant processes.

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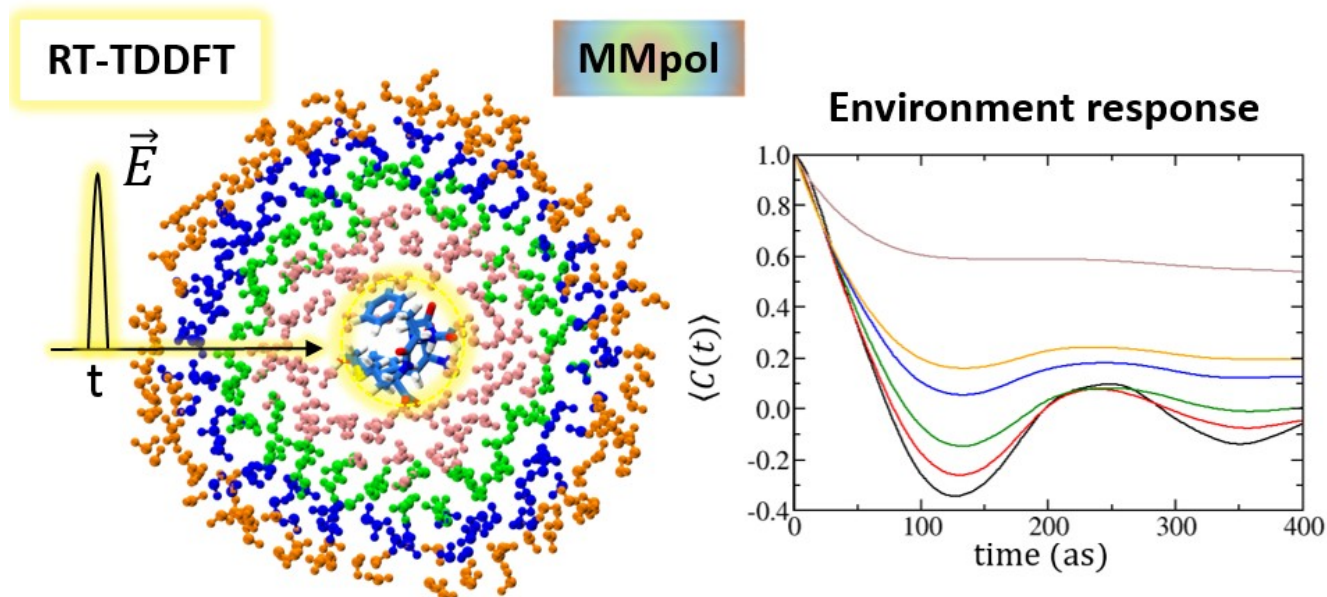
## Simulating Electron Dynamics in Polarizable Environments

Xiaojing Wu<sup>a</sup>, Jean-Marie Teuler<sup>a</sup>, Fabien Cailliez<sup>a</sup>, Carine Clavaguéra<sup>a</sup>, Dennis Salahub<sup>b,c</sup> and Aurélien de la Lande<sup>a</sup>

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We propose a methodology for simulating attosecond electron dynamics in large molecular systems. Our approach is based on the combination of Real-Time Time-Dependent-Density-Functional-Theory (RT-TDDFT) and polarizable Molecular Mechanics (MMpol) with the point-charge-dipole model of electrostatic induction. We implemented this methodology in the software deMon2k that relies heavily on auxiliary fitted densities. In the context of RT-TDDFT/MMpol simulations, fitted densities allow the cost of the calculations to be reduced drastically on three fronts i) the Kohn-Sham potential, ii) the electric field created by the (fluctuating) electron cloud which is needed in the QM/MM interaction, and iii) the analysis of the fluctuating electron density on-the-fly. We determine conditions under which fitted densities can be used without

jeopardizing the reliability of the simulations. Very encouraging results are found both for stationary and time-dependent calculations. We report absorption spectra of a dye molecule in the gas phase, in non-polarizable water and in polarizable water. Finally, we use our method to analyze the distance-dependent response of the environment of a peptide perturbed by an electric field. Different response mechanisms are identified. It is shown that the induction on MM sites allows excess energy to dissipate from the QM region to the environment. In this regard, the first hydration shell plays an essential role in absorbing energy. Overall our methodology opens the possibility of simulating radiation-induced electronic phenomena in complex and extended molecular systems.



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## **New Surface Hopping Methods for Simulating Nonadiabatic Dynamics in Molecules and Clusters**

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In this talk, we discuss the quantum-classical dynamics of nonadiabatic transitions from the perspective of trajectory surface hopping. Our approach builds on the semiclassical Liouville formalism for describing the dynamics of generalized phase space distributions representing elements of the electronic density matrix. The result is a new method for trajectory surface hopping “by consensus”, where individual trajectories interact and influence each other in a

way that captures the underlying features of exact quantum dynamics. We describe modifications to the existing trajectory surface hopping method of Fewest Switches Surface Hopping (FSSH) to incorporate the insights gained from our consensus formalism while retaining the numerical advantages of FSSH. Finally, we describe applications to electronic nonadiabatic dynamics and vibrational predissociation of clusters.

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## Trajectory surface hopping study of the photodissociation dynamics of methyl radical from the 3s and 3p<sub>z</sub> Rydberg states.

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The methyl radical is employed commonly in both, applied and fundamental studies of Chemistry. Although it has been historically used as a benchmark system in molecular orbital theory for the photochemistry of larger open-shell hydrocarbons[1]; it is used also in areas like atmospheric[2] and interstellar chemistry[3] or hydrocarbon combustion[4]. Recently, experimental studies of the excited states of this radical has been carried out employing the resonance enhanced multiphoton ionization (REMPI) technique[5, 6].

**Table 1.** Lifetimes of studied vibrational levels of the 3s and 3p<sub>z</sub> Rydberg states. The third and fourth columns correspond to the results of this work( $\tau$ ). In the last column, lifetimes reported in [5] for vibrational levels of 3p<sub>z</sub> Rydberg state ( $\tau_{exp}$ ) are showed for better comparison. Subpicosecond lifetimes between 60 and 80 fs were reported by Westre et al [9] for the 3s Rydberg state presenting a smooth J dependency.

$\nu_1$	$\nu_2$	$\tau$ (fs)		$\tau_{exp}$ (fs)
		3s	3p <sub>z</sub>	
0	0	31.90	763.56	720 ± 70
0	1	49.89	435.20	500 ± 50
0	2	21.67	156.80	320 ± 100
0	3	19.82	94.79	-
1	0	21.96	74.87	410 ± 70
1	1	20.23	93.63	310 ± 90
1	2	19.00	84.59	300 ± 40
1	3	17.47	43.25	-
2	0	19.36	66.57	-
2	1	17.92	42.62	-

In order to validate the results of such experiments the photodissociation of the methyl radical (CH<sub>3</sub>) from the 3s and 3p<sub>z</sub> Rydberg states has been studied using a quasi-classical approximation. Specifically, we build a code that employs the trajectory surface hopping method together with the fewest switches algorithm (TSH-FS) [7, 8].

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## Photoinduced energy relaxation and redistribution in chlorophylls

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Optical properties of chlorophylls have drawn considerable attention because of their fundamental and biological relevance. Chlorophylls play an essential role in the conversion of sunlight into chemical energy in Green plants and various algae. Furthermore, they are also widely studied as candidates for molecular electronics applications. In this work, Non-Adiabatic Excited-State Molecular Dynamics simulations (NA-ESMD)[1] have been performed to study the internal conversion process in chlorophylls. We aim to achieve a detailed comprehension of the ultrafast intramolecular electronic and vibrational energy transfer that takes place after photoexcitation. Within our NA-ESMD framework, direct nonadiabatic molecular dynamics simulations can be applied to describe photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such NA-ESMD simulations are performed by combining the molecular dynamics with quantum transitions (MDQT) approach with “on the fly” analytical calculations of excited state energies, gradients, and non-adiabatic couplings terms. We present results of the intra- and intermolecular redistribution of the electronic transition density during the internal conversion process[2],[3]. Excited state trajectories are analyzed in terms of the ground state equilibrium normal modes[4]. Our analysis of the time evolution of the average mode energies uncovers that only a

small subset of the medium-to-high frequency normal modes actively participate in the electronic relaxation processes. These active modes are characterized by the highest overlap with the nonadiabatic coupling vectors (NACRs) during the electronic transitions. Further statistical analysis of the nonadiabatic transitions reveals that the electronic and vibrational energy relaxation occurs via two distinct pathways with significantly different time scales.

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## Photoinduced dynamics in weakly coupled equivalent chromophores

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Dendrimers are arrays of coupled chromophores, with the energy of each unit depending on backbone structure and conformation. Light harvesting and energy funneling properties are strongly dependent on their highly branched conjugated architecture. Herein, the photoexcitation and subsequent ultrafast electronic energy relaxation and redistribution of a first generation dendrimer (Ph<sub>3</sub>PG-1)[2] is analyzed combining theoretical and experimental studies. Ph<sub>3</sub>PG-1 consists of three linear phenylene-ethynylene (PE) units, or branches, attached in *meta* position to a central group opening the possibility of inter-branch energy transfer. Excited state dynamics are explored using either time-resolved spectroscopy and non-adiabatic excited state molecular dynamics simulations (NA-ESMD)[1]. Our results indicate a subpicosecond loss of anisotropy due to an initial exciton delocalization, induced by couplings among branches, followed by a random exciton self-trapping on different units. The absence of an energy gradient leads to an ultrafast energy redistribution among isoenergetic chromophore units. We observe final similar probabilities for each branch to retain significant contributions of the lowest excited-state electronic transition density. The observed unpolarized emission is attributed to the contraction of the electronic wavefunction in a single branch rather than corresponds to its expansion over the whole dendrimer.

On the other hand, NA-ESMD approach was applied to investigate photoexcited dynamics and relaxations pathways in a spiro-link conjugated polyfluorene at room (T=300K) and low (T=10K) temperatures. These dimeric aggregates consist of two perpendicularly oriented weakly interacting  $\alpha$ -polyfluorenes oligomers. The negligible cou-

pling between the monomer chains results in an initial absorption band composed of equal contributions of the two lowest excited electronic states, each localized on one of the two chains. After photoexcitation, an efficient ultrafast localization of all the electronic population to the lowest excited state is observed on the timescale of about 100 fs. Both internal conversion between excited electronic states and vibronic energy relaxation on a single electronic state contribute to this process. Thus, photoexcited dynamics of the polyfluorene dimer follows two distinct pathways with substantial temperature dependence of their efficiency. One relaxation channel involves resonance electronic energy transfer between the monomer chains, whereas the second pathway concerns the relaxation of the electronic energy on the same chain that has been initially excited due to electron-phonon coupling. Our numerical simulations analyze the effects of molecular geometry distortion during the electronic energy redistribution and suggest spectroscopic signatures reflecting complex electron-vibrational dynamics.

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## About the electric properties of spatially confined molecular systems

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Studies concerning the spatial confinement phenomenon and its influence on the variety of physical and chemical properties of quantum objects have been attracting an increasing research attention. This is triggered by the great advances in nanotechnology, as well as the rapid development of chemical synthesis methods, particularly in the supramolecular chemistry [1, 2, 3]. These factors open up a fascinating possibility of constructing molecular systems with entirely new properties, mostly determined by the size effects (e.g. endohedral complexes, inclusion compounds or low-dimensional semiconductor structures). One area of research of increasing prominence concerns the linear and nonlinear (L&NLO) electric properties of spatially restricted atoms, ions and molecules. Basically, it is expected that embedding of a quantum system in the confining cages will affect its electronic density distribution. This, in turn, may be reflected through changes in a variety of L&NLO phenomena.

In the present contribution we focus on the theoretical description of the interactions between the molecular matter and the electric field under the spatial confinement (orbital compression). Particularly, the main objective of this work is the qualitative and quantitative analysis on the spatial restriction influence on the linear and nonlinear properties of different type of molecules (polar diatomic molecules,  $\pi$ -electron molecules, noble gas compounds) [4, 5, 6, 7] as well as hydrogen bonded complexes [8]. Among the evaluated molecular quantities are properties that govern the NLO processes in the resonant (TPA probability) as well as nonresonant (dipole moment, polarizability, first hyperpolarizability) regime upon confinement. All results, presented within this study, are obtained employing quantum chemistry methods based on the wave function, primarily those which go beyond the independent particles approximation.

The results of theoretical studies, conducted for the considered molecular systems, demonstrate that together with the increasing strength of spatial confinement one may observe an increase, decrease, or non-monotonic changes in the values of studied electric properties [4, 5, 6, 7]. This conclusion is particularly true for the dipole moment and first hyperpolarizability of analyzed molecules. Moreover, the obtained data provide an evidence that the orbital compression might have a significant influence on the magnitude of two-photon absorption response of molecular system [8]. On the other hand, the presented results allow to formulate a thesis that the pure orbital compression effect causes a reduction of the linear dipole polarizability [4, 5, 6, 7].

Summing up, our results indicate the possibility of strengthening the nonlinear electrical response of molecular systems under the influence of spatial confinement of cylindrical symmetry.

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## **Energy dissipation in abstraction processes from metallic surfaces**

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The rationalization of elementary processes at surfaces is of prime importance for numerous natural and technological areas. From a fundamental point of view, the way the energy concomitant to any chemical reaction is distributed among the desorbing molecules degrees-of-freedom and the surface is not entirely pictured. Over the last few years, we have been developing molecular dynamics simulations to investigate this issue for the recombination of H<sub>2</sub> and N<sub>2</sub> resulting from atomic adsorbate abstraction by atom scattering off the W(100) and W(110) covered

surfaces. Potential energy surfaces, built from density functional (DFT) theory calculations, have been used to simulate, within the framework of classical dynamics (including semi-classical corrections), the subpicosecond Eley-Rideal and Hot-Atom processes. The implementation of effective models to account for energy dissipation to surface phonons and electron-hole pair excitations, have allowed to rationalize the non-adiabatic dynamics of atom abstraction at metal surfaces. Some examples of this ongoing research will be here shown.

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## On carbon clusters: A general purpose wave function-based method for calculation and automated location of multiple structural isomers

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Carbon clusters have fascinated chemists and physicists throughout the years. The smaller  $C_n$  clusters play a key role in the chemistry of carbon stars, comets, and interstellar molecular clouds, while acting as building blocks for the formation of complex carbon-containing compounds. Added to such a vast astrophysical significance, carbon chains can act as intermediates in chemical vapor deposition systems for production of carbon-rich thin films, and be predominant species in terrestrial sooting flames. All the above stems from their physico-chemical properties, which find a justification on the exceptional bonding flexibility of carbon as demonstrated by its unique ability to form single, double, and triple (even quadruple for  $C_2$  ( $X^1\Sigma_g^+$ ) [1]) bonds; the field has been much reviewed, and hence we address the reader to our recent papers [2, 3] for references. Naturally, the elucidation of the possible mechanisms that lead to formation of such aggregates is only attainable once the properties of the smaller ones have been clarified [4]. It turns out that the existence of nearly isoenergetic isomers, a high-density of low-lying singlet/triplet electronic states, and a significant multi-reference character, makes their study theoretically challenging [2, 3].

Density functional theory (DFT) is commonly regarded as the leading first-principles method in computing electronic structures and properties in molecular science, particularly when dealing with large-sized molecules [4, 7]. Of concern here is its mainstream: Kohn-Sham [6] (KS) DFT. Although offering an exact formulation of quantum mechanical electronic structure theory, KS DFT relies on approximate exchange-correlation functionals: were these known, and it would fully account for all complex many-body effects at a cost characteristic of mean-field approximations. As a result, one meets a proliferation of DFT functionals, with the best for one application being often not the best for another. Recently [8], we have found that second-order Moller-Plesset perturbation theoretic results extrapolated from the first steps of the

hierarchical staircase to the complete basis set limit, MP2/CBS( $d, t$ ), can rival DFT/M06-2X [7], both in time and accuracy. Such findings extend to other popular functionals.

After introducing the various involved issues, we show that by combining second-order Møller-Plesset perturbation theoretic calculations with extrapolation of the energy to the complete basis set limit, a fully ab initio approach emerges capable of rivaling with KS DFT both in accuracy and cost-effectiveness. In fact, spin-scaling may even be used to give the calculated energies couple-cluster-like quality: first to the MP2/*VDZ* and MP2MP2/*VTZ* energies, then to the MP2/CBS( $d, t$ ) ones. The results are shown to compare well with the much more expensive CCSD(T)/CBS( $d, t$ ) energies, which are consider-red the golden rule of quantum chemistry.

By further combining the approach with a stimulated breakup of the molecule, the present wave function based method is shown to offer a near automated tool for locating all structural isomers at a high level of theory. Further adaptations suggest themselves for locating unstable intermediates.

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## Exploration of irradiation/collision induced processes in Meso-Bio-Nano (MBN) systems by means of MBN Explorer and MBN Studio

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A new molecular dynamics (MD) approach for computer simulations and analysis of irradiation/collision driven chemical transformations of complex molecular systems, called irradiation driven molecular dynamics (IDMD), was recently suggested [1] and implemented in MBN Explorer [2]. The approach is based on the fact that irradiation induced quantum transformations can be treated as random, fast and local processes involving small molecules or molecular fragments. On this basis the quantum transformations, such as molecular bond breaks, creation and annihilation of dangling bonds, electronic charge redistributions, changes in molecular topologies, etc, can be incorporated into the molecular force fields, including the recently developed reactive CHARMM force field [3]. IDMD opens new possibilities to explore the irradiation/collision driven MD and chemistry in many complex MBN systems ranging from atomic clusters, nanoparticles and biomolecules to irradiated cells, surfaces, materials, as well as novel technologies such as radiotherapies, or focused electron/ion induced beam deposition (FEBID/IBID).

*MBN Explorer* is a multi-purpose software package for advanced multiscale simulations of complex molecular structure and dynamics [2]. It has many unique features and a wide range of applications in Physics, Chemistry, Biology, Materials Science, and Industry [4]. A broad variety of algorithms and interatomic potentials implemented in the program allows simulations of structure and dynamics of a broad range of systems with the sizes from the atomic up to the mesoscopic scales. A distinct feature of the package, which makes it significantly different from other codes, is in its universality and the implemented algorithms for multiscale modelling which make it very useful tool in to the exploration of many very different MBN systems beyond the limits of the classical MD schemes.

*MBN Studio* is a special multitask software toolkit with graphical user interface developed for

*MBN Explorer* [5]. It helps setting up calculations with *MBN Explorer*, monitoring their progress and examining the calculation results. The graphical utility enables to visualise selected inputs and outputs. A number of built-in tools allows for the calculation and analysis of specific systems' characteristics. A special modelling plug-in allows constructing a large variety of molecular systems built of different atomic and molecular constituents.

The talk will give an overview of the main features of the software, its application areas and will highlight a number of recent case studies of irradiation/collision induced processes in MBN systems explored by means of *MBN Explorer* and *MBN Studio*. Particular attention will be devoted to simulations of the fusion and multifragmentation process in collisions involving metallic clusters, fullerenes and biomolecules [4,6] and the computational exploration of the FEBID processes [1,4]. It will be demonstrated that one can reproduce reasonably well experimental observations and make predictions about the morphology and molecular composition of nanostructures that emerge on the surface in the FEBID process.

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## Probing dimerization effects on the $e^-$ -( $\text{H}_2\text{CO}$ )<sub>2</sub> scattering cross sections

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**Synopsis** We computed electron scattering cross sections for the two most stable structures of the formaldehyde dimer.

Electron-induced DNA damaging have been associated to subionization and subexcitation processes [1]. Hence, several studies on electron scattering with biological molecules have appeared in the literature in the recent past, however quite a few explored weakly bound systems [2,3]. Formaldehyde dimer ( $\text{H}_2\text{CO}$ )<sub>2</sub> present one of the simplest examples of systems containing a C-H...O interaction, that is often found in the structures of important biomolecules such as amino acids, sugars, DNA and RNA. Therefore, the system can serve as a prototype for investigations about the damage caused by low-energy electrons when interacting with larger biochemical units present in living tissue.

In this work we present a theoretical investigation on  $e^-$ -( $\text{H}_2\text{CO}$ )<sub>2</sub> scattering. Several cross sections for the two most stable structures reported by Dolgonos [4] (the Cs and the C<sub>2h</sub> ones) were computed in the 1-25 eV energy range. For comparison purposes, all the cross sections of the monomeric system were also determined.

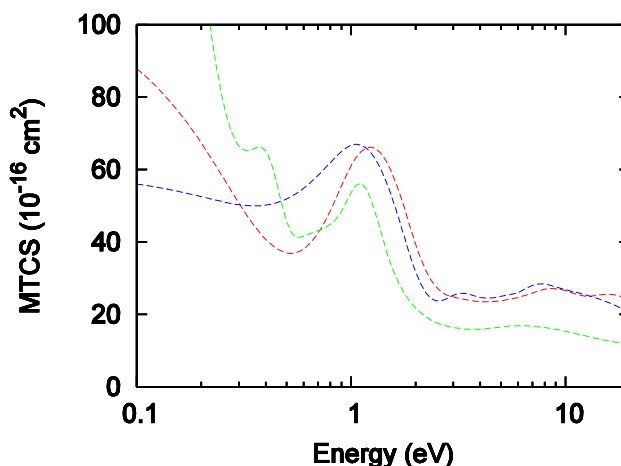
The EPolyScatD code (originally developed by Gianturco *et al.* [5] and modified by de Souza *et al.* [6]) was applied to solve the scattering equations. A complex optical potential, given by:

$$V_{opt} = V_{st} + V_{ex} + V_{cp} + iV_{ab}$$

is used to represent the collisional dynamics. In the above equation,  $V_{st}$  and  $V_{ex}$  are the static and the exchange components, respectively.  $V_{cp}$  is the correlation-polarization contribution obtained in the framework of the free-electron-gas model [7], and  $V_{ab}$  is the improved model absorption potential developed by our group [8].

In Fig. 1 we show our calculated results of momentum transfer cross sections (MTCS). It is possible to notice the occurrence of a shape resonance (around 1.0 eV) in all three species. Interestingly, the feature seen in the Cs dimer presents a blue shift (about

0.3 eV) when compared to the monomer, while the C<sub>2h</sub> dimer show the feature at the same energy (or slightly red shifted by 0.05 eV). Additional results will be presented at the Conference.



**Figure 1.** MTCS of electron scattering. Green dashed curve, results of  $e^-$ -formaldehyde monomer; red dashed curve, results of  $e^-$ -(Cs dimer); blue dashed curve, results of  $e^-$ -(C<sub>2h</sub> dimer).

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## Ion radiation damage of biomolecules in aqueous solutions

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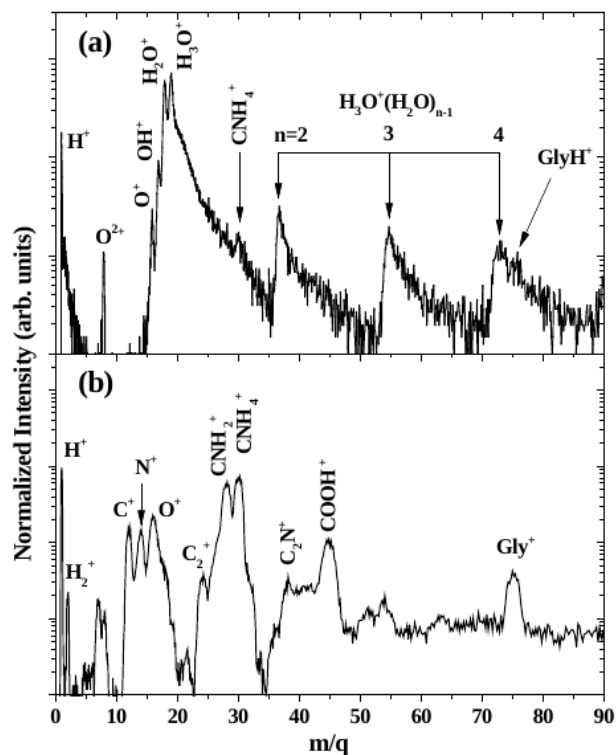
Investigations of the radiation damage to human bodies have been of longstanding interest in radiobiology and radiotherapy. The radiation damage processes of DNA are mainly divided into two categories: direct and indirect actions. The latter is closely related to radiolysis of the water molecules. Therefore, it is important for understanding of the effects of liquid water environments on radiation damage to biomaterials. To elucidate its detailed mechanism at the atomic or molecular level, basic research has been conducted on a variety of model biomaterials in the form of gas-phase targets (isolated single molecules and their cluster), as well as liquid-phase targets (aqueous solutions).

In this work, we study radiation damage of biomolecules in aqueous solutions under fast heavy-ion irradiation [1]. The purpose of this study is to understand radiolysis of biomolecules in liquid water. We performed mass spectroscopic analysis of products emitted from a biomolecule solution by ion irradiation, using the vacuum liquid microjet technique combined with a secondary ion mass spectrometry. A microjet target of aqueous solution was irradiated with 4.0-MeV carbon ions. We examined ionization and dissociation processes of the solvent molecules. We also performed the experiments with a biomolecule target in the vapor-phase.

Figure 1 shows a TOF spectrum of positively charged secondary ions emitted from (a) a 0.1-M glycine (Gly:  $C_2H_5NO_2$ ) solution and (b) gas-phase target produced by sublimating a glycine powder, under 4.0-MeV  $C^{2+}$  irradiation. For the solution target, observed secondary ions from glycine molecules were protonated glycine  $GlyH^+$  and dissociated glycine  $CNH_4^+$ . The former is formed via the addition reaction between neutral Gly and  $H^+$  generated from dissociated water molecules. The latter is formed by the cleavage of the C- $C_\alpha$  bond. A

comparison of the TOF spectra for the solution and gas-phase targets shows that the yield of products formed by the multifragmentation, such as  $CNH_2^+$  and  $C^+$  was significantly reduced for the solution target. The suppression of molecular multifragmentation could be an effect of the liquid water environment.

In this presentation, we will discuss the environmental effects on dissociation of biomolecules, comparing with experiments with other targets in the form of isolated single and cluster biomolecules.



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## Free Electron Production From Nucleotides Upon Collision With Charged Carbon Ions

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Over the last decade Ion Beam Cancer Therapy (IBCT) has become increasingly favored worldwide in the treatment of certain types of cancer. Whereas its effect and usage within cancer therapy is well documented, the understanding of the physical mechanisms behind the therapy is still not entirely understood. The complexity stems from the multiscale nature of the physical phenomena underlying IBCT and span across quantum mechanical to macroscopic scales [1].

The current investigation reports on modelling of the collision process between a highly charged carbon ion and a fragment of a DNA molecule inside a cell. In particular, the quantum mechanical code Octopus 6.0 [2] was employed to simulate the collisions, using a cytosine-guanine nucleotide pair as a representative target. The results suggest that such a collision triggers the release of a large amount of free electrons into the cellular environment, where they might interact with the surrounding medium, possibly

creating free radicals or causing direct damage to the DNA. It is furthermore observed that the number of released electrons and the fraction of them that become localized around the carbon ion is highly dependent on the initial kinetic energy of the ion and its impact parameters.

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## Capture of heliophilic atoms by quantized vortices in $^4\text{He}$ nanodroplets

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**Synopsis** We present a computational study, based on time-dependent Ar and Xe atoms by superfluid  $^4\text{He}$  nanodroplets either pure or Density Functional theory, of the real time trapping of hosting a quantized vortex line.

Recent experiments have shown evidence that quantized vortices in superfluid helium induce coalescence of solvated impurities, which become trapped along their cores, eventually resulting in the formation of nano-sized filaments[1], thus pointing forward to a potentially new method of producing nanowires and nanotubes[2, 3, 4]. Moreover, doping vortices with impurities has emerged as a valuable practical tool to image the vortex presence and dynamics, especially in the presence of vortex tangles and vortex reconnections.

In this work we present results obtained within TDDFT[5] for the collision and capture of Xe and Ar atoms by a  $^4\text{He}$  droplet at different kinetic energies and impact parameters. Due to the relevance of the interaction of foreign impurities with quantized vortices, special attention is paid to the time-dependent interaction of Xe and Ar atoms with helium nanodroplets hosting a vortex line.

- We study the capture of Xe atoms by a  $^4\text{He}$  nanodroplet, both for head-on collisions and for different impact parameters, with velocities ranging from thermal values up to several hundreds m/s. The results of peripheral collisions with different values of the impact parameter are used to estimate the cross section for the Xe capture;

- We study how a Xe atom dynamically interacts with a droplet hosting a vortex line, under different initial conditions resulting in different velocity regimes of the impurity as it collides with the vortex core: (i) a Xe atom initially located in the interior of the droplet and close to the vortex core; (ii) a Xe atom initially at rest on the droplet surface sinking under the effect of solvation forces; (iii) a head-on collision of Xe and Ar atoms against the  $^4\text{He}$  nanodroplet.

We find that Xe and Ar atoms at thermal velocities are readily captured by helium droplets, with a capture cross section similar to the geometric cross section of the droplet.

Also, upon capture, during 50 ps the Xe (or Ar) atom wanders in the bulk of the droplet at velocities of a few tens of m/s. If the droplet hosts a vortex line along the diameter of the droplet, the thermal impurity is captured by the vortex line (see also Ref. [6]).

We have found that the capture is helped by an additional energy transfer from the impurity to the droplet as compared to a capture by a non-vortical state[5]; indeed, large amplitude displacements of the vortex line take place in the course of the capture of the impurity by the vortex, constituting the main source of the kinetic energy lost by the impurity.

In short, what is of fundamental interest is that at thermal energies, most of the impurity energy is lost in the collision process. Then, if the impact parameter is such that the impurity is captured, there are two facts that contribute to the eventual meeting and capture of the Xe/Ar atom and the vortex line, namely that the vortex line is fairly robust (angular momentum conservation) and remains near the droplet symmetry axis, and that the equilibrium position of Xe/Ar is in the bulk of the droplet.

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## Particles with similar LET values generate DNA breaks of different complexity and reparability: a high-resolution microscopy analysis of $\gamma$ H2AX/53BP1 foci

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Biological effects of high-LET (linear energy transfer) radiation have received increasing attention, particularly in the context of more efficient radiotherapy and space exploration. Efficient cell killing by high-LET radiation depends on the physical ability of accelerated particles to generate complex DNA damage, which is largely mediated by LET. However, the character of DNA damage and repair upon exposure to different particles with similar LET parameters remains unexplored. We employed high-resolution confocal microscopy to examine phosphorylated histone H2AX ( $\gamma$ H2AX)/p53-binding protein 1 (53BP1) foci streaks at the microscale level, focusing on the complexity, spatiotemporal behaviour and repair of DNA double-strand breaks generated by boron and neon ions accelerated at similar LET values ( $\sim 135$  keV/ $\mu$ m) and low energies (8 and 47 MeV/n, respectively). Cells were spatially (3D) fixed and irradiated using a sharp-angle geometry to maximize the resolution of these analyses. Both high-LET radiation types generated highly complex  $\gamma$ H2AX/53BP1 foci clusters with a larger size, increased irregularity

and slower elimination than low-LET  $\gamma$ -rays. Surprisingly, neon ions produced even more complex  $\gamma$ H2AX/53BP1 foci clusters than boron ions, which is consistent with DSB repair kinetics. Although cells exposed to  $\gamma$ -rays and boron ions eliminated a vast majority of foci (94 % and 74 %, respectively) within 24 h, this value was only 55 % in cells irradiated with neon. Our calculations suggest that the complexity of DSB damage critically depends on the particle track core diameter. Thus, different particles with similar LET and energy may generate different types of DNA damage, which should be considered in future research.

### Acknowledgement

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## Quasi-Classical Trajectory Study of Atom-Diatomic Molecule Collisions in Symmetric Hyperspherical Coordinates

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We investigate the reactive dynamics of triatomic systems of the heavy + light-heavy type (e.g., F + HCl and F + HI reactions) for total angular momentum equal zero and for different low-lying rovibrational states of the diatomic molecule. For each of the initial vibrational quantum numbers, the time evolution of the atom-diatom collision process is investigated for a wide range of impact angles and collision energies. To this purpose, the Quasi-Classical Trajectories (QCT) method was implemented in a hyperspherical configuration space. The Hamilton equations of motion are solved numerically in an intermediate effective Cartesian space to exploit the relative simplicity of this intermediate representation. Interatomic interactions are described by London-Eyring-Polanyi-Sato

potential energy surfaces specifically developed for the target reactions, and the results of the QCT simulations are discussed in terms of the time-evolution of the hyperangles. The analysis of the collision dynamics using symmetric hyperspherical coordinates provides, in addition to the description in terms of a natural reaction coordinate (the hyperradius), a more striking representation of the exchange dynamics, in terms of the time-dependent probability distribution along the kinematic rotation hyperangle, and a precise distinction between direct and indirect mechanisms of the reaction. The extension of the present study to incorporate quantum effects within the framework of the Quantum Trajectory Method is described.

## **Mechanisms of Energy Redistribution in Laser-Driven Dynamics in Interconnected Quantum Dot - Metal Nanoparticle Systems**

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The ultrafast energy redistribution mechanisms in interconnected quantum dot-metal nanoparticle systems upon laser pulse excitation are studied using a quantum dynamical approach based on the time-dependent version of the Fermi Golden Rule. The quantum dot is modeled as a single-particle system, within the effective mass theory and using model confining potentials. In the case of the metal nanoparticles, the equation of motion for the electronic wavefunction is derived using time-dependent density functional theory. This model is combined with quantum wave packet propagation to

account for the main dynamical features of the interconnected system. The approach allows to compute the lifetime of the excited resonances, the time-evolution of the electronic wavepacket, and the detailed analysis of the ultrafast mechanism of the energy transfer between the two subsystems. The present analysis paves the way to investigate the possibility to achieve the coherent control of the electron relaxation pathway via the manipulation of macroscopic excitations such as the plasmon resonance in metal nanoparticles.

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|--|---|
| 1.- Alberto Rodríguez-Fernández (Havana, Cuba) | Quasi-classical study of the photodissociation dynamics of the methyl radical.                                  |
| 2.- Shinji Nomura (Kyoto, Japan)               | Fast ion-induced dissociation of biomolecules in liquid water environments                                      |
| 3.- B. Rodríguez-Hernández (Havana, Cuba)      | Dynamics of excited states in carbon nano-rings   |
| 4.- Alfred Z. Msezane (Atlanta, USA)           | Large fullerenes for nanocatalysis, sensors and organic solar cells   |
| 5.- Lázaro H. Negrín-Yuvero (Havana, Cuba)     | Spectroscopy and Dynamics of Atomic Zinc Trapped in Xenon Matrices: Molecular Dynamics with Quantum Transitions |
| 6.- Iva Falková (Brno, Czech Republic)         | Chromosomal rearrangements in myelodysplastic syndromes   |
| 7.- Ricardo García Vázquez (Havana, Cuba)      | Approximations of Statistical Quantum Mechanical model for atom-diatom insertion reaction studies               |
| 8.- Pedro Pajón-Suárez (Havana, Cuba)          | Inter-molecular potentials in complexes of the Nitrogen Monoxide (NO) calculated by <i>ab initio</i> methods    |

## Quasi-classical study of the photodissociation dynamics of the methyl radical.

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The photodissociation dynamics of the methyl radical from selected vibrational levels of the 3s and 3pz Rydberg states has been studied using the trajectory surface hopping method. One-dimensional ab initio potential energy surfaces along the carbon-hydrogen dissociative coordinate have been used. Lifetimes and the distribution over the dissociation channels have been reported for all the studied vibrational levels and compared with previous theoretical and experimental works. The obtained lifetimes show a decreasing trend as

vibrational excitation in the symmetric stretch and bending umbrella modes increases. The results have been compared with recent experiments [1] showing very good accordance for the lowest energy levels.

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## Fast ion-induced dissociation of biomolecules in liquid water environments

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Studies on the effect of ionizing radiation on biological molecules are important for an understanding of radiation damage to normal cells during radiotherapy. Basic research has been conducted on a variety of model biomaterials such as amino acids and nucleobases in the form of gas-phase target. Radiation damage of biomolecules is caused by the direct or indirect action. In the indirect action, it is considered that the effect of water molecules surrounding a biomolecule plays an important role in radiation damage to normal cells.

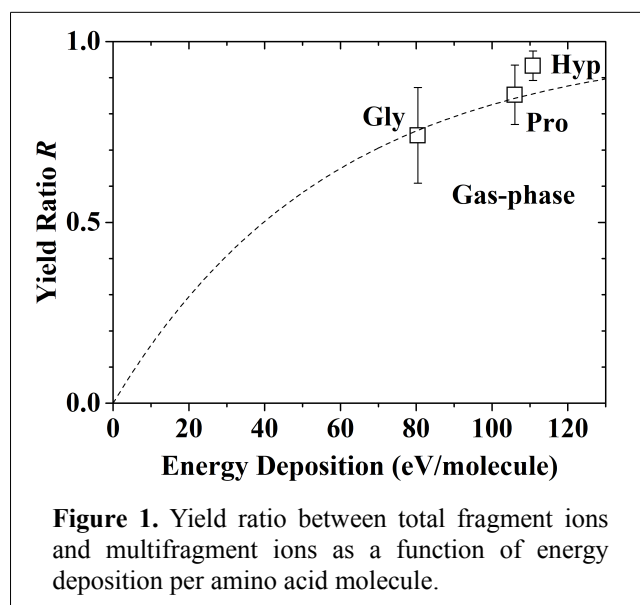
In this work, we investigate fast ion-induced dissociation of biomolecules in aqueous solutions. The purpose of this study is to understand aqueous environmental effects on radiation damage of biomolecules. Three types of amino acids with different molecular structures were used as targets. These targets in aqueous solutions or in the form of gas-phase were irradiated by 4.0-MeV C<sup>2+</sup> ions. Reaction products were analyzed by a time-of-flight mass spectrometry.

Secondary ions emitted from the aqueous solution targets are dissociated amino acid, protonated amino acid, and ions formed via chemical reaction with water molecules. Compared to the relative intensities of fragment ions, the fragment resulting in the cleavage of the C-C<sub>α</sub> bond and the loss of the COOH radical is formed in the highest intensity. Interestingly, the yield of fragment ions for the solution targets is significantly low compared with that for the gas-phase targets. In particular, the yield of multi-fragment ions is reduced by approximately half. This result implies that molecular dissociation is suppressed in liquid water environments.

To see variation of the fragment ion yield, Fig. 1 shows the yield ratio between total fragment ions and multi-fragment ions as a function of

energy deposition per amino acid molecule for the gas-phase targets. The energy deposition was estimated using the core-and-bonds approach [1]. There is a clear correlation between them, and it follows the fitting result shown by dashed line. Based on this result, we deduce the amount of energy deposition for the solution targets. The energy becomes approximately half in comparison with the result of the gas-phase targets. This may result from the energy dispersion to water molecules surrounding an amino acid molecule.

In this presentation, we will discuss the effects of water molecules on dissociation of biomolecules by comparing results for solution and gas-phase targets.



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## Dynamics of excited states in carbon nano-rings

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The nano-rings of cycle-para-phenylenes (CPPs) and related compounds represent model systems to study the optical properties of carbon nanotubes. Because of their cyclic conjugation, these structures present unique and interesting photophysical properties [1]. In the present work, we investigate the excited-state, non-adiabatic dynamics of a set of nano-rings which are composed by a segment of seven phenylene interconnected units. The rings are closed by an alyphatic chain of variable length [2], which join the extremes of the phenylene segments. We analyze the effect of the curvature of the nano-rings on the photoexcitation dynamics, and on the subsequent relaxation and redistribution of the excess energy among the electronic and the vibrational degrees of freedom. Specifically, we focus our attention on the influence of the curvature on the localization/delocalization of the electronic transition density, the mechanism of the energy transfer (i.e.,

through bond or through space), the non-adiabatic couplings, and the impact of the thermal fluctuations on the population transfer to the lowest excited state. Since the relaxation process involves many coupled electronic states, we employ standard tools for dynamical calculations of excited states in non-adiabatic systems [3], in order to compute the electronic state energies, their gradients and couplings.

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## Large fullerenes for nanocatalysis, sensors and organic solar cells

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**Synopsis** We report here on first low-energy electron elastic scattering total cross sections (TCSs) for C<sub>94</sub>, C<sub>96</sub>, C<sub>98</sub>, C<sub>112</sub> and C<sub>120</sub> fullerenes calculated using our robust Regge pole methodology. The TCSs are found to be characterized by correlation and polarization induced dramatically sharp resonances manifesting long-lived metastable negative ion formation. We extract the binding energies (BEs) of the resultant anions formed during the collision.

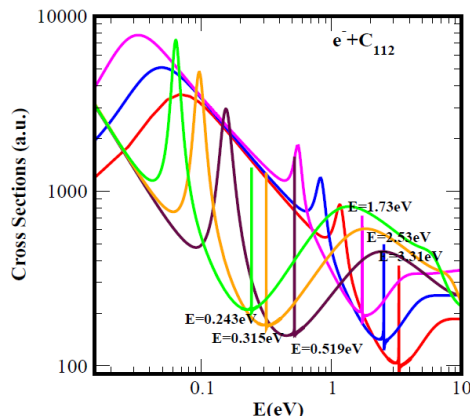
Fullerenes have extensive and crucial applications in science, nanotechnology and industrial research. In particular, in modern organic solar cells the photons absorbed by the donor, usually a polymer create hot-carriers (electrons/holes) which move into the acceptor material, usually a fullerene derivative[1]. Understanding the stability and degradation mechanism of organic solar cells is essential before their commercialization. To overcome the rate of irreversible polymer photobleaching in blend films (polymer: fullerene), designing polymers and fullerenes with larger electron affinity (EA) has been proposed [2]. This has motivated this study to search for fullerenes with larger EAs.

Recently, our robust Regge pole methodology, wherein is fully embedded the electron-electron correlations and the vital core-polarization interaction achieved a theoretical breakthrough in low-energy electron scattering from fullerenes [3]. Entirely new in the field of cluster/fullerene collisions, the Regge pole methodology was benchmarked on the measured EAs of C<sub>60</sub> and C<sub>70</sub> [4, 5] and used to produce the unprecedented theoretical BEs for the anions C<sub>n</sub><sup>-</sup> (n=60 through 92) that matched excellently the measured EAs [3].

Here the method has been used to calculate TCSs for C<sub>94</sub>, C<sub>96</sub>, C<sub>98</sub>, C<sub>112</sub> and C<sub>120</sub> fullerenes and extract the BEs of the resultant anions. The typical calculated TCSs for the large C<sub>112</sub> fullerene are displayed in Fig. 1. The results demonstrate that when subjected to varying gentle electron impact energy the investigated fullerenes respond through rich resonance structures, representing doorway states to stable ground anions. These results significantly widen the selection scope of tunable fullerenes for multiple functionalization through their anions. In particular the series of resonances could provide a mechanism for dumping out the hot-carriers thereby eliminate their liability in the efficient operation of robust organic solar cells.

The long-lived metastable resonances support the conclusion that the experimentally detected fullerene isomers correspond to metastable states [6]. We also found

relatively large ground state BEs as high as 3.56 eV for C<sub>98</sub><sup>-</sup> and 3.74 eV for C<sub>120</sub><sup>-</sup> anions. Importantly, a single large fullerene such as the C<sub>120</sub> could replace the Au, Pd and Sn atoms in the catalysis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub>O in the experiments [7] for water purification in the developing world.



**Fig. 1:** Total cross sections (a.u.) for C<sub>112</sub>. The red, blue and pink curves represent results for the ground and induced meta-stable (first and second), respectively; the black, orange and green curves are the TCSs for the first, second and third excited states, respectively. Sharp lines represent C<sub>112</sub><sup>-</sup> anion formation.

### Acknowledgement

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## Spectroscopy and Dynamics of Atomic Zinc Trapped in Xenon Matrices: Molecular Dynamics with Quantum Transitions

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Experimentally, it is observed the emission and absorption bands -see figure 1- associated to the transition  $^1S_0$ - $^1P_1$ , that take place in Zn atoms trapped in cryogenic matrices (Ne, Ar and Kr) upon the photoexcitation of the impurity [1]. In the particular case of Kr solids, it is also observed an emission band associated to  $^3P_1$ - $^1S_0$  transition [1]. This behavior has been studied for diatomic and triatomic complexes [2] and those studies shown the possibility to take place intercrossing among  $^1P_1$  and  $^3P_2$  states, followed by intramultiple transitions  $^3P_2$ - $^3P_1$ .

The picture is very different when the Zn atom is trapped in Xe matrices. Experimentally, there is not observe emission bands associated to the  $^1P_1$ - $^1S_0$  transition [1]. It means a high efficiency for intercrossing among  $^1P_1$  and  $^3P_2$  states. In the experiments were recorded two bands red shifted respect to  $^3P_1$ - $^1S_0$  atomic emission. Similar picture was recorded when Cd atoms were photoexcited to their  $^1P_1$  state, being trapped in Xe matrices []. But in this case one of the emission bands was associated to

$^3P_1$  transition while the other one to the emission from the metastable state  $^3P_0$ .

The aim of the current work is concentrated on the study of the photoexcitation of atomic zinc trapped in Xe matrices. The study was carried out using the Molecular Dynamics with Quantum Transitions method. The Potential Energy Surfaces were built in the framework of the Diatomic in Molecule approximation. The results allowed to correlate the experimental data with the results obtained in the simulations during the photoexcitation of the impurity (see figure 2).

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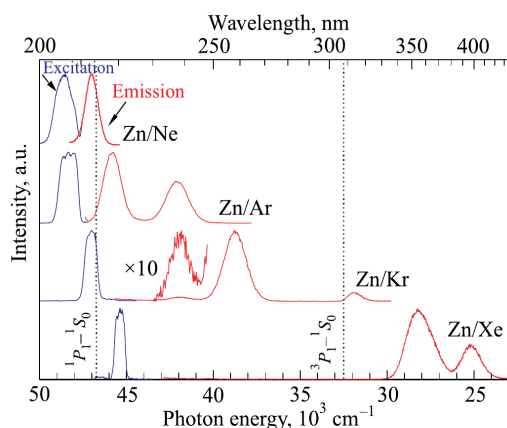


Figure 1. Experimental absorption and emission bands [1].

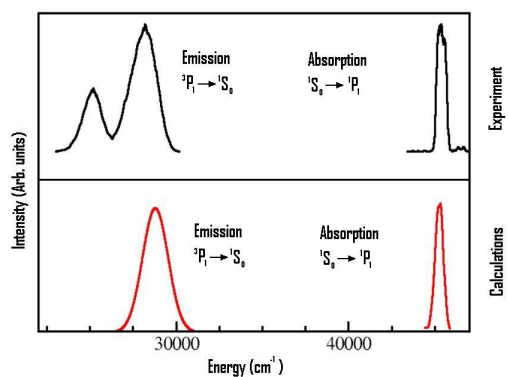


Figure 2. Experimental [1] and calculated absorption and emission bands for Zn trapped in Xe matrices.



## Chromosomal rearrangements in myelodysplastic syndromes

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Myelodysplastic syndromes (MDS) are group of clonal hematologic disorders. The molecular basis are deletions and/or rearrangements of chromosomes 5, 7 and 8. Large interstitial deletions of the chromosome 5 (5q) appear most frequently.

Since the breakpoints are variable but still clustered in specific chromosomal regions, the instability of 5q-arms could not be simply explained by the presence of DNA fragile sites. We hypothesize that the higher-order chromatin (HOC) structure may cause 5q fragility. Chromosomal regions encompassing frequent MDS deletions might adopt specific HOC structure, potentially in MDS precursor cells or some individuals only, which facilitates their damage.

We addressed this question by reconstructing 3D HOC structure of the 5q31.1 - 5q32 chromosomal region, which we identified to be deleted with the highest frequency. Using 3D-FISH and high-resolution confocal microscopy, we determined unclear and mutual positions of 5 BAC probes, hybridizing to individual G-bands between 5q23.3 and 5q32 (in human G0-lymphocytes isolated from healthy donors, CD34+ cells isolated from patients and healthy donors, and human skin fibroblasts).

Centromeric, telomeric, and whole chromosome

probes were used in combinations with the BAC probes to reveal the arrangement of the affected locus inside the chr. 5 territory. Our results indicate the formation of a large chromatin loop between the 5q23.3 and 5q32 loci that sometimes protrudes out of the chromosome 5 territories. This substantial level of chromatin decondensation and protrusion of the loop into the interchromatin channels might contribute to the region fragility. The flexibility of the loop structure we observed might then explain the variability of MDS deletion breakpoints. In accordance with these results, we suggest that HOC organization of the affected region could contribute to formation of chromosomal aberrations in MDS.

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## Approximations of Statistical Quantum Mechanical model for atom-diatom insertion reaction studies

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Atom-diatom insertion reactions are characterized by the formation of an intermediate complex between reactants and product. Therefore, is possible to use statistical approaches in the theoretical investigation of this kind of reactions. The primary assumption of such techniques consists of the division of the whole process in two stages: the formation of the compound after the collision and its further fragmentation. The problem is resumed to the determination of a capture probabilities reactants and products. During the last decades, different approaches have been developed for estimate thus probabilities such as the Statistical Quantum Mechanical (SQM) model. Although this method introduces a considerable reduction of the computational time, in some cases (e.g., O+HCl, Si+OH) is quite complicated the use of the SQM

approach, due to the existence of deep potential wells –which support many bound and quasi-bound states.

To address that challenges Barrios and coworkers introduced different approximations into the SQM model. In this work, we validate them by analyzing the typical insertion reaction O+H<sub>2</sub>. Furthermore, we investigate, the Si+OH reaction, which plays a significant role in the formation of molecular SiO found in the interstellar medium. It is important to highlight that the standard SQM calculations for this system are extremely time-consuming, as a result, this study represents the first investigation of Si+OH system using the SQM approaches. From the results obtained we can conclude that the implemented approximations represent a tool of great benefit for the study of atom-diatom insertion reaction.

## Inter-molecular potentials in complexes of the Nitrogen Monoxide (NO) calculated by *ab initio* methods

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The Nitrogen monoxide properties, have been and continue being of great concern in several research areas, both from the fundamental and applicative point of view. In this work we present several intermolecular potentials for the complexes of NO calculated using *ab initio* methods by our research group.

The main features of the intermolecular potential of: I. the first Rydberg state (A) of the NO-Ne system [1], II. the ground state of the NO-NO system [2] and III. NO – H<sub>2</sub> system in the ground and first Rydberg state(A) [3], are shown.

The inter-molecular potentials shown, have been used successfully in several molecular dynamics research, for example in the references [4] and [5].

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