# ISACC 2015, 18-21 JULY 7<sup>TH</sup> INTERNATIONAL SYMPOSIUM "ATOMIC CLUSTER COLLISIONS"



# **BOOK OF ABSTRACTS**

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#### - 17<sup>th</sup> JULY

 19:00 - 20:30
 REGISTRATION.

 20:30 - 22:00
 WELCOME RECEPTION.

18<sup>th</sup> JULY

09:30 - 10:00 **OPENING**.

1<sup>st</sup> SESSION, CHAIR PERSON: Andrey V. Solov'yov

- 10:00 10:30 Manuel Barranco, "Quantized vortices in superfluid helium nano droplets".
- 10:30 11:00 Nadine Halberstadt, "Quantum molecular dynamics of doped helium clusters".
- 11:00 11:30 **COFFEE BREAK**.

2<sup>nd</sup> SESSION, CHAIR PERSON: Elena Orlenko

- 11:30 12:00 Attila G. Császár, "Energy levels of  $H_3^+$ ,  $H_5^+$  and their deuterated isotopologues".
- 12:00 12:30 Andrey V. Solov'yov, "Structure and dynamics of MesoBioNano systems unraveled with MBN Explorer".
- 12:30 13:00 Michael Gatchell, "Collision Induced Growth Processes in PAH Clusters".
- 13:00 13:20 **Bernd Schütte**, "Time-resolved investigation of charge recombination in clusters driven by strong extreme-ultraviolet and near-infrared fields".
- 13:30 15:00 LUNCH.

### 3<sup>rd</sup> SESSION, CHAIR PERSON: Nadine Halberstadt

- 15:00 15:30 **Paul-Antoine Hervieux**, "High-harmonic generation by nonlinear resonant excitation of surface plasmon modes in metallic nanoparticles".
- 15:30 16:00 José Récamier, "Coherent states for nonlinear systems".
- 16:00 16:20 Alberto García-Vela, "Interference between overlapping resonances: A route to coherent control of resonance lifetimes and photofragment distributions in the weak-field limit".

- 16:20 16:40 **Jaime Suárez**, "Quantum treatment of post-collisonal fragmentation of  $H_2O^+(\tilde{B}^2B_2)$ ".
- 16:20 17:00 Luís Pedro Viegas, "Effect of water clusters on the natural cycle of ozone depletion: the  $HO_2 + (H_2O)_n + O_3$  reaction".
- 17:00 17:30 **COFFEE BREAK**.

4<sup>th</sup> SESSION, CHAIR PERSON: Bernd A. Huber

- 17:30 18:00 Manuel Alcamí-Pertejo, "Key factors governing isomer relative stability of fullerene anions and cations".
- 18:00 18:30 **Himadri Chakraborty**, "Photoemission time delay explores the plasmon resonance, molecular cavity, and hybridization in fullerene materials".
- 18:30 19:00 Shiv N. Khanna, "Reactivity of Free, Ligated and Supported Clusters and Designer Catalytic Mimics".
- 19:00 19:20 Masahiko Ichihashi, "Collision of Rare-Gas Clusters with Size-Selected Cobalt Cluster Ions".
- 19:20 21:00 **POSTER SESSION**.

19<sup>th</sup> JULY

5<sup>th</sup> SESSION, CHAIR PERSON: Sylvio Canuto

- 09:00 09:30 Antonio J.C. Varandas, "Accurate ab initio potentials and quantum dynamics".
- 09:30 10:00 Elena Orlenko, "Scattering of charged particles by Lithium atom with electron exchange".
- 10:00 10:30 Alexander I. Kuleff, "ICD and ICD cascades in multiply excited clusters".
- 10:30 11:00 **Sarantos Marinakis**, "Collisions of hydroxyl radicals with helium, argon and xenon".
- 11:00 11:30 **COFFEE BREAK**.

6<sup>nd</sup> SESSION, CHAIR PERSON: Shiv N. Khanna

- 11:30 12:00 Julius Jellinek, "Structural and dynamical complexities in finite heterogeneous systems: analysis and characterization".
- 12:00 12:30 Chris-Kriton Skylaris, "Large-scale DFT calculations on platinum nanoparticles".
- 12:30 13:00 María J. López, "Competition between molecular and dissociative adsorption of hydrogen on free and graphene-supported palladium clusters".
- 13:00 13:20 Massimiliano Bartolomei, "First principles investigation of hydrogen physisorption on graphynes' layers".
- 13:30 15:00 LUNCH.
- 15:00 19:00 **FREE TIME**.
- 19:00 21:00 **GUIDED VISIT**.
- 21:00 22:30 **DINNER**.

20<sup>th</sup> JULY

7<sup>th</sup> SESSION, CHAIR PERSON: Manuel Barranco

- 09:00 09:30 Eric Suraud, "Dissipation in quantum time dependent mean field".
- 09:30 10:00 **Sylvio Canuto**, "Investigating molecular properties and spectroscopy along the phase diagram".
- 10:00 10:30 Manuel Ruíz-López, "Hydrogen polyoxides: structure, stability and dynamics in gas phase, water clusters and aqueous solution".
- 10:30 11:00 **Paola Bolognesi**, "Molecular mechanisms leading to mutagenesis unraveled via ion-induced mass spectrometry".
- 11:00 11:30 **COFFEE BREAK**.

#### 8<sup>th</sup> SESSION, CHAIR PERSON: Julius Jellinek

- 11:30 12:00 Alicja Domaracka, "Charge and energy flows in ionized thymidine".
- 12:00 12:30 Kaline Coutinho, "Understanding the effect of the hydrogen bonds and the preferential solvation of mixtures in electronic properties of solutes".
- 12:30 13:00 **Eva G. Noya**, "Quantum effects in water clusters: role of the molecular flexibility and applicability of quantum thermal baths".
- 13:00 13:20 Daniel J. Arismendi-Arrieta, "Modelling ion hydration with the iTTM model".
- 13:30 15:00 LUNCH.

9<sup>th</sup> SESSION, CHAIR PERSON: Antonio J.C. Varandas

- 15:00 15:30 Víctor J. Herrero, "Bombardment of solid glycine by 2 keV electrons: Implications for astronomical environments".
- 15:30 16:00 M. Eugenia Sanz, "Conformational Studies of Biomolecules by Broadband Rotational Spectroscopy".
- 16:00 16:20 **Isabelle Braud**, "Attachment of Water and Alcohol Molecules onto Water and Alcohol Clusters".
- 16:20 16:40 Álvaro Valdés de Luxán, "Quantum Dynamics of Encapsulated Linear Triatomic Molecules: Carbon Dioxide in the Cages of the sl Clathrate Hydrate".
- 16:20 17:00 **Dongbin B. Qian**, "Does an isolated  $C_{60}$  molecule have a liquid phase?".
- 17:00 17:30 **COFFEE BREAK**.

10<sup>th</sup> SESSION, CHAIR PERSON: Alicja Domaracka

- 17:30 18:00 Jan M. Rost, "Proton ejection in hydride clusters and large molecules following illumination with short X-ray pulses".
- 18:00 18:30 Alexey Verkhovtsev, "Electron production by noble metal nanoparticles irradiated with photons and fast ions".
- 18:30 18:50 **Dariusz G. Piekarski**, "Dynamics of excited clusters of  $\beta$ -alanine in the gas phase".
- 18:50 19:10 Néstor F. Aguirre, "Theoretical Modeling of Mass Spectrometry".
- 19:10 19:30 Alfred Z. Msezane, "Photoabsorption spectra of Xe atoms encapsulated inside Fullerenes".
- 19:30 20:30 **FREE TIME**.
- 20:30 22:30 CONFERENCE DINNER.

21<sup>st</sup> JULY

11<sup>st</sup> SESSION, CHAIR PERSON: Paola Bolognesi

- 09:00 09:30 **José Campos-Martínez**, "Quantum approaches to the interaction and processes between rare-gas atoms and carbon-layered materials".
- 09:30 10:00 **Bernd A. Huber**, "Experimental study of ion-induced chemistry in PAH and PANH nanosystems".
- 10:00 10:30 **Henning Zettergren**, "Fragmentation of fully aromatic and hydrogenated PAH molecules: H<sub>2</sub> formation and carbon backbone protection?".
- 10:30 11:00 **Henrik Cederquist**, "Relaxation of cluster anions in the cryogenic electrostatic storage ring DESIREE".
- 11:00 11:30 **COFFEE BREAK**.

12<sup>nd</sup> SESSION, CHAIR: Attila Császár

- 11:30 12:00 Ignacio L. Garzón, "Chiral metal clusters and their interaction with chiral molecules".
- 12:00 12:30 **Pablo de Vera**, "Molecular dynamics study of fast ion collisions with biomolecular systems and nanoparticles".
- 12:30 13:00 Christophe Prigent, "Short time dynamics of van der Waals cluster under strong Coulomb perturbation induced by femtosecond laser pulses or highly charged ions".
- 13:00 13:20 **Bruno Manil**, "Experimental alternative to investigate the radiation-induced radical chemistry at the molecular level".

13:20 - 13:30 **CLOSING**.



## Invited Talks: 1-36 Oral Contributions: 37-50 Posters: 51-60



## He droplets as nanolabs for cluster growth and ultracold chemistry

## Andreas W. Hauser<sup>†1</sup> and Wolfgang E. Ernst<sup>†2</sup>

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**Synopsis** We report on combined experimental and theoretical studies of metal cluster formation, electronic excitations and ultracold chemistry in superfluid helium nanodroplets.

Droplets of superfluid helium can be used as nano-sized containers, offering the possibility to study processes of metal cluster formation and chemical reactions at utracold temperatures. This talk gives an overview of our current research in the field with an outlook on helium-isolation-techniques for future studies of surface reactions and photochemistry on mixedmetal nanoparticles.

The growth and deposition of metallic alloys is demonstrated given the example of the coinage metal atoms Cu, Ag and Au. Recently, we published on the formation of elongated Au/Ag coreshell nanostructures in superfluid helium nanodroplets and their subsequent surface deposition under soft landing conditions. [1, 2] The Hedroplet approach can be exploited for the deliberate formation of core-shell nanowire structures with predefined core and shell materials, offers a novel route to a large variety of new material combinations.<sup>[3]</sup> The phenomenon of quantized, local distortions of the He density in the droplet, so-colled vortices, cause atoms and clusters to agglomerate along their core lines, which serve as personal cryo-templates for each nanowire. This finding triggered the question of time scales for initial steps of clustering, Ostwald-ripening and the process of capturing single atoms in vortices. A basic theoretical analysis was performed with the help of molecular dynamics and helium density functional theory in a classical model, [4] which allows us to predict particle collision times within a droplet of a given size.

The concept of reaction studies for ultracold chemistry is illustrated given the example of a double dotation of He droplets with Rb and Xe.[5] The heliophilic Xe resides inside the droplet, while its heliophobic reaction partner, the Rb atom, stays on the surface of the droplet. The effect of this spatial separation, the stability of the system and its properties are described theoretically in the context of future experiments.

Finally, the ability to investigate the electronic structure of unstable or highly reactive compounds such as mixed alkali-metal clusters is demonstrated on the example of the RbSr dimer, an interesting molecule in the context of quantum computation and applications of quantum measuring due to the combination of an unpaired spin and an electric dipole moment in its ground state. Fluorescence spectra of RbSr on helium droplets in combination with ab initio calculations give direct insights into selected electronic states, which allows us indirectly to learn about formation processes of this molecule in cold collisions.[6, 7]

- [1] P. Thaler et al. 2014 Phys. Rev. B 90 155442
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- [4] A. W. Hauser, A. Volk, P. Thaler and W.
   E. Ernst 2015 Phys. Chem. Chem. Phys.
   17 10805-10812
- [5] J. Poms, A. W. Hauser and W. E. Ernst 2012
   Phys. Chem. Chem. Phys. 14 15158-15165
- [6] F. Lackner, G. Krois, T. Buchsteiner, J V. Pototschnig and W. E. Ernst 2014 Phys. Rev. Lett. 113 153001
- G. Krois, F. Lackner, J. V. Pototschnig, T. Buchsteiner and W. E. Ernst 2014 Phys. Chem. Chem. Phys. 16 22373-22381

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## Quantized vortices in superfluid helium nano droplets

### Manuel Barranco $^{\dagger 1}$

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**Synopsis** Whereas most of the phenomena associated with superfluidity have been observed in helium nano droplets, the nucleation of quantized vortices has proven elusive. In this talk I will present DFT and TDDFT results for the appearance of quantized vortex rings and loops. Motivated by recent experimental work, I will also discuss the appearance of vortex arrays in helium droplets.

Helium-4 droplets created by expanding a cold helium gas [1] or fragmentation of a jet of liquid helium attain a limiting temperature below 0.4 K [2], and constitute the only selfbound superfluid systems. Superfluidity in helium droplets was established through the dissipationless rotation of an OCS molecule inside them, as indicated by the appearance of a clean ro-vibrational spectrum [3]. More recently, the indirect evidence of quantum vortices [4, 5, 6] and the existence of a critical Landau velocity below which impurities displace inside helium droplets without experiencing any friction [7] point towards a superfluid character of helium nano droplets.

If a rotating helium droplet in the normal phase above the superfluid transition temperature  $T_{\lambda} = 2.17$  K is cooled down reaching the superfluid phase, it reacts by storing its angular momentum either into quantized vortices or into travelling capillary waves [8]. Conversely, a critical angular velocity  $\omega_c$  has to be supplied to the superfluid droplet for the nucleation of vortices with quantized velocity circulation in units of h/M, where h is the Planck constant and M is the mass of a <sup>4</sup>He atom. When the angular velocity is increased above  $\omega_c$ , larger amounts of angular momentum may be stored into the superfluid by increasing the number of nucleated vortices. These vortices arrange themselves into lattices whose existence in bulk superfluid <sup>4</sup>He was established long ago.

Very recently, superfluid He nanoscopic droplets in fast rotation have been studied by coherent X-ray scattering [9]. The existence of vortex lattices inside the droplets was established by the appearance of Bragg patterns from Xe clusters trapped in the vortex cores in droplets made of  $N = 10^8 - 10^{11}$  atoms (corresponding to radii from 100 to 1000 nm) produced by the fragmentation of liquid helium expanding into vacuum.

The shapes of the droplets were consistent

with those of axially symmetric oblate pseudospheroids with large aspect ratio, defined as the ratio of the long half-axis length b to the short half-axis length a along the rotational axis. While normal liquid drops change their shape as rotation becomes faster to resemble a "peanut" (multi-lobe shape) or a "blood cell", no evidence of such shape shifting has been seen in the helium nano droplets. Rather, their shape at high angular velocities look "wheel-like" [9, 10].

In this talk I will review recent progresses made –within Density Functional Theory– in the study of vorticity in nanoscopic helium droplets.

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- [10] F. Ancilotto, M. Pi, and M. Barranco, Phys. Rev. B **91**, 100503(R) (2015).

## Quantum molecular dynamics of doped helium clusters

#### We sley UNN TOC<sup> $\dagger 1$ </sup> and Nadine HALBERSTADT<sup>§ 2</sup>

<sup>†</sup> Institut des Sciences Moléculaires d'Orsay, Université Paris Sud 91405 Orsay, France <sup>§</sup> LCAR-IRSAMC, CNRS and Université Paul Sabatier Toulouse 3, 31062 Toulouse, France

Synopsis Development and test of a method for quantum dynamics of doped helium nanodroplets at the molecular level.

Our aim is to describe at a microscopic level the time-dependent behavior of these many-body systems under excitation of the host, and to reproduce the results of recent time-resolved experiments. To this end, we have developed a real-time quantum dynamics method which can take into account the bosonic nature of <sup>4</sup>He by including exchange symmetry and correlations. Hence the influence of each of these factors can be examined separately, and their relative importance can be assessed depending on the dynamical regime (high or low kinetic energy).

Our approach is based on the Multi-Configuration Time-Dependent Hartree (MCTDH) method [1]. We will present the details of the model, and our first results on simple few-particle systems. They will be compared to results using single configuration dynamics (TDH, or mean field dynamics), with or without bosonic exchange, and to zero-point averaged dynamics [2,3] (ZPAD), a frozen wave packet-type dynamical method which incorporates zero-point quantum effects on average.

#### References

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## Energy levels of H<sub>3</sub><sup>+</sup>, H<sub>5</sub><sup>+</sup> and their deuterated isotopologues

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**Synopsis** Energy levels obtained from a MARVEL (Measured Active Rotational-Vibrational Energy Levels) analysis of the experimental high-resolution spectra of  $H_3^+$ ,  $H_2D^+$ , and  $D_2H^+$  are compared with results obtained from variational nuclear motion computations based on a highly accurate potential energy surface for  $H_3^+$ . Characteristics of the rovibrational energy level structure of the astructural  $H_{5-n}D_n^+$  ions (n = 0, ..., 5) are discussed and interpreted.

The MARVEL (Measured Active Rotational-Vibrational Energy Levels) algorithm [1,2], based on the theory of spectroscopic networks [3], has been used to determine experimentalquality rotational-vibrational energy levels of  $H_3^+$  and two deuterated isotopologues:  $H_3^+$  [4],  $H_2D^+$  [5], and  $D_2H^+$  [5]. Characteristics of the experimental sources are collected into Table 1.

The high-quality experimental rotationalvibrational energy levels are compared to energy levels obtained from variational nuclear motion computations utilizing exact kinetic energy operators and a highly accurate, global, adiabatic potential energy surface (PES) which also includes relativistic effects [6]. This PES is accurate to about 0.1-0.2 cm<sup>-1</sup> all the way to dissociation.

A particularly interesting development concerning the computed rovibrational energy levels of  $H_{3^+}$  is the introduction of the motiondependent mass concept and the coordinatedependent mass surfaces (CDMS) [7]. Employing optimized motion-dependent masses yields an improvement of almost two orders of magnitude in the prediction of rovibrational enegy levels; then the quality starts approaching the accuracy of the related experiments.

The rovibrational level structure of the astructural molecules  $H_5^+$  and all of its deuterated isotopologues show puzzling characteristics [8,9,10] which requires models distinctly different from the usually employed (perturbed) rigid-rotor and harmonic oscillator treatments.

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Figure 1. Deviations between adiabatically and non-adiabatically computed rovibrational energy levels of  $H_{3^+}$ 

The modeling results for  $H_5^+$  [9] can be extended to systems containing two weakly coupled internal rotors. The question of the number of deuterated isotopomers is addressed.

- T. Furtenbacher *et al.* 2007 *J. Mol. Spectrosc.* 245, 115.
- [2] T. Furtenbacher, A. G. Császár 2012 J. Quant. Spectr. Rad. Transfer 113, 929.
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- [10] J. Sarka et al. 2015 manuscript in preparation.

## Structure and dynamics of MesoBioNano systems unraveled with MBN Explorer

Ilia A. Solov'yov<sup>†</sup>, Gennady Sushko<sup>‡§</sup>, and <u>Andrey V. Solov'yov<sup>§1</sup></u>

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**Synopsis** There will be presented the universal software package MBN Explorer and its applications for studies of structure and dynamics of MesoBioNano (MBN) systems.

MBN Explorer [1] is a multi-purpose software package designed to study structure and dynamics of molecular systems of various degrees of complexity. A broad variety of interatomic potentials implemented in the MBN Explorer allows to simulate the structure and dynamics of different molecular systems, such as atomic clusters [2], fullerenes [3], nanotubes [4], metallic nanomaterials [5], proteins and DNA [6], crystals [7] composite bio-nano systems and nanofractals [8-10]. A distinct feature of the package, which makes it significantly different from other codes, is in its universality and implemented multiscale features that make it applicable to really a broad range of problems involving complex molecular systems.



Fig. 1 Illustration of different areas of application of MBN Explorer [1].

The talk will give an overview of the main features of the package and will highlight a number of recent case studies of structure and dynamics of MesoBioNano systems carried out with the use of MBN Explorer some of which are illustrated in Fig.1. The professional version of MBN Explorer can be ordered via the website [11]. MBN Explorer is being under the permanent development carried out by the MBN Research Center in Frankfurt [12]. In July 2015 the MBN Explorer release 2.0 will be issued. The new features of MBN Explorer implemented in its most recent version as well as corresponding case studies will be presented.

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[12] http://www.mbnresearch.com/

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## **Collision Induced Growth Processes in PAH Clusters**

### M. Gatchell<sup>\* 1</sup>, R. Delaunay<sup>‡,¶</sup>, P. Rousseau<sup>‡,¶</sup>, A. Domaracka<sup>¶</sup>, S. Maclot<sup>‡,¶</sup>, Y. Wang<sup>b,‡</sup> M. H. Stockett<sup>\*,†</sup>, T. Chen<sup>\*</sup>, L. Adoui<sup>‡,¶</sup>, M. Alcamí<sup>b,‡</sup>, F. Martín<sup>b,‡,‡</sup>, H. Zettergren<sup>\*</sup>, H. Cederquist<sup>\*</sup>, and B. A. Huber<sup>‡,¶</sup>

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Synopsis We have observed growth processes in clusters of PAH molecules induced by collisions with keV ions.

Clusters of Polycyclic Aromatic Hydrocarbon (PAH) molecules are believed to form the building blocks for small carbonaceous grains in the interstellar medium [1]. The cluster environment both protects the individual molecules and provides conditions where new chemical reactions can occur. We will present experiments where we collided keV ions with clusters of Pyrene  $(C_{16}H_{10})$  molecules [2]. In these experiments we observed the formation of a wide range of new molecules of the form  $C_{16+m}H_x$ , where m =1-21. The growth of new molecules is the result of prompt non-statistical fragmentation, where molecules fragment on femtosecond timescales due to nuclear scattering processes between the projectile ion and atoms in the cluster. The rapid fragmentation is unique to collisions involving projectile atoms or ions and is crucial for the forming of the new molecules, as highly reactive fragments may form new bonds with neighboring molecules before the surrounding cluster has time to dissociate. In addition to the experiments we have performed classical and quantum chemical molecular dynamics simulations of the collisions and subsequent reactions [2]. With these theoretical tools we are able to reproduce the experimental findings, an example of which is shown in Figure 1. We find that the prompt atomic knockout process starts the reaction and that the cluster environment is essential and works as a heat bath to protect the remaining fragments.



**Figure 1.** Experimental and simulated mass spectra from collisions between 12 keV  $Ar^{(2+)}$  and Pyrene clusters.

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## High-harmonic generation by nonlinear resonant excitation of surface plasmon modes in metallic nanoparticles

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**Synopsis** The nonlinear electron dynamics in metallic nanoparticles is studied using a hydrodynamic model that incorporates most quantum many-body features, including spill-out and nonlocal effects as well as electron exchange and correlations. We show that, by irradiating the nanoparticle with a chirped laser pulse of modest intensity (autoresonance), it is possible to drive the electron dynamics far into the nonlinear regime, leading to enhanced energy absorption and complete ionization of the nanoparticle on a time scale of the order of 100 fs. The accompanying radiated power spectrum is rich in high-order harmonics.

Experimentally, the electron dynamics in a metallic nanoparticle can be probed with great precision using ultrafast spectroscopy techniques in the femtosecond regime. From the theoretical point of view, the linear response has been the object of intense investigations in the past decades. In contrast, the nonlinear regime is much harder to assess using many-body approaches such as the time-dependent density functional theory (DFT) or Wigner function methods [1]. A possible alternative relies on the use of macroscopic models based on a set of quantum hydrodynamic (QHD) equations [2], which were successfully used in the past to model the electron dynamics in molecular systems, metallic nanoparticles, thin films [3], and semiconductor quantum wells [4]. A further degree of simplification can be achieved by means of a variational approach [5], which expresses the QHD model in terms of a Lagrangian function. By postulating a reasonable ansatz for the electron density, it is possible to obtain a set of ordinary differential equations for some macroscopic quantities, such as the center of mass and the radial extension of the electron gas.

Using this approach, we have studied [6] the dynamics of collective electron modes (surface plasmons) excited with laser pulses in the visible range. Using chirped pulses with slowly varying frequency (autoresonance), it is possible to drive the plasmon mode far into the nonlinear regime, leading to the emission of electromagnetic radiation with a power spectrum rich in high-order harmonics (see Fig. 1). The autoresonant technique [7] is very flexible and efficient, the required laser intensities are modest  $(10^{10})$  $W/cm^2$ ) and no feedback mechanism is needed to match the driving frequency with the oscillator frequency. Further, this technique is expected to work even in the case of nanoparticles of unequal sizes, which is the most common situation

in the experiments. Thus the electron response of an assembly of metallic nanoparticles could be excited well into the nonlinear regime, leading to a dramatic increase of the absorbed energy.



Figure 1. Frequency spectrum of the total radiated power in a gold nanoparticle with N = 200, for two cases, below the autoresonance threshold (a) and above the threshold (b) [6].  $\Omega_{\rm d}$  is the surface plasmon frequency.

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## Coherent states for nonlinear systems

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**Synopsis** In this work we generalize two definitions for the construction of nonlilnear coherent states (NLCS) and apply them to two essentially different systems: (i) systems supporting a finite number of bound states exemplified by the Morse and the modified Pöschl-Teller potentials, and (ii) systems with an infinite number of bound states, exemplified by the trigonometric Pöschl-Teller potential.

The idea of creating a coherent state for a quantum system was first proposed by Schrödinger, in 1926, in connection with the classical states of the quantum harmonic oscillator; he referred to them as states of the minimum uncertainty product. Almost forty years later in 1963, Glauber introduced the field coherent states which can be obtained from any one of three mathematical definitions: (i) as the right-hand eigenstates of the boson annihilation operator  $\hat{a}|\alpha\rangle = \alpha |\alpha\rangle$ , with  $\alpha$  being a complex number; (ii) as the states obtained by application of the displacement operator  $D(\alpha) =$  $\exp(\alpha \hat{a}^{\dagger} - \alpha^* \hat{a})$  upon the vacuum state; and (iii) as those states with a minimum uncertainty relationship  $(\Delta q)^2 (\Delta p)^2 = 1/4$ , with  $q = (\hat{a} + \hat{a}^{\dagger})/\sqrt{2}$ and  $p = i(\hat{a}^{\dagger} - \hat{a})/\sqrt{2}$  the position and momentum operators respectively and  $\Delta q = \Delta p$ . The same states are obtained from any one of the three mathematical definitions when one makes use of the harmonic oscillator algebra. At the same time, Klauder developed a set of continuous states in which the basic ideas of coherent states for arbitrary Lie groups were contained. The complete construction of coherent states of Lie groups was achieved by Perelomov and Gilmore almost ten years later; the basic theme of this development was to connect the coherent states with the dynamical group for each physical problem thus allowing the generalization of the concept of coherent state. Gazeau and Klauder proposed a generalization for systems with one degree of freedom possessing discrete and continuous spectra. Man'ko and collaborators introduced coherent states of a *f*-deformed algebra as eigenstates of a deformed annihilation operator  $\hat{A} = \hat{a}f(\hat{n})$ , where  $\hat{a}$  is the usual annihilation operator of the harmonic oscillator algebra and  $f(\hat{n})$  is a number operator function that specifies the potential.

On the basis of the f-deformed oscillator formalism, in previous works we put forward the construction of generalized coherent states for nonlinear systems by selecting a specific deformation function in a way such that the energy spectrum of the Hamiltonian it seeks to describe is similar to that of a f-deformed Hamiltonian [1, 2, 3, 4]. In this talk we present two alternative forms to obtain the coherent states pertinent to nonlinear Hamiltonians.

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## Key factors governing isomer relative stability of fullerene anions and cations

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**Synopsis:** Here we show that the concepts of cage connectivity and frontier  $\pi$  orbitals allow us to understand the stability of both anionic and cationic species, and to predict the energy ordering of all their possible isomers without performing elaborate quantum chemistry calculations. The latter is not a trivial matter, since the number of possible isomers for a medium-size fullerene largely exceeds 100,000. The model correctly predicts the structures observed experimentally and explains why, for fullerene anions, the isolated-pentagon rule is often violated, while, for fullerene cations, the opposite is found

Fullerene anions and cations present unique physical and chemical properties and are abundant in nature. They play an important role in organic photo-voltaics, biomedicine, material science and astrophysics. An unusual behavior of charged fullerenes is that the isomer relative stability could be substantially different from that of neutral counterparts their [1]. The wellestablished stability rules for neutral fullerenes, such as isolated-pentagon rule (IPR), are no longer valid for many experimentally observed structures.

Some approximate rules, based on different physical arguments, such as maximum aromaticity [2], minimum electrostatic repulsion [3] or minimun strain [4] have been proposed for fullerene anions. However, these models often lead to conflicting predictions [5]. In this presentation, we propose a new simple and general scheme [5] based on the concepts of cage connectivity and frontier  $\pi$  orbitals that allow to fully understand the stability of both anionic and cationic fullerenes. The model proposed does not need neither geometry optimizations nor iterative electronic structure calculations, but just the knowledge of cage connectivity, allowing to explore the stability of a very large number of potential isomers.

We have proposed the charge stabilization index,  $CSI_i^q$ , for a given fullerene isomer i with charge q. The predictive power of CSI has been systematically checked, by considering all fullerene isomers from  $C_{28}$  to  $C_{104}$  with charges between +6 and -6. The model correctly predicts the structures observed experimentally for endohedral metal fullerenes and those determined by DFT computations. It also allows to identify the key factors determining fullerene stability and gives new insights on the underlying physics. For instances it explains why, for fullerene anions, the IPR is often violated, while, for fullerene cations, the opposite is found.

This new approach should allow to explore the stability of larger fullerenes and fullerene derivatives, where millions of isomers are possible.

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## Photoemission time delay explores the plasmon resonance, molecular cavity, and hybridization in fullerene materials

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**Synopsis** Time-dependent local density approximation is used to predict photoemission quantum phases and time delays at the giant plasmon resonance and at a series of cavity minima in  $C_{60}$ . Studies also probe temporal structures of atom-fullerene hybrid emissions from the Ar@ $C_{60}$  endofullerene molecule.

Resolving electron dynamics in real-time offers access into a plethora of electron-correlation driven processes in matters. The advent in technology of producing isolated ultrashort laser pulses and pulse trains dovetails a new landscape of active and precision research of light-matter interactions on ultrafast time scales. In the interferometric measurements, namely, reconstruction of attosecond beating by interference of two-photon transitions (RABITT), photoelectrons emitted by odd harmonics of an XUV pulse train subsequently absorb or emit an IR photon. This produces even harmonic sidebands in the spectrogram. The ionization time delay is then obtained by the ratio of the difference of the measured phases at consecutive sidebands and the harmonic separation. This phase-frequency difference approach approximates the energy differential of the phase of the photoamplitude, the Wigner-Smith time delay, which can be calculated by many-body perturbative techniques.

We will first present a combined experimenttheory study [1] that shows that the surface plasmon resonance in  $C_{60}$  alters the valence photoemission quantum phase, resulting in powerful effects in the photoelectron angular distribution and time delay. Electron momentum imaging spectroscopy is used to measure the angular distribution that agrees well with the calculations from the time-dependent local density approximation (TDLDA). Significant structures in the valence emission delay are simultaneously detected by TDLDA over the plasmon energies. Results unravel a unified spatial and temporal asymmetry driven by the plasmon resonance.

Photoelectron spectroscopy earlier probed oscillations in  $C_{60}$  valence emissions, producing a series of minima whose energy separation depends on the molecular cavity. It will be shown that the quantum phase at these cavity minima exhibits variations from electron correlations, causing rich structures in the emission time delay [2]. Therefore, these minima offer unique spectral zones to explore multielectron forces via the RABITT interferometry not only in fullerenes, but also in clusters and nanostructures for which such minima are likely abundant.



**Figure 1.** Schematic for probing the relative delay between photoemissions from fullerene materials [3].

Finally, effects of confinement on the TDLDA relative delay between the 3s and 3p photoemissions of Ar confined endohedrally in C<sub>60</sub> will be discussed [3]. At energies in the neighborhood of 3p Cooper minimum, correlations with C<sub>60</sub> electrons are found to induce opposite temporal effects in the emission of Ar 3p hybridized symmetrically versus that of Ar 3p hybridized antisymmetrically with C<sub>60</sub>. A recoil-type interaction model mediated by the confinement is found to best describe the phenomenon.

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## Reactivity of Free, Ligated and Supported Clusters and Designer Catalytic Mimics

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Due to quantum confinement, the electronic states in metal clusters are grouped into electronic shells. This shell structure controls the reactivity of clusters with reagents like O2. Earlier experiments on the reactivity of Al<sub>n</sub> clusters with oxygen had indicated that an  $Al_{13}$  cluster is relatively inert. This reactivity could be reconciled within an electronic shell closure. More recently, silver cluster anions  $[Ag_n]^-$  have been found to exhibit variable reactivity with  $[Ag_{13}]^{-1}$ exhibiting unique stability against reactivity with oxygen. Experiments on cations also indicate that Ag<sub>15</sub><sup>+</sup> shows remarkable resistance to reactivity with oxygen. I will demonstrate that these reactivity patterns are all related to the spin accommodation. The ground state of O<sub>2</sub> is a spin triplet and the reactivity entails a spin multiplicity  $3 \rightarrow 1$  excitation of the cluster. The reactivity is then correlated with the spin excitation energy and clusters with filled shells and the large separation between filled and unoccupied shells require large energy for spin excitation and exhibit reduced reactivity.

While the electronic shells control the reactivity with  $O_2$ , reactivity with molecules having polar covalent bonds exhibits different patterns. Experiments on the reactivity of aluminum cluster anions with water, methanol and formaldehyde show that while some clusters with open electronic shells such as  $Al_{20}$  do not show significant reactivity, selected clusters with closed electronic shells exhibit strong reactivity. I will show that these behaviors are rooted in the nonuniform distribution of charge densities and have a geometric origin. Clusters with non-uniform charge distributions are marked by Lewis-acid and Lewis-base complementary sites that stimulate the breaking of polar bonds. Such pairs can break hydroxyl and even stronger C=O carbonyl bond of formaldehyde.

Ligands including halogens or thiols modify the electronic structure through bonding resulting in stable clusters with filled electronic shells that are resistant to oxygen etching. I will demonstrate that the stabilization afforded by ligands is partially confounded because the ligands perturb the charge density of the metallic core, inducing Lewis acid-base sites that make the cluster reactive in a protic environment. I will demonstrate these intriguing effects through studies of  $Al_{13}I_x$  and  $Al_{14}I_y$  clusters.

For practical applications, the clusters need to be supported on substrates. Here the stability of clusters and the energy needed to remove oxygen play an important role on the reactivity of clusters. I will present our recent results on the Pd<sub>n</sub> and Pt<sub>n</sub> clusters supported on TiO<sub>2</sub>. In particular, I will show how the binding energy of metal clusters or oxygen atoms to the substrate can be controlled (enhanced/reduced) by doping the surface with donor or acceptor atoms.

Finally, I will describe our recent work on modifying the reactivity of 3d transition metals by combining them with C, Si, or O. I will show that some of these designer compounds have reactivity patterns close to precious metals and may provide catalytic mimics to replace Rh, Pd, or Pt clusters.

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## Accurate *ab initio* potentials and quantum dynamics

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The talk begins with some remarks on the BO approximation. The emerging concept of potential energy surface is examined, and a strategy to get it accurately via conventional electronic structure calculations followed by extrapolation to the complete basis set limit (CBS) discussed. The approach can therefore be of interest in studies of molecules, ions and clusters as well as in reaction dynamics. The emphasis will be on the correlation energy by far the most computationally demanding component of the molecular potential. Optimally, the sought extrapolation should require a single raw ab initio point and a basis of arbitrary hierarchy, with a CBS scheme presented that satisfies such a requirement and performs accurately against a test set of 106 systems involving atoms from H to Ne. A strategy to model analytically the calculated energies is next examined, jointly with the long-standing issue of fitting "conical" cusps at arbitrary geometries with a

single-sheeted (adiabatic) form. Developed so far for triatomics, such an approach is illustrated for ground-state C<sub>3</sub> where 4 conical intersections arise due to combined Jahn-Teller E' $\otimes$ e' plus pseudo-Jahn-Teller [(E'+A'<sub>1</sub>) $\otimes$  e'] interactions. The remaining part of the talk addresses the solution of the equations of nuclear motion by focusing on the calculation of the photoelectron spectra of CH<sub>4</sub>. Besides the good agreement between the calculated and measured vibronic bands of CH<sub>4</sub><sup>+</sup>, it is shown that "attosecond" resolved dynamics occurring at the triply-degenerate ground electronic manifold of CH<sub>4</sub><sup>+</sup> can be studied with regular dynamics by simulating the ratio of the emitted high-harmonic signals. Some remarks on ongoing work conclude the talk.

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Synopsis Time dependent exchange perturbation theory, Scattering matrix with respect to electron exchange, Charge exchange scattering.

We present the formalism of Timedependent Exchange Perturbation Theory (TDEPT) built to all orders of perturbation, for the arbitrary time dependency of perturbation. The theory takes into account the rearrangement of electrons among centres. The elements of the scattering S-matrix and transitions T-matrix and the formula for the electron scattering differential cross section are derived. The application of the theory to scattering and collision problems is discussed on an example of charged particles ( $\alpha$ particle, proton positron) scattering on a Lithium atom, calculating the differential and total cross-sections. The strength of the interaction between particles during collisions is described by a scattering cross-section, or a differential cross-section. We consider the collision associated with the redistribution of electrons, as the collisions of ion with neutral atoms accompanied by charge transfer. As for example the collisions of charged particle  $(Pa^{n+})$  scattering on Lithium atom:  $\text{Li} + Pa^{n+} \rightarrow \text{Li}^{+} + Pa^{(n-1)+}$ , accompanied by charge transfer.

Here we would like to emphasize the advantages of applying the EPT method. The obtained expression for the differential cross section is

$$\frac{d\sigma_{_{fi}}}{d\Omega} = j^{^{-1}}\frac{dw_{_{fi}}}{d\Omega} = \frac{\mu_i\mu_fk_f}{\left(2\pi\hbar^2\right)^2k_i} \left|\left\langle\Psi_f^0\left|\hat{T}\right|\Phi_i^0\right)\right|^2.$$

The transition operator  $\hat{T}$  given in the form

$$\hat{T} = V_0^{\mathbb{N}} + V_0^{\mathbb{N}} \left(\frac{f_0^2}{P}\right)^{-1} \left(E_i - H + i\eta\right)^{-1} V_0^{\mathbb{N}},$$

where H is the total Hamiltonian of the sys-

tem and where  $V_0^{\mathbb{N}} = \left(\frac{f_0^2}{P}\right) V_0$  is a renormalized

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perturbation operator. The initial state is described by the vector  $|\Phi_i^{0(0)}\rangle$ , corresponding to the initial electron permutation between the centers, the antisymmetric vector  $|\Psi_f^0\rangle$  of the final state is obtained by applying the normalized Young operator onto the wave function  $\hat{A} | \Phi_f^{0(0)} \rangle$  with respect to all electron permutations between the centers.

The obtained matrix element contains the exchange integrals. These integrals take into account the permutations of the electrons between the centers. The signs of these integrals are defined by the Young diagrams and depend on the total spin value.

A simulated differential cross section as a function of the scattering angle at different energies of the incident positron or proton. One can observe regions of a "twisted ridge" for certain values of wave vector k and a scattering angle  $\theta$ . It has been previously reported that under similar conditions, but when an alpha-particle is colliding with a Lithium atom [1], the differential cross-section has a smooth appearance without ridges. The same "twisted ridge" were theoretically predicted for the scattering of proton by Lithium atom, for other values of vector k and angle  $\theta$  [2].

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## ICD and ICD cascades in multiply excited clusters

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**Synopsis** The recently predicted interatomic Coulombic decay (ICD) process in multiply excited rare gas clusters will be discussed. It will be shown that in clusters exposed to moderately intense XUV pulses with single-photon energy below the ionization threshold of the individual cluster constituents, but on resonance with a low-lying excitation, may be the dominant ionization mechanism of the cluster. Moreover, it will be shown that if higher lying excited states are populated, the cluster may undergo a cascade of such ICD processes. First experimental indications for such cascades in rare-gas clusters will also be presented.

Exposing atomic or molecular clusters to intense laser pulses will typically result in a multiple ionization of the cluster, even in the cases when the single-photon energy is not enough to directly ionize the cluster constituents. The atoms or molecules of the clusters can absorb more than one photon and use the accumulated energy to eject an electron in a process known as multiphoton ionization. Recently, we have shown [1] that if the photon energy of the pulse is on resonance with a particular excitation of the cluster constituents, another very efficient pathway for multiple ionization of the cluster is open. Due to the resonant transition, the cluster first gets multiply excited and then relaxes by emitting electrons via a process in which a pair of neighboring cluster constituents undergo interatomic (intermolecular) Coulombic decay [2], as schematically shown for a dimer in Fig. 1.



Figure 1. Schematic representation of the ICD process in a dimer [1].

It will be shown that for pulses of moderate

intensity the ICD process is by far the dominant ionization mechanism of the cluster [1]. Since the efficiency of the ICD process grows with the increase of the number of excited species, it is important to know the optimum conditions for achieving multiple excitation of a cluster. It will be shown by reporting high-level *ab initio* calculations of the double-excitation of Ne dimers [3] that the so-called dipole (or Rydberg) blockade actually facilitates the multiple excitation process.

First experimental indications for the importance of electronic decay processes that involve two (or more) excited species have already been reported in the literature [4, 5] for helium droplets. These experiments, as well as our earlier calculations, were done for lowest excitations of the cluster constituents.

Here we will show that for clusters containing species excited to higher-lying states another interesting and very efficient relaxation pathway becomes operative. Such kind of multiply excited cluster can undergo a cascade of ICD processes. First calculations and experimental results demonstrating the efficiency of such cascades in large neon clusters will be presented and discussed.

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## Collisions of hydroxyl radicals with helium, argon and xenon

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**Synopsis** Collisions of hydroxyl radicals (OH) with helium (He), argon (Ar) and xenon (Xe) have been studied using crossed-beam experiments and quantum mechanical calculations. A comparison between experimental and theoretical results is presented and discussed. The results reveal common and different characteristics between He + OH(X), Ar + OH(X) and Xe + OH(X) collisions.

Product-state-selective differential cross sections (DCSs) for inelastic scattering of OH(X  ${}^{2}\Pi$ ) with He/Ar/Xe have been measured via a crossed-beam technique. OH was prepared in the unique  ${}^{2}\Pi_{3/2}$ , v = 0, j = 1.5, *f* level by hexapole field selection. Products were detected state-selectively by [2+1] resonance-enhanced multiphoton ionization of OH, combined with velocity-map imaging (VMI) for the first time [1,2].

Complementary exact close-coupled quantum scattering calculations on *ab initio* potential energy surfaces (PESs) were carried out. The agreement between experimental and theoretical DCSs is generally very satisfactory for OH + Ar, but is less good for OH + He/Xe [3]. This highlights the ability of such vector measure-

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ments to identify potential shortcomings in the best-available PESs for such a benchmark openshell system.

Finally, hyperfine rate coefficients for OH(X) + He collisions, which are related with maser emission models, were calculated and discussed [4].

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## Structural and dynamical complexities in finite heterogeneous systems: analysis and characterization\*

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Synopsis Please replace this text with your synopsis. Keep it short, as it should not have more than 700 characters including spaces.

A number of descriptors to analyze structural and dynamical complexities in finite heterogeneous systems will be presented. Their utility will be illustrated through applications to bimetallic clusters. \*This work was supported by by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

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## Large-scale DFT calculations on platinum nanoparticles

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Metallic systems pose a challenge for density functional theory (DFT) calculations as their lack of band gap does not allow a numerically stable description of "occupied" and "virtual" molecular orbitals. The Kohn-Sham formulation of Mermin's extension [1] of DFT to finite electronic temperature overcomes these difficulties by using fractional occupancies for the molecular orbitals. In this approach, the Helmholtz free energy rather than the energy of the electronic system is computed. Methods for calculations based on this theory have been developed in terms of delocalised molecular orbitals [2, 3]. We will present a new direct energy minimization method for metals [4] based on the localised Wannier functions of the ONETEP [5] linearscaling DFT code. The localization constraint results in substantial matrix sparsities. In its original formulation [4] our method contains a cubic-scaling computational bottleneck due to a required diagonalization of the Hamiltonian matrix but with greatly reduced impact on computational cost due to the minimal size of the Hamiltonian matrix and the use of parallel eigensolvers. Our more recent developments are in the spirit of the Fermi Operator Expansion (FOE) methods and completely avoid the diagonalization.

Using our method, we have performed large-scale adsorption calculations on cubooctahedral and experimentally determined platinum nanoparticles, for a range of ligands chosen for their importance in fuel cell reactions such as the oxygen reduction reaction (ORR) on the cathode catalyst of a proton exchange membrane fuel cell. In the set of cubooctahedral nanoparticles we compare the difference in adsorption energies between constrained, but pre-optimised nanoparticles and the ligands, and between fully geometry optimised systems of nanoparticles

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and ligands, which show significant deviations in binding strength between the fully relaxed and constrained systems. We have also performed atomic oxygen adsorption calculations on experimentally derived (using quantitative ADF STEM [6]) Pt nanoparticles.



**Figure 1.** Electronic density of a Pt nanoparticle from DFT calculations with ONETEP

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## Competition between molecular and dissociative adsorption of hydrogen on free and graphene-supported palladium clusters

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**Synopsis** The storage and the dissociation of hydrogen are two key problems for the technological use of hydrogen, as a source of energy or in catalysis. The adsorption of hydrogen on metal-doped nanoporous carbon materials has been proposed as an efficient storage technique. We have performed density functional calculations, DFT, to investigate the competition between the molecular and the dissociative adsorption channels of hydrogen on palladium clusters as a function of hydrogen concentration. Realistic palladium clusters supported on graphene are compared with ideal free-standing clusters.

Hydrogen adsorption on nanoporous carbon materials is one of the most promising technologies for hydrogen storage. However pure carbon materials do not meet the technological requirements due to the small adsorption energy of hydrogen to the graphitic walls of the pores [1]. Experimental work [2] has shown that doping with Pd atoms and clusters enhances the storage capacity of porous carbons. Therefore, it is of high interest to unravel the role played by the Pd dopant on the enhancement mechanisms.

We have performed simulations based on the Density Functional formalism to study the adsorption of hydrogen on free palladium clusters, clusters supported on pristine graphene [3] and clusters anchored at a graphene vacancy. In all three cases we found that hydrogen adsorbs following two channels i) molecular adsorption and ii) dissociative chemisorption. The adsorption energies of hydrogen on the Pd clusters are higher than on the graphitic walls, a feature that would justify the observed enhancement in the storage capacity of Pd-doped porous carbons. We have shown, however, that desorption of Pd-H complexes from the surface of pristine graphene competes with desorption of hydrogen [4], what would spoil the beneficial effect of the dopant. As a way to overcome this difficulty, we proposed to anchor the Pd atoms and clusters to defects of the graphene layer, for instance to graphene vacancies. Our results are very promising since the Pd clusters anchored to vacancies [5] retain their capacity of adsorbing hydrogen and completely prevent the desorption of Pd-H complexes. The competition between molecular adsorption and dissociative chemisorption of hydrogen on Pd clusters is investigated as a function of hydrogen concentration from a single hydrogen molecule till the saturation limit (see Figure 1). The more realistic palladium clusters supported on pristine graphene and anchored at a graphene vacancy are compared with ideal free-standing clusters.



Figure 1.  $Pd_6$  cluster anchored at a graphene vacancy saturated with nine hydrogen molecules. Three of them are dissociated.

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## Dissipation in quantum time dependent mean field

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Mean field provides an essential starting point to understand the dynamics of numerous many-body systems, from nuclei to molecules and nano structures. But the analysis of energetic dynamical processes requires correlations beyond mean field, especially incoherent ones. The inclusion of dissipative features in current mean field theories for finite electronic systems is thus a key issue. The underlying mean field theory is provided by Density Functional Theory (DFT) in its simplest Local Density Approximation (LDA), which is a robust and flexible low energy approach [1,2]. We discuss extensive studies to include incoherent correlations on top of Time Dependent LDA or Time Dependent Hartree Fock (TDHF). We propose a quantum Relaxation Time Ansatz (RTA) providing an approximate quantum kinetic treatment [3] and a stochastic extension of mean field, Stochastic TDHF [4]. The RTA has allowed us to access realistic laser irradiation scenarios and study in particular the impact of dissipation on electron emission in moderate size clusters. The STDHF approach is much richer but still at a more schematic level. We have explored it in simple mo-

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lecular systems and analysed its capabilities in detail [5,6].

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## Investigating molecular properties and spectroscopy along the phase diagram.

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**Synopsis:** A combined use of Quantum Mechanics and Statistical Mechanics is used to study atomic and molecular properties and spectroscopy in different points of the phase diagram, thus including the liquid and supercritical phases. The behavior of the dielectric constant of Ar is analyzed near the critical point  $(T=T_c+2K)$ .

The combination of quantum mechanics with molecular modeling is a powerful tool for studies of simple and complex liquids. In addition, it may also be used to study the spectroscopic and reactivity of molecules in solution, a situation that is germane in chemical laboratories. The understanding of the solvent effects is thus a major concern in the rationalization of experimental results. In the last two decades theoretical treatments have been developed to incorporate solvent effects. An important direction of research uses some sort of computer simulation to perform hybrid calculations. This is generally called QM/MM method, because both classical and quantum methodologies are employed. Conventional QM/MM methodology can be so costly that normally only a small fraction of the system is indeed treated by quantum mechanics. A systematic procedure based on a sequential Monte Carlo (or Molecular Dynamics) quantum mechanics (S-QM/MM) methodology has been developed in our group [1] that treats the solvent as an explicit liquid system. Different applications [2] have been made including absorption and emission spectra, NMR parameters, vibrational circular dichroism, chemical reactivity, etc. As long as the thermodynamic condition can be imposed this opens a large avenue for applications in other parts of the phase diagram. Hence, we have also addressed the technologically and environmental friendly condition of supercritical fluids. Several applications will be shown indicating the accuracy of the calculated results. In particular we discuss the structural aspects of supercritical  $CO_2$  and its role on the spectrum of para-nitroaniline as obtained from Born-Oppenheimer Molecular Dynamics [3].

More recently we have pointed our focus to the vicinities of the critical point. Theoretical studies of the critical behavior of fluids have been conducted mostly by universal scaling functions and renormalization theories. We have given the first explicitly calculated values of the dielectric constant in the close vicinity of the critical point  $(T > T_c)$ . Thus, the behavior of the dielectric constant, only slightly above the critical point, is determined using first-principle quantum mechanical calculations for the first time. Our multiscale results [4] obtained by combining statistical mechanics and first-principle quantum mechanics indicate that the dielectric constant of Ar only 2K above T<sub>c</sub> and around the critical isochoric (0.531 g/cm<sup>3</sup>) becomes density-independent (Figure 1).



Figure 1. Change of the dielectric constant of Ar.

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## Hydrogen polyoxides: structure, stability and dynamics in gas phase, water clusters and aqueous solution

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**Synopsis** Ab initio calculations and QM/MM Molecular Dynamics simulations have been carried out to get insights into the molecular structure of hydrogen polyoxides, which are reactive oxygen species (ROS) playing an important role in the atmospheric and water chemistry of ozone.

Small hydrogen polyoxides (n=3-4) are thought to be formed during  $O_3$  decomposition in water by recombination of highly reactive HO and HO<sub>2</sub> radicals. Direct experimental evidence of H<sub>2</sub>O<sub>3</sub> formation has been reported after photolyzing hydrogen peroxide–ozone mixtures in argon matrices. Formation of H<sub>2</sub>O<sub>3</sub> in biochemical processes has been established too. H<sub>2</sub>O<sub>4</sub> formation has been observed in electrical discharge studies and other experiments. Larger hydrogen polyoxides have not been observed yet but they are likely to form in ozone decomposition from the combination of HO<sub>n</sub> radicals.

The physical and chemical properties of these systems are not completely understood and in the last years, we have carried out a series of theoretical studies trying to get some insights into their electronic and molecular structure. Calculations have been carried out in the gas phase and in aqueous environments, namely in water clusters, in bulk water solution and at the air-water interface.

Hyperconjugation effects have been shown to play an important role. They are responsible for the helical structure of these molecules and for a remarkable chain parity effect: in even-n chains, there is a clear systematic alternation of long and short O-O bonds. Actually, O-O distances do not become uniform as the chain length increases (Figure 1). Besides, formation enthalpies for n= 3-10 have been calculated in gas phase using high-level ab initio calculations. Formation enthalpies are negative for n<5, close to zero for n=5 and positive for n>5. They go up by approximately 12-16 kcal/mol per O atom although the increase is not regular; it presents an oscillatory behavior that is clearly connected with the above mentioned odd/even effect.

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Computations in aqueous media have focused on hydration energies, structural modifications through the effect of interactions with water, and on some chemical properties such as dissociation energies and  $pK_a$  values. The calculations in bulk water solution and at the air water interface have been carried out with an elaborated Molecular Dynamics approach that employs the socalled QM/MM force-field, in which the solute is described quantum mechanically and the water molecules are described using a classical (molecular mechanics) potential.

Some of these results will be presented and discussed in this talk.



**Figure 1.** Remarkable OO bond-length variation in even (*vs* odd) polyoxide chains due to hyperconjugation effects.

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## Molecular mechanisms leading to mutagenesis unraveled via ion-induced mass spectrometry

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**Synopsis.** The study of the ion induced fragmentation of 5-bromouracil (5BrU) hydrated clusters demonstrates that several series of hydrated fragments are formed. The structure of these fragments provides evidence of the water mediated keto-enol tautomerisation in 5BrU.

The bi-helical complementary base pairing structure of DNA, adenine-thymine (A-T) and guanine-cytosine (G-C) [1] is widely considered one of the most important scientific discoveries of the 20th century. In the original formulation of mechanisms of replica of DNA, the possibility of base mispairing due to a base occasionally occurring in one of its less likely tautomeric forms was suggested as the main cause for spontaneous mutations in DNA. These non-Watson-Crick complementary bases [2] constitute a mispair due to keto-enol and amino-imino tautomerisations.

Spontaneous tautomerisation is unlikely, but it can be stimulated by external factors, like the presence of base analogues, as 5BrU, or of the water environment itself [3,4]. The mutagenic action of 5BrU is widely accepted [5]. Even though the basic mechanisms of such effect are still much debated, the crucial role played by the water environment has been often emphasized. In our experiments we show that mass spectrometry performed on free biomolecules and small clusters in condition of nanosolvation, provide valuable insights into tautomerisation mechanisms.

In this work we report a study of the fragmentation of hydrated clusters of Uracil(U) and 5BrU induced by 36 keV  $^{12}C^{4+}$  ions. The hydrated clusters have been produced by using a gas aggregation cluster source [6]. The fragment products have been analyzed via a time of flight mass spectrometer. The experiments have been performed at the low energy beamline, ARIBE, of the GANIL facility in Caen (France).

The measured mass spectra of the 5BrU hydrated clusters have shown the presence of several series of hydrated fragments, i.e. molecular fragments bound to an increasing number of water molecules. Such phenomenon, barely present in the unsubstituted U case, has allowed to observe that a relatively small number of water molecules in specific sites promotes the H migration from the N to the O atom producing the keto  $\rightarrow$  enol tautomerisation, which is the main cause of the mutagenic effect observed in 5BrU (see figure 1).



**Figure 1.** Schematic of some of the fragments whose hydrated series are observed in the mass spectrum of hydrated clusters of 5BrU. The blue arrows indicate the suggested sites of hydration and the red dashed lines surround the charged (detected) fragment; M indicates the parent ion. The proposed tautomerisation processes mediated through the presence of a sufficient number of water molecules is also shown.

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## Charge and energy flows in ionized thymidine

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**Synopsis** The ionization and fragmentation of the nucleoside thymidine in the gas phase have been investigated. We used two sources of ionization/excitation: VUV photons and low-energy multiply charged ions, associated with coincidence analysis of photoelectron/photoion or ion/ion pairs. The synergy between experimental works and quantum chemistry calculations, allowed to obtain a complete picture of the fragmentation dynamics, in particular the charge and energy transfers within the molecular system.

Dynamics of different relaxation processes, reflecting energy and charge flow processes in complex systems that can imply a vast number of relaxation pathways (e.g. evaporation, structural reorganization, fragmentation). In the present work, we study response of the thymidine molecule (nucleoside, component of DNA) after interaction with ions or photons in the gas phase. Moreover, we have coupled the experimental investigations with quantum theoretical calculations to obtain a complete picture of charge and energy flows in the case singly ionized thymidine molecules.

The experiments have been performed with two different crossed beam devices relying on coincidence measurements: valence shell ionization (GASPHASE beamline, Elettra synchrotron, Trieste) and low energy ions (ARIBE facility of the GANIL, Caen). Quantum chemistry calculations have been performed using the GAUSSIAN09 package (UAM, Madrid, Spain).

The thymidine cation, produced in collisions with 48 keV  $O^{6+}$  ions, hardly survives. It dissociates via the glycosidic bond cleavage. Interestingly, an intramolecular H-transfer is observed when the charge is localized on the base part yielding  $(B+1)^+$  ions. This does not occur when the charge is localized on the sugar part  $(S^+)$ . From the quantum chemistry calculations it has been shown that such products are the most stable ones.

The photoelectron-photoion coincidence method (PEPICO) [1] was used to investigate the fragmentation dynamics as a function of the electronic excitation energy. Particularly, the comparison of the PEPICO mass spectrum with

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the calculated orbitals shows the strong dependence of the charge localization on the excited orbitals. From the comparison of the stateselected mass spectra with the calculated energies associated with the different fragmentation pathways for the ground state, we suggest that the electronic state correlates to the nearest fragmentation channel already opened and that the coupling between the electronic excitation and the vibrational one is highly efficient. Therefore, we propose a method to evaluate the energy transferred to the system during ion collisions by fitting the contributions of the PEPICO mass spectra obtained for different photon energies in order to reproduce the ion-mass spectrum. The obtained excitation energy distribution agrees very well with the predicted one [2].

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## Understanding the effect of the hydrogen bonds and the preferential solvation of mixtures in electronic properties of solutes

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**Synopsis:** We used a sequential molecular mechanics and quantum mechanics approach to study the effect of mixtures in electronic properties of molecules of interest. In particular we analyzed and quantified the most important contributions of each moiety of the mixture in the non-linear behavior of the electronic absorption spectral shift with respect to the concentration of the mixture.

The solvent effects in molecular properties are of great interest and have been studied by theoretical and experimental methods [1]. In particular a solvent composed by mixture of two liquids presents interesting properties and large applicability. Changing the concentration of one species of the mixture a specific property can be varied gradually from one value to another (example: the dielectric constant in the 1,4dioxanewater mixture can vary from 2.8 to 78.5 increasing the water concentration).

El Seoud and coworkers [2-6] performed extensive investigations of the solvatochromism of betaine family probes in different mixtures. In Figure 1, we show some experimental data obtained by them [2-6] for the reduced electronic excitation,  $(E_r)$ , of 1-methilquinolin-8-olato (QB) in solvent-water mixtures varying the concentration of water.



**Figure 1.** Experimental behavior of the reduced electronic excitation of QB in different solvent-water mixtures with respect to the concentration of water in the mixture [2-6]. The dashed line is the ideal behavior.

The reduced electronic excitation energy is defined as  $E_r = (E-E_W)/(E_S-E_W)$ , where *E* is the excitation energy of the probe in the mixture,  $E_W$  in pure water and  $E_S$  in pure solvent.

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We performed a theoretical investigation on the QB absorption excitation energy in methanolwater and acetone-water mixtures in several concentrations using a sequential approach with molecular mechanics and quantum mechanics (QM). Initially, we perform Molecular Dynamics (MD) simulations of the mixtures and compare their theoretical and experimental densities in several concentrations of water to validate the classical force field of molecules of the mixture. Then, we refine the classical force field of the solute comparing the molecular dynamics in vacuum and the QM calculations of the isolate solute. Additionally, we considered in the classical force field the solute polarization due to different mixture in different concentrations.

The results of the electronic excitation energies showed that our theoretical procedure was able to well describe the experimental solvatocromism of QB in mixtures. Then, we build a model that describes the experimental solvatocromism data using the microscopic solvation details revealed by the configurations generated in the MD simulations. With this model we could identify that the most important solvation contributions, which causes the non-linear behavior the solvatocromism, are the number of solute-solvent hydrogen bonds and the preferential solvation of the solute that compete with each other.

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## Quantum effects in water clusters: role of the molecular flexibility and applicability of quantum thermal baths

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**Synopsis** We have investigated the properties of water clusters by means of molecular simulation methods that incorporate nuclear quantum effects. Firstly we will show that rigid models can provide a rather accurate description of many properties with about one fifth of the cost of flexible models. Secondly, we will also discuss the applicability of the semiclassical Quantum Thermal Bath method for water cluster. It will be shown that this method, with a computational cost comparable to that of classical simulations, can provide a reasonable description of the thermodynamics of clusters as long as that the vibrational delocalization is not too strong.

Due to the light mass of hydrogen, water properties are affected by quantum effects even at room temperature. This is reflected, for example, on the increase of both the melting temperature and the temperature of maximum density upon isotopic substitution of hydrogen. These nuclear quantum effects can be relatively easily incorporated in simulations using the path integral formalism[1], in which each quantum particle is described by a ring polymer with a number of beads P. Rigorously this formalism is only exact for an infinite number of beads, but in practice the main contribution of quantum effects is caputured for  $P > \hbar \omega / k_B T$ ,  $\omega$  being the maximum vibrational frequency of the system.

Water is a flexible molecule and such flexibility should be taken into account when designing realistic potential models. As in the water molecule the frequencies of intramolecular vibrations are quite high  $(\omega_{max}/2\pi c \approx 4000 cm^{-1})$ , a rather large number of replicas is required (P =120-200 at T=120K). However, since many condensed matter properties are likely to be more affected by intermolecular vibrations rather than by intramolecular contributions, the number of replicas can be reduced using rigid models. Considering water as a rigid molecule, the maximum frequency of the system is  $\omega_{max}/2\pi c \approx 900 cm^{-1}$ , thus reducing the number of required replicas to about P = 30 - 50 at T=120K[2]. With the aim of assessing the effect of flexibility on the properties of small water clusters we have performed simulations using the rigid TIP4PQ/2005[3] and the flexible q-TIP4P/F[2] models. We found that the geometry of the water molecule is affected by intermolecular interactions and, as a consequence of this distortion, the formation energies of the clusters for the rigid model are about 0.6 kcal/mol lower than those for the flexible model. However, as this difference remains practically constant with size, the results obtained with rigid models can be corrected in an *ad hoc* way[4].

Another possible route to reduce the computational cost of simulation of quantum effects in water is by resorting to the use of semiclassical methods, such as the Quantum Thermal Baths (QTB). This approach consists on propagating the phase space variables within a Langevin equation formalism, but using a correlated (colored) noise. Our results show that this method performs relatively well against alternative approaches in predicting correct energetic properties, including in presence of phase changes, provided that vibrational delocalization is not too strong. In contrast, the dynamical behaviour inferred from global indicators such as the root-mean-square bond length fluctuation index or the vibrational spectrum reveals more marked differences caused by zero-point energy leakage, except in the case of isolated molecules with well separated vibrational modes [5].

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## Bombardment of solid glycine by 2 keV electrons: Implications for astronomical environments.

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**Synopsis** The stability of glycine under 2 keV electron bombardment is analyzed at various temperatures by means of IR spectroscopy. Radiolysis yields and half-life doses are in good agreement with recent MeV proton experiments. The results of the measurements indicate a low probability of survival of hypothetic pre-solar glycine in the present Solar System.

Glycine, the simplest amino acid, has been detected in a comet and in carbonaceous chondrites and, although its detection in interstellar space remains uncertain, its presence is not unlikely, since organic molecules of comparable complexity have been observed [1]. The estimate of the survival probability of this amino acid under the harsh conditions of many extraterritorial environments, subjected to UV irradiation and cosmic ray bombardment, is thus of great interest.

Recent investigations on the irradiation of glycine with high energy protons [2] and electrons [3] have led to conflicting results and have cast doubt on the widespread assumption that the effects of energetic particles on matter depend rather on the deposited energy dose than on the specific nature of the particle.

In this work the destruction of solid glycine under irradiation with 2 keV electrons has been investigated by means of IR spectroscopy. Destruction cross sections, radiolysis yields and half-life doses were determined for samples at 20, 40, 90 and 300 K. The thickness of the irradiated samples was kept below the estimated penetration depth of the electrons. No significant differences were obtained in the experiments below 90 K, but the destruction cross section at 300 K was larger by a factor of two (Figure 1). The radiolysis yields and half-life doses are in good accordance with recent MeV proton experiments [2], which confirms that electrons in the keV range can be used to simulate the effects of cosmic rays if the whole sample is effectively irradiated. In the low temperature experiments, electron irradiation leads to the formation of residues. IR absorptions of these residues are assigned to the presence CO<sub>2</sub>, CO, OCN<sup>-</sup>, and CN<sup>-</sup> and possibly to amide bands I to III.

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**Figure 1.** Normalized intensity decay of the 1405 cm<sup>-1</sup> band of glycine as a function of electron fluence.

The protection of glycine by water ice is also studied. A water ice film of  $\sim 150$  nm is found to provide efficient shielding against the bombardment of 2 keV electrons. The results of this study show also that current Monte Carlo predictions provide a good global description of electron penetration depths. The lifetimes estimated in this work for various environments ranging from the diffuse interstellar medium to the inner Solar System, show that the survival of hypothetical primeval glycine from the solar nebula in present Solar System bodies does not seem very likely.

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## **Conformational Studies of Biomolecules by Broadband Rotational Spectroscopy**

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**Synopsis** Results on the structures and conformations of several biologically-relevant molecules determined by broadband rotational spectroscopy will be presented and discussed.

Biologically-relevant molecules are highly flexible, existing in different conformations and interconverting between them along corrugated potential energy surfaces. What are the preferred conformations that a biomolecule adopts and why? What is the influence of the environment? Rotational spectroscopy is uniquely placed to answer these questions as it relates directly to molecular structure and its high resolution and sensitivity allows unequivocal identification of co-existing conformers and relevant stabilising interactions. Over the last decade, technical improvements had made possible to extend the range of biomolecules amenable to rotational studies. In this contribution we will describe these advances and several examples of our recent work on isolated biomolecules and their clusters will be discussed, namely results on amino alcohols and on odorants. In all cases val-

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uable information was obtained on the intra and intermolecular interactions determining molecular structure.



**Figure 1.** Observed clusters of the complex 1:1 complex of prolinol with water.

## Proton ejection in hydride clusters and large molecules following illumination with short X-ray pulses

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The illumination of atoms with short and intense Xray pulses leads to very high charging of the remaining ion due to efficient ionization from within and subsequent resonances with the photon energy in the highly charged ion allowing for efficient twophoton ionization even against high ionic charge.

One would expect this phenomenon to carry over to atomic clusters; however, there another effect comes into play, namely the delocalization of valence electrons reducing Auger decay. Making the step to hydride clusters on the way to large molecules with many hydrogen atoms, one finds surprisingly that for a certain (relevant) intensity range of the X-ray pulse, high charges of the heavy ions are efficiently

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suppressed. We will explain these phenomena and finally investigate how they influence the Coulomb explosion of Lysozyme, a large molecule recently frequently studied as a test case for coherent diffractive imaging.

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## Electron production by noble metal nanoparticles irradiated with photons and fast ions

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**Synopsis** We analyzed electron production by noble metal nanoparticles irradiated with photons and fast ions. Two dominant peaks in the emission spectra of low-energy (with kinetic energy of 0 - 30 eV) electrons ejected from gold clusters were assigned to two distinct types of collective electron excitations, namely plasmons and giant atomic resonances. We demonstrated that the decay of the collective excitations formed in noble metal nanoparticles is an important mechanism of generation of low-energy electrons which play a significant role in producing damage to biological systems.

It is currently acknowledged that low-energy secondary electrons having the kinetic energy from a few eV to several tens of eV and other reactive species (mostly, free radicals), which are produced when fast ions propagate through a biological medium, largely cause the biological damage [1, 2]. As was proposed recently, cancer treatments with ionizing radiation can be improved by injecting metal nanoparticles (noble metal, in particular) which may increase the number of secondary species in the target region. However, the nanoscale mechanisms leading to an improvement of existing techniques are still to be thoroughly substantiated.

We performed a theoretical and numerical analysis of electron production by noble metal (gold, platinum, silver) nanoparticles irradiated with photons and fast ions. For that, we calculated the photoabsorption spectra of  $Au_N$  (N = 18 - 42) clusters in a broad photon energy range by means of the time-dependent densityfunctional theory (TDDFT) approach. Two prominent features of the spectra were assigned to the two distinct types of collective electron excitations (Fig. 1). Plasmons, i.e. collective excitations of delocalized valence electrons, dominate the spectra of electron emission from metallic nanoparticles in the energy range of 1-10 eV. For higher electron energies (of a few tens of eV), the main contribution to the electron yield arises from the atomic giant resonance associated with the collective excitation of 5d electrons in individual atoms of a nanoparticle.

Similar to the photoionization, the two distinct types of collective electron excitations appear in the process of impact ionization. We demonstrated that noble metal nanoparticles, especially those made of gold and platinum, significantly enhance the electron yield due to the collective response to an external electric field of a charged projectile. Consequently, the number of the low-energy electrons generated by small noble metal nanoparticles significantly exceeds that produced by an equivalent volume of liquid water [3, 4]. Thus, the decay of the collective electron excitations in the nanoparticles represents an important mechanism of generation of low-energy electrons.



Figure 1. Photoabsorption cross section of the Au<sub>32</sub> cluster calculated within TDDFT (thin curve). Thick solid and dashed curves represent the contributions of the plasmon-type and the localized (giant resonance) excitations, respectively [3, 4]. Vertical lines mark the 5*d* and 5*p* ionization thresholds in the atom of gold.

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### Quantum approaches to the interaction and processes between rare-gas atoms and carbon-layered materials

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**Synopsis** We will present recent results on the interaction and processes taken place between rare gases (mainly He) and carbon layered materials and their precursors or prototypes. In particular focus will be put in the characterization of the potential between the gas particle and the substrate, the way in which it can be fit to provide an adequate force field, as well as several results concerning the cluster formation, the evolution with size and the dynamics at the quantum level.

The interaction between atoms or molecules with Polycyclic Aromatic Hydrocarbons (PAHs) or their extensions such as graphene and related carbon layered materials are important topics in several areas covering from astrophysics to more basic research and possible future technological applications in the case of graphene and derivatives.

For the study of these atom-molecule substrate interactions is necessary the construction of reliable potential energy surfaces that properly describe both the short and the long range part of the interaction. We have recently reported a global potential energy surface (GPES) for the adsorption of He on the surface of coronene[1]. The comparison of these GPES with ab-initio calculations shows a general good agreement.

In this report we will show[2] some results concerning the energetics and structure of Heatoms on the coronene molecule ( $C_{24}H_{12}$ ). The structure has been elucidated by means of a Diffusion Monte Carlo (DMC) approach where the coronene molecule has been treated as a rigid body.

The dynamics of He atoms with graphynetype surfaces will also be discussed by using a time-dependent quantum wave packet propagation method[3], in full dimensions and within a reduced dimensionality model.



He-C<sub>24</sub>H<sub>12</sub>

**Figure 1**. Probability density in the coronene plane for He@Coronene

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**Synopsis**. We have studied the production of carbon and hydrogen containing nano-systems. On the one hand, we have used a cluster aggregation source including a He-discharge with and without the admixture of nitrogen. On the other hand, we have irradiated pure clusters of PAH and PANH molecules with low-energy singly charged ions. We will compare the mass spectra obtained with both methods and we will discuss the influence of different parameters, like the relative content of nitrogen in the discharge, the ion collision energy, the initial cluster size as well as the delay of the particle detection.

Molecular clusters can be excited and ionized in the gas phase by collisions with ions. They represent, although only nano-sized, a relatively high density target, the fragmentation of which can be studied with high resolution coincident mass spectrometry. Our recent experiments have shown, that not only fragmentation can be observed, but also highly reactive species can be produced which can initiate chemical reactions within the cluster before this decays [1,2]. Thus, well-prepared ion-irradiated cluster systems can be considered as nano-laboratories which allow to perform ion-induced chemistry in a controlled manner.

In collision experiments we have studied the formation of new molecules when Ar<sup>+</sup> ions at 1.2 keV collide with clusters of Anthracene  $(C_{14}H_{10})_k$  and Phenazine  $(C_{12}N_2H_8)_k$ . In both cases, a large variety of new molecules has been detected with masses much larger than the initial molecular masses (178 and 180 amu, respectively), namely reaching sizes up to about 1000 amu. The different molecules are separated by a carbon unit with the addition or loss of several Hatoms. The underlying process is described by the creation of reactive fragments by nuclear collisions and their following reaction with neighbored molecules. This model is confirmed by classical Molecular dynamics calculations in the case of pyrene clusters [2]. In the top part of Figure 1 we show a corresponding mass spectrum for Pyrene clusters (see also contribution of M. Gatchell et al. in these proceedings).

In order to confirm the reaction model experimentally, we have produced these molecules with the aid of the cluster source (CS) by adding a discharge device. In this case, the PAH molecules which are leaving the evaporation oven will be fragmented by collisions with electrons and He<sup>+</sup> ions in the discharge region. Subsequently the formed fragments react in a condensation channel which is cooled down to liquid nitrogen temperature. The obtained distribution of cationic molecules is shown in the middle part of Figure 1 and shows a surprisingly high similarity with the ion-collision-induced spectrum. When nitrogen is added to the discharge, the peak positions change indicating the inclusion of nitrogen atoms.

In addition we will compare mass spectra obtained for molecules and clusters of anthracene and phenazine obtained with different projectiles and discuss the effect of nitrogen atoms on the growth processes.



**Figure 1:** Mass spectra: top:  $Ar^{2+}$  collisions with Pyrene clusters; middle part: results of a He-discharge; lower part: mixed He/N<sub>2</sub> discharge.

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## Fragmentation of fully aromatic and hydrogenated PAH molecules: H<sub>2</sub> formation and carbon backbone protection?

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**Synopsis** We have studied the fragmentation of internally heated fully aromatic PAHs and hydrogenated PAHs. We find that  $H_2$  may be efficiently formed for internal PAHs temperatures exceeding about 2200 K and that the carbon backbone is *not* protected from damage when the PAHs are hydrogenated.

Polycyclic Aromatic Hydrocarbons (PAHs) consist of fused aromatic rings, typically in planar hexagonal structures. They are formed in incomplete combustion of organic compounds and are considered as pollutants of concern for the human health. PAHs are also believed to be important in many astrophysical environments. It has for instance been suggested that PAHs may act as catalytic centers in the formation of molecular hydrogen, which then may be a key step in the formation of new stars and in the evolution of gas phase species in the interstellar medium [1]. Possible routes (see e.g. Ref [2]) involve internally heated fully aromatic PAHs and hydrogenated PAHs (see Fig. 1).



**Figure 1.** Left: Fully aromatic pyrene ( $C_{16}H_{10}$ ). Right: Fully hydrogenated pyrene ( $C_{16}H_{26}$ ).

It is thus important to establish if  $H_2$  can be formed directly from internally heated PAHs, and how hydrogenation and the excitation agent (photons, electrons, or ions) influence the formation rate. Interestingly, hydrogenation increases the heat capacity (degrees of freedom) but at the same time decreases the dissociation energies (there are only single bonds in fully hydrogenated PAHs, see Fig. 1). This delicate balance determines how hydrogenation affects the  $H_2$  formation rate and if the PAH carbon backbone becomes protected from damage for a given energy input [3]. In the present work we have investigated some of these aspects [2,4]. The experiments were carried out at the ARIBE facility in Caen [2], where atomic ions collide with neutral PAH targets ( $\geq$ 10 keV center of mass energies) and at Stockholm University [3] where fully aromatic and hydrogenated PAH cations collide with neutral atoms (<1 keV center of mass energies). A simple collision model, molecular structure calculations, and molecular dynamics simulations were used to aid in the interpretations of the results.

We find that  $H_2$  formation becomes an important first step process for internal PAH temperatures above about 2200 K, regardless of the PAH size and the way they were excited [2]. This suggests that keV ions may effectively induce such reactions, while they are unlikely due to, e.g., absorption of single photons with energies below 13.6 eV. Our measured absolute, total, fragmentation cross sections shows that the pyrene carbon backbone (see Fig. 1) is more easily destructed when hydrogenated [4]. This is consistent with the results from our quantum chemical molecular dynamics simulation of internally heated PAHs and hydrogenated PAHs.

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## Relaxation of cluster anions in the cryogenic electrostatic storage ring DESIREE

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**Synopsis** We will discuss the relaxation of  $C_n^-$  and  $C_nH^-$  anions, Cu-cluster anions, and some dimer anions during storage in the 13-Kelvin electrostatic ion storage ring DESIREE.

The DESIREE infrastructure at Stockholm University is now in operation [1,2]. DESIREE stands for Double ElectroStatic Ion Ring ExpEriment and it has two ion storage rings. Anions and cations can be stored simultaneously in the two rings, which both are cooled to 13 Kelvin and have a common section for low-energy anion-cation reaction studies [3]. Ions stored in the cold rings exchange heat with their surroundings and gradually approach the same low temperature [3]. This typically means that cluster ions will reach their electronic and vibrational ground states.

The capability of DESIREE to store ions for very long times (hours) was demonstrated in a recent experiment measuring the eight-minute radiative lifetime of the only bound excited state in  $S^{-}[1]$ . In this presentation, we will discuss the storage and cooling of a range of anions. These were produced with wide internal energy distributions in a sputter ion source. The ions were accelerated to energies of 10 keV, mass selected by a 90°-bending magnet and injected in one of DESIREEs ion storage rings. Neutral decay products from spontaneous electron detachment and/or dissociation events are counted by means of a microchannelplate detector placed in the forward direction of one of the rings' straight sections [3]. As the stored ions initially have a broad distribution of internal energies and as the ones with the highest excitation energies decay first, the recorded count rate of neutrals typically follows  $t^{-1+\delta}$  power laws [4]. Here, t is the time at which the ions were produced. The exponent is often (but not always) close to -1 ( $\delta$  small).

Stored internally excited cluster anions may also decay by emission of photons. In such cases no neutrals will be produced and the ions will just continue to circulate in the ring. This is a way for the ions to cool, which means that the signal due to the neutrals will be quenched at a characteristic rate.

We will compare the cooling behaviors of  $C_n^{-1}$ and  $C_nH^-$  cluster ions with n=2, 4, 6, 8, and 10. The  $C_nH^-$  cooling is much slower than the corresponding  $C_n^-$  cooling for n=4, 6, and 8. The fast cooling of these C<sub>n</sub><sup>-</sup> ions are due to fast internal conversion processes to low-lying electronically excited states in these open shell systems. These states decay rapidly by emitting eV photons. The internal conversion processes are not effective for  $C_nH^-$  (n=4,6,8), which have closed outer shells and large HOMO-LUMO gaps. Thus these systems must decay by much slower emissions of infrared photons (vibrational transitions). The  $C_2H^2$  and  $C_{10}H^2$  decays are similar to those of the  $C_nH^-$  ions discussed above while  $C_2^{-}$  and  $C_{10}^{-}$  decay much slower than other  $C_n^{-1}$  ions. The  $C_{10}^{-1}$  decay is complex possibly reflecting different isomers (linear and ring formed) in the stored beam. This may also be the case for the  $Cu_n^-$  ions for which we measure complex decay behaviors. The cooling rates of the  $C_nH^-$  and  $C_n^-$  ions are particularly important as this relates to their possibilities to stabilize when formed in the interstellar medium where  $C_4H^-$ ,  $C_6H^-$  and  $C_8H^-$  have been identified [5].

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### Chiral metal clusters and their interaction with chiral molecules

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Chirality in metal clusters is investigated through geometrical measures, circular dichroism calculations and experimental measurements, and interactions with chiral molecules.

Chirality is a fundamental property of many molecules, including biomolecules like most amino acids. This property has also been found at the nanoscale, as it is evident from recent theoretical and experimental studies. In particular, bare and ligand-protected metal clusters, with size under 2 nm, display chiral behavior [1,2]. In this work, I will briefly review the most recent results on the this topic, focusing on a possible geometrical quantification of chirality through a calculation of the Hausdorff chirality measure for several well-known bare and ligand protected gold clusters [1,3].

I will also discuss recent results on first principles calculations and experimental measurements of the circular dichroism for mononuclear and trinuclear metal-coordinated chiral complexes [4]. This study, based on time-dependent density functional theory, allowed us to gain insights into the origin of the optical activity displayed by larger ligand protected metal clusters.

Finally, I present results, based on density functional theory calculations, on the enantiospecific adsorption of the cysteine amino acid on a chiral Au<sub>34</sub> cluster (see Fig. 1). These results confirm that the adsorption energy of the amino acid depends on which enantiomer of cysteine is interacting with the chiral gold cluster [5,6]. We found that this effect is mainly related with the strength and relative orientation with respect to the cluster surface of the COOH functional group. We also calculated the vibrational spectrum of the cysteine-Au<sub>34</sub> complex to investigate the existence of a vibro-enantiospecific effect, that will be related with different vibrational frequencies of the cysteine normal modes, depending on which enantiomer is adsorbed on the Au<sub>34</sub> cluster surface. The results indicate that indeed there exists frequency shifts between the L- and R- enantiomers of cysteine, mainly localized in the stretching and scissoring modes of

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the COOH functional group. In order to verify this theoretical prediction it would be necessary the design and implementation of novel and accurate enantio-separation methods to perform vibrational spectroscopy measurements. Recent experimental progress along this direction will be mentioned.



**Figure 1.** Geometric structure of the (top panel): chiral  $C_3$ -Au<sub>34</sub> cluster; (bottom panel): cysteine amino acid.

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## Molecular dynamics study of fast ion collisions with biomolecular systems and nanoparticles

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**Synopsis** This work presents recent progress in molecular dynamics simulations of energetic ion interactions with biomaterials, studying new phenomena discovered in this field, such as thermo-mechanical DNA damage, or the properties of nanoparticles which are used as radiation sensitizers in radiotherapy.

A great interest is arising in the collision phenomena between fast atoms and biomolecular systems as well as their interaction with nanoclusters. This interest appears especially because of their application in medicine, as for example in ion beam cancer therapy, where energetic charged particles are used to treat deeply seated tumors [1]. Also, the use of nanoparticles to enhance this kind of therapy is being explored, and this is the main subject of projects such as ARGENT [2].

However, the applications are not motivating this interest alone, since new physical phenomena, which play a relevant role in the interaction of fast ions and nanoclusters with biomolecules, are being discovered. For instance, in Ref. [3], it was predicted that the shock waves on nanometer scale are produced following the ions passage through the tissue-like medium. Moreover, such a shock wave is predicted to be an instrument in biodamage, either directly breaking chemical bonds, or effectively transporting reactive species [4]. Also a new challenge is the understanding of the mechanism of enhancement of biodamage by nanoparticles: although it is known that they can improve the performance of radiation, the physical and chemical pathways are not vet understood, and several possibilities are being currently considered, such as the induction of collective electronic excitations, which could enhance the production of free electrons as compared with the biological media [5, 6], or the catalytic properties of their surfaces [7].

In this context, molecular dynamics simulations are very useful, since the radiation interaction phenomena and the properties of nanoclusters can be studied on the atomic scale, bringing insight on how exactly these new phenomena occur and can be tailored to improving the effectiveness of radiotherapy. In this work, we present simulations performed with the code MBN Explorer [8], related both to DNA damage by shock waves formed around energetic ion tracks, and the study of properties of nanoparticles used for radiosensitization. Previous studies about the interaction of shock waves with DNA are extended, with a better description of energy deposited around ion tracks [9] and the implementation of a reactive force field in MBN Explorer for describing bond breaking. Also, the structure of gold nanoparticles up to 4500 atoms is studied, and the organic coatings commonly found in experiments are introduced in the calculations to simulate its interactions with the nanoparticles.

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## Short time dynamics of Van der walls clusters under strong Coulomb perturbation by femtosecond laser pulses and highly charged ions.

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Gaseous targets are unquestionably a very important tool in physic and chemistry experiments due to their versatility in terms of density and accessibility to a wide range of atomic species. Nowadays, supersonic cluster beam techniques are applied in a large number of experiments such as, for example, laser plasma formation, absolute cross section measurement and X-ray generation [1]. Atomic clusters stand out their versatility (in density, size and accessibility to a wide range of species) as unique objects for studying the nonlinear response of finite systems. Combining advantages of both gaseous and solid targets, they often exhibit specific features that are not observed with atoms, small molecules or even solids when they are submitted to strong Coulomb excitation like intense laser pulses or Highly Charged Ions (HCI) collisions.

On one hand, large clusters, similarly to solids, couple very efficiently to intense femtosecond laser pulses. Nearly 100 % of the laser radiation can be absorbed, leading to the emission of highly charged ions with energies reaching MeV and the ejection of electrons with energies up to a few keV [2]. Another fascinating feature of this interaction is its efficiency for converting photons in the eV range to X-rays with keV energies. Since the late 90's, studies of short laser pulses interacting with atomic clusters have provided a wealth of physics results, often directed towards the concept of short-pulse sources of particles, from neutrons to HCI, including high energetic photons. X-ray emission from HCI provides an ultra-short time probe of the dynamics, giving access to the heating mechanisms on the early first stages of the laser-cluster interaction. Exploring deep inner-shell vacancy production by systematic measurements of the absolute x-ray emission with different parameters governing the interaction (namely laser intensity, pulse duration, cluster size), it was found that the theoretical description should go beyond a "cold-plasma" approximation. Furthermore, we have developed a theoretical model involving collective effects, such as cluster polarization that combines the cluster charge building-up and competes with electronic rearrangements and cluster expansion [3].

On the other hand, the investigation of collisions of Highly Charged Ions (HCI), in the low energy regime (below a few tens of keV/q) with matter is important for fundamental understanding of atomic processes occurring, for example, in various plasma environments as well as astrophysics phenomena. The x-ray spectroscopy of HCI excited states formed by capture of target electrons has proved to be a very powerful tool to study the interaction dynamics of ions with atoms [4] or solids (bulk or surfaces) [5]. In the case of the interaction of a cluster jet consisting of a mixture of clusters and free atoms with slow HCI, the classical capture radius is of the same order of magnitude as the cluster radius (~ nm). Consequently, in the single collision regime, the X-ray yield is drastically reduced due to the clustered part of the jet compared to an effusive jet (at same mean atomic density). This cluster effect signs the HCIcluster interaction when X-ray spectroscopy technique is used [6]. Moreover, clusters offer the possibility to easily change the surface/volume ratio and two extreme cases can be considered : at high impact parameter, the interaction behaves as in ion/atom's collision case with mostly single electron capture while at low impact parameter the interaction looks like ion/solid collision leading to a huge number of electrons captured ("hollow atoms") and then a lower stabilized charged state of the projectile.

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## Time-resolved investigation of charge recombination in clusters driven by strong extreme-ultraviolet and near-infrared fields

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**Synopsis** We report on the first time-resolved investigation of electron-ion recombination in nanoplasmas that are generated during the interaction of intense extreme-ultraviolet or near-infrared pulses with atomic clusters. In both cases, charge recombination is most efficient in the Xe core of mixed Ar-Xe clusters, where a large number of excited atoms and ions are formed during the first few ps of the cluster expansion that are probed by a time-delayed weak near-infrared pulse.

The ionization mechanisms of clusters exposed to intense near-infrared (NIR) and extreme-ultraviolet (XUV) pulses are fundamentally different. For NIR pulses, multiphoton and resonantly driven electron impact ionization can strongly heat the cluster [1], while single-photon ionization processes dominate when using XUV pulses [2]. Nevertheless, we show here that very similar relaxation processes are observed in the nanoplasma formed by ions and electrons that remain confined by the cluster potential.

For the experiments in the XUV range, we employ a newly developed intense high-order harmonic generation (HHG) source [3]. In the timedependent Xe<sup>+</sup> ion kinetic energy spectra from mixed Ar-Xe clusters in Fig. 1(a), the signal is increased by a weak NIR probe pulse. At time delays < 10 ps, the enhancement of the ion yield at higher kinetic energies is explained by a resonance effect, where the laser frequency matches the plasmon frequency of the expanding cluster. At time delays > 10 ps, the probe pulse reionizes excited atoms that are formed by electronion recombination in the nanoplasma, leading to additional strong ion emission that can even exceed the ion emission obtained by the XUV pump pulse only. In the electron spectra, clear signatures of different excited states are found [4].

A very similar behavior is observed for NIR pump pulses in Fig. 1(b), where a pronounced resonance effect is found. Ions that are formed by the reionization of excited atoms from recombination at large delays have much higher kinetic energies in this case. This is explained by the more efficient heating during the interaction of the clusters with intense NIR pulses. The generated ions are accelerated until they form neutral atoms due to recombination [5].

Our results demonstrate that electron-ion recombination plays a dominant in nanoplasmas generated by the interaction of intense laser pulses with nanometer-scale particles at different wavelengths. The use of novel intense HHG sources opens up the path for the investigation of cluster dynamics during the ionization with intense XUV pulses on an attosecond time scale.



Figure 1. Kinetic energy spectra of Xe<sup>+</sup> ions from mixed Ar-Xe clusters at different time delays between an intense pump and a weak NIR probe pulse. In (a) an XUV pump pulse at an intensity of  $2 \times 10^{12}$  W/cm<sup>2</sup> is used, and in (b) an NIR pump pulse at I=1×10<sup>14</sup> W/cm<sup>2</sup> is employed. In both cases, the difference spectra between the pump+probe pulses and the probe pulse only are shown.

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## Interference between overlapping resonances: A route to coherent control of resonance lifetimes and photofragment distributions in the weak-field limit

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**Synopsis** Two different coherent control schemes in the weak-field regime are discussed. They are based on the manipulation of the mechanisms of interference between overlapping resonances when they are simultaneously populated in a coherent superposition. With the first control scheme, enhancement by a factor of three of the life-time of a specific single resonance state of the superposition created, is achieved. The second control scheme allows one to control the transient photofragment distributions by means of pure phase modulation of the pump laser pulse for a long time window after the pulse is over.

Overlapping resonances possess two very interesting features: (1) They are nonorthogonal states that can interfere between themselves; (2) they have a finite lifetime that can vary remarkably for different resonances. The combination of these two features makes possible a rather flexible control of the mechanisms of interference when the overlapping resonances are populated simultaneously in a coherent superposition. Thus, preparing such a superposition provides a powerful tool to design and develop coherent control schemes.

It has been recently shown that the lifetime of an overlapping resonance strongly depends on the amplitudes of the other overlapping resonances populated in a superposition [1]. This is the basis of a control scheme which, in its simplest version, creates a superposition of two overlapping resonances in the complex Ne- $Br_2(B,v'=27)$ , using one pump laser pulse to excite each of the two resonances. By varying the delay time and the ratio of amplitudes between the two pump pulses, it is possible to control the amount of population that is simultaneouly excited to both resonances, and therefore to control the intensity of interference between them [2,3]. In this way, an enhancement by a factor of three of the lifetime of one of the resonances is achieved (see Figure 1) [2].



**Figure 1.** Resonance lifetimes vs delay time and three different ratios of amplitudes between pulses.

In the second control scheme, a single fixed bandwidth pump pulse is used to excite the same superposition of two resonances in Ne-Br<sub>2</sub>(B,v'=27). By applying different linear chirps to the pulse, interference between the resonances can be controlled. As a result, phase effects of increasing intensity are produced in the transient vibrational populations of the Br<sub>2</sub>(B,v<sub>f</sub><v') fragment as the chirp rate  $\beta_0$  increases (see Figure 2) [4]. These pure pulse phase modulation effects occur for a long time window (about 200 ps) after the pulse is over.



**Figure 2.** Transient  $Br_2(B,v_f=v'-1)$  fragment vibrational populations using different pulse chirps.

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**Synopsis** We present a quantum dynamical study of the post-collisonal fragmentation of the ionized water molecule. The nuclear wave packet propagations involve several potential energy surfaces, which are connected by nonadiabatic couplings. The wave packet is initially located at the  $\tilde{B}^{-2}B_2$  electronic state, assuming a Franck-Condon transition from the water ground state. The results show a quick transfer of nuclear wave packet between  $\tilde{B}^{-2}B_2$  and  $\tilde{A}^{-2}A_1$  electronic states due to a conical intersection, while a Renner-Teller coupling between  $\tilde{A}^{-2}A_1$  and  $\tilde{X}^{-2}B_1$  yields in a ps timescale OH<sup>+</sup> / H<sup>+</sup> fragmentation ratios that reproduce the experimantal data.

The H<sub>2</sub>O<sup>+</sup> cation is formed by single ionization of water molecules in collisions with electrons, ions or photons. Removing one electron from the three highest occupied molecular orbitals of H<sub>2</sub>O leads to the formation of H<sub>2</sub>O<sup>+</sup> in the electronic states  $\tilde{X}$  <sup>2</sup>B<sub>1</sub>,  $\tilde{A}$  <sup>2</sup>A<sub>1</sub> and  $\tilde{B}$  <sup>2</sup>B<sub>2</sub>. While the first two states present high dissociation energy barriers that inhibit the fragmentation of the cation into OH<sup>+</sup>+H and H<sup>+</sup>+OH, respectively, the energies of the  $\tilde{B}$  <sup>2</sup>B<sub>2</sub> electronic state lie above the dissociation limits of the  $\tilde{X}$ and  $\tilde{A}$  channels in a broad region, resulting in the predissociation of the molecule at a high rate.

We have carried out nuclear wave packet propagations in several potential energy surfaces (PESs) of  $H_2O^+$ , including nonadiabatic transitions between the different electronic channels. The GridTDSE parallel code [1] was employed in order to solve the corresponding Time Dependent Schrödinger equation (TDSE) in jacobi coordinates, taking a set of  $83 \times 80 \times 73$  grid points in the space of coordinates. We have analyzed the fragmentation dynamics of water ions by considering five *ab initio* PES and their corresponding nonadiabatic couplings, assuming that the wave packet lands in  $\tilde{B}^2B_2$  through Franck-Condon transitions from the H<sub>2</sub>O ground state.

Previous simulations [2] showed that the fragmentation process involves two mechanisms of different time-scales. On the one hand, most of the initial wave packet is readily transfered through a conical intersection to  $\tilde{A}$  within 10 fs. On the other hand, the Renner-Teller coupling between the  $\tilde{A}^2A_1$  and  $\tilde{X}^2B_1$  states that takes place at linear geometries drives to a subsequent distribution in the population of the electronic channels that dissociate into H<sup>+</sup> and OH<sup>+</sup>. The calculated fragmentation branching ratios nicely reproduce previous experimental values [3].

Figure 1(a) displays the time evolution of the populations of the  $\tilde{X}$ ,  $\tilde{A}$  and  $\tilde{B}$  for K = 1, with K the quantum number corresponding to the projection of the total angular momentum along the internuclear axis at linear geometry configurations. Figure 1(b) shows the probabilities of formation of the different ions and radicals.



**Figure 1.** Time evolution of (a) the populations of  $\tilde{X}$  <sup>2</sup>B<sub>1</sub>,  $\tilde{A}$  <sup>2</sup>A<sub>1</sub> and  $\tilde{B}$  <sup>2</sup>B<sub>2</sub> electronic states of H<sub>2</sub>O<sup>+</sup> and (b) probability of production of the different fragments.

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## Effect of water clusters on the natural cycle of ozone depletion: the $HO_2 + (H_2O)_n + O_3$ reaction

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**Synopsis** We report results of our theoretical investigations concerning the influence of water on the  $HO_2 + O_3$  reaction, rate limiting step in the natural cycle of ozone depletion. After a brief revision of the work carried out for n = 0 - 1, we will place emphasis on our latest results concerning the effect of the water dimer and trimer (n = 2 - 3) on the title reaction. Unreported radical-water complexes will also be presented and discussed, as they occur in the reaction mechanism and may be considered a sink for OH and  $HO_2$  in the atmosphere. Ongoing work involving larger water clusters (n = 4, 60) will also be shortly outlined.

The reaction of hydroperoxyl radical with ozone is the rate limiting step in the natural cycle of ozone depletion:

$$\mathrm{HO}_2 + \mathrm{O}_3 \xrightarrow{k_1} \mathrm{OH} + 2\mathrm{O}_2$$
 (1)

$$\mathrm{HO} + \mathrm{O}_3 \xrightarrow{k_2} \mathrm{HO}_2 + \mathrm{O}_2$$
 (2)

$$net: 2O_3 \to 3O_2 \tag{3}$$

This process is mostly active in the lower stratosphere over much of the globe, and it is believed to be responsible for approximately half of the global ozone loss in this atmospheric layer [1]. The intricate nature of reaction (1) has led to a fruitful debate between experimentalists and theoreticians. The importance of studying the influence of water molecules has two sources. One is related to the fact that there is no conclusive evidence from the publications that the experiments on the  $HO_2 + O_3$  reaction do not have the presence of water. Secondly, and besides knowing that water vapour is present in the atmosphere, it is well known that hydroperoxyl-water complexes can act as sinks of  $HO_2$ , with the best example being the  $HO_2$ . $H_2O$  complex, which can account for approximately 30% of HO<sub>2</sub>.

It is therefore evident that in order to achieve a global and detailed understanding of reaction (1), theoretical investigations of the title reaction may be extremely useful. We will start by giving a brief introduction, where we report our main results for reaction (1) (n = 0) [2, 3, 4] and for reaction (1) including one water molecule (n = 1) [5, 6, 7, 8].

We will then proceed by giving a detailed insight of our latest results concerning the effect of the water dimer (n = 2) and trimer (n = 3)on the HO<sub>2</sub> + O<sub>3</sub> reaction. This will include the qualitative and quantitative analyses of the several available reaction paths, where we will focus on the structure of the key stationary points and their energy relative to reactants, calculated at the DFT/aug-cc-pVTZ level of theory. It will also be shown that radical-water complexes are of crucial importance in the reaction mechanism and we will present unreported versions of such complexes involving the water trimer.

Finally, we will briefly discuss the appearance of a hydrogen transfer mechanism along water wires (n = 3, 4) and the possibility of having the HO<sub>2</sub> + O<sub>3</sub> reaction inside a (H<sub>2</sub>O)<sub>20</sub> water cage.

The results will show that the presence of water molecules in the  $HO_2 + O_3$  reaction inverts the initial (n = 0) relative energies between the oxygen- and hydrogen-abstraction saddle points, and therefore the title reaction should not be discarded from dynamics and atmospheric modelling studies of ozone depletion.

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## **Collision of Rare-Gas Clusters with Size-Selected Cobalt Cluster Ions**

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**Synopsis** We have built up an apparatus to study the low-energy collisions between a size-selected metal cluster ion and a neutral molecular cluster by using a merging-beam technique in a pulsed mode. By use of this apparatus, we demonstrate the production of the cluster complexes in the collision of a cobalt dimer ion with a neutral rare-gas cluster,  $Ar_N$  or  $He_N$ , as an example. The production efficiency of cluster complexes is measured as a function of the relative velocity of the collision, and the incorporation process is explained on the basis of the electrostatic interaction and the hard-sphere interaction.

Electronic and geometric structures of metal clusters in gas phase are understood by spectroscopic measurements with rare-gas messenger atoms. Furthermore, helium nano-droplets or clusters are used as a nano-matrix for cryogenic cooling to elucidate them in a high-resolution spectroscopy [1]. In the present stage, we have developed a novel merging-beam method using pulsed cluster beams to incorporate a massselected metal cluster ion into a rare-gas cluster, and show some recent results.

Helium clusters were produced by the supersonic expansion of He gas from a cryo-cooled (~20 K) pulsed valve. The He clusters were ionized by electron impact to confirm the cluster production. Then the ionization source was removed, and we started the collision experiment between cobalt cluster ions and the He clusters. The Co cluster ions were produced by laser ablation, and mass-selected by a quadrupole mass selector (QMS). The mass-selected Co cluster ion beam was deflected by a quadrupole bender and merged with the He cluster beam in an octopole ion beam guide (OPIG). The translational energy of the Co cluster ions was adjusted by changing the DC voltage of the OPIG. The formed cluster complexes,  $Co_2He_n^+$ , were massanalyzed by the second QMS.

Figure 1 shows a typical mass spectrum of the ionized He clusters. The largest size of the ionized clusters,  $\text{He}_m^+$ , detected was  $m \cong 50$  at the stagnation pressure of 18 bar. At higher pressures, the total intensity of the ionized He clusters decreased probably due to the scattering by the background He gas. On the other hand, Figure 2 shows a mass spectrum of the cluster complexes between  $\text{Co}_2^+$  and He clusters. The inten-

sity of  $\text{Co}_2\text{He}_n^+$  decreases with the number of He atoms, but it is clearly observed up to n = 20.



20

10

30

40

50



**Figure 2.** Mass spectrum of  $\text{Co}_2\text{He}_n^+$ . Relative velocity of collision was 1.7 km/s.

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Intensity / 10<sup>4</sup> cps

3

2

1

0

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He"

 $\times 10$ 

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## First principles investigation of hydrogen physisorption on graphynes' layers

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**Synopsis** The adsorption energy of  $H_2$  on graphynes' layers is obtained by means of accurate first principles computations. A novel porous graphite composed of stacked graphtriyne sheets is proposed and it is found to provide large interaction energies for both intercalation and in-pore storing.

Graphynes are novel two-dimensional (2D) carbon-based materials, naturally presenting a nanoweb-like structure characterized by triangular and regularly distributed subnanometer pores[1]. These intriguing features make them appealing for molecular filtering as shown by recent theoretical predictions[2]. The possibility to exploit multilayer graphynes as ideal media for the reversible storage of molecular hydrogen (H<sub>2</sub>) is here theoretically studied.

First principles adsorption energies of  $H_2$  on graphene, graphdiyne and graphtriyne molecular prototypes are obtained at the MP2C[3] level of theory. First, the case of a single layer is investigated and it is found that graphynes are more suited than graphene for  $H_2$  physical adsorption since they provide larger binding energies at equilibrium distances much closer to the 2D plane. In particular, for graphtriyne a flat minimum located right in the geometric center of the pore is identified.

A novel graphite composed of graphtriyne stacked sheets is then proposed and an estimation of its 3D arrangement is obtained at the DFT level of theory by considering a periodic model of the involved bilayers. In contrast to pristine graphite this new carbon material allow both  $H_2$  intercalation and out-of-plane diffusion by exploiting the larger volume provided by its nanopores. Related  $H_2$  binding energies for intercalation and in-pore adsorption are around 0.1 eV (see Figure) and they could lead to high storage capacities exceeding those found to date for carbon nanostructures of different nature.

The proposed layered carbon allotrope should be considered as a very promising material for a safer and potentially cheaper alternative for hydrogen on-board storage than conventional

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solutions based on cryogenic liquefaction and/or high compression.



**Figure.** Adsorption energy evolution of one  $H_2$  molecule crossing a porous graphite composed of stacked graphtriyne layers. A prototype consisting of three parallel graphtriyne pores in a Bernal-like 3D arrangement is used.

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## Modelling ion hydration with the iTTM model

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**Synopsis** Ion hydration plays a key role for the understanding of many natural, industrial and technological processes. In this regard, a crucial issue to be resolved is the extent to which ions influence the structural and dynamical properties of the surrounding hydrogen bond network and, at the same time, to provide a direct molecular-level interpretation of the experimental measurements.

During the last decade, progress on the understanding of these systems have been made by both experimentalists and theorists. On the experimental side, diffraction techniques, linear and non-linear IR spectroscopy and X-ray adsorption measurements have been used to understand the hydration of ions, while for their interpretation rather simplified models have been employed in the post-processing of raw data. On the theoretical side, computational simulations have been mainly limited by the lack of accurate and realistic representations of the underlying interactions, as well as due to the computational cost for an effective sampling of the molecular configurations.

Motivated by the interest of the ion-absortion propensity in droplets and interfaces, as well as its single and collective transport properties in bulk. In this contribution we present the i-TTM (ion-Thole-type) model [1], which includes an explicit treatment of two-body repulsion, electrostatics, and dispersion energies, with the latter contribution being derived within the exchangehole dipole moment dispersion model, and manybody effects represented as classical polarization. The family of potentials include anisotropy in both short and long-range interactions, and their parameters were determined by a two-step fitting procedure to ab initio data at the CCSD(T)-F12 level of theory for the  $X^-H_2O$  (X=F,Cl,Br,I) and  $Y^+H_2O$  (Y=Li,Na,K,Rb,Cs) complexes.

In principle, the quality of the i-TTM model is validated through comparisons with high level electronic structure calculations for alkali and halide water systems. The obtained data suggest that such effective many-body i-TTM potentials can indeed be used to describe ion-water gas phase interactions [2], while in conjunction with the MB-pol water-water model [3] can be also used at condensed phase simulations. Further investigations of structural, spectroscopy and transport properties in condensed-phase environments such as ionic solutions and surfaces of aqueous electrolytes are currently in progress.



Figure 1. Representation of the tetrahydrate cluster-ions for the  $Na^+H_2O$  (left) and  $Cl^-H_2O$  (right) systems, embedded in a water droplet.

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## Attachment of Water and Alcohol Molecules onto Water and Alcohol Clusters

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**Synopsis** We measured the absolute attachment cross-sections of water and alcohol molecules colliding with protonated water and alcohol clusters. Dynamical arguments are used to explain the lower than geometrical cross-sections at small sizes.

By studying the collision between clusters and molecules we can have a better understanding of the growth (nucleation) process. We focused on H-bonded systems such as water, methanol and ethanol that are solvent involved in many physical and chemical processes, in particular as nucleation seeds in atmospheric physics [1].

In the present study we report the measurement of absolute attachment cross-sections of single molecules M (M = water, methanol, or ethanol) onto positively charged mass-selected clusters  $X_nH^+$  (X = water, methanol, or ethanol). Cluster sizes range from tens to hundreds of molecules and the center-of-mass collision energies vary from 0.1 to ~ 1 eV [2].

The attachment cross-sections converge towards the geometrical (hard-sphere) crosssections at large cluster sizes, whereas they are noticeably lower for small sizes as shown in figure 1.

For homogeneous attachment reactions  $X_nH^+ + X \rightarrow X_{n+1}H^+$ , this decrease in the cross-section is well explained by a dynamical collisional model. Indeed when the collision time is short compared to the main vibrational period of the cluster's surface vibration mode, the cluster cannot absorb all the collision energy. From our previous results on water [3] and using a mass-scaling, the experimental results are well reproduced for both methanol and ethanol

clusters.



Figure 1. Log-log plot of the attachment crosssections for methanol molecules onto protonated methanol clusters for two kinetic energies in the laboratory frame [2]. Red triangles: 12 eV. Black squares: 22 eV. Dashed line: geometrical crosssection. Full lines: predictions from the dynamical model.

For inhomogeneous attachment reactions  $X_nH^+ + Y \rightarrow X_nYH^+$  (X, Y = water, ethanol, or methanol), however, this simple dynamical model does not satisfactorily account for the measured data, although the global size dependences are qualitatively reproduced.

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## Quantum Dynamics of Encapsulated Linear Triatomic Molecules: Carbon Dioxide Encapsulated in the Cages of the sI Clathrate Hydrate

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**Synopsis** The translational, rotational and vibrational dynamics of the linear  $CO_2$  molecule inside the sI clathrate is studied employing a quantum treatment within the MCTDH framework.

In this work we present the methodology developed to perform quantum multiconfiguration time-dependent Hartree (MCTDH) calculations for encapsulated triatomic linear molecules. We report, for first time, results on the translational, rotational, and vibrational states of the encapsulated  $CO_2$  molecule. [1]

We carried out five-dimensional (5D), translational and rotational (T-R) and seven dimensional (7D) calculations, treating the two vibrational, two rotational, and three translational degrees of freedom of the trapped  $CO_2$  as anharmonic and fully coupled.



The exact kinetic energy operator is derived and applied to the CO<sub>2</sub> molecule inside the different cages of the sI clathrate hydrate. We employed a set of seven coordinates  $(x,y,z,\theta,\phi,r_1,r_2)$  to describe the caged linear CO<sub>2</sub> molecule. The x,yand z are the Cartesian coordinates of the center of mass of the CO<sub>2</sub> molecule,  $\theta$  and  $\phi$  are the polar and azimuthal angles specifying the orientation of the linear CO<sub>2</sub> molecule within the cage, and  $r_1/r_2$  are the CO bondlengths. The Hamiltonian for the caged linear CO<sub>2</sub> molecule is:

$$\begin{split} H &= -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &+ T_{int} + V(x, y, z, \theta, \phi, r_1, r_2) \end{split}$$

where  $m = m_C + 2m_O$  is the mass of the CO<sub>2</sub> molecule,  $T_{int}$  is the internal kinetic energy term, that in case of a linear molecule has the form

$$\frac{T_{int} = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r_2^2} + \frac{1}{m_C}\left(\frac{\partial^2}{\partial r_1\partial r_2} - \frac{1}{r_1r_2}\right)}{^{1}\text{E-mail: avaldes}}$$

$$+\frac{J^2}{4}\left(\frac{1}{2\mu_1r_1^2}+\frac{1}{2\mu_2r_2^2}-\frac{1}{m_Cr_1r_2}\right)$$

with J being the total angular momentum of the CO<sub>2</sub> molecule, and  $\mu_1 = \mu_2 = \frac{m_C m_O}{m_C + m_O}$ . The potential surface is constructed by the

The potential surface is constructed by the semiempirical SPC/E water model and pairwise additive interactions between the  $CO_2$  molecule and all water molecules forming each cage, while a spectroscopic-determined potential is used for the  $CO_2$  monomer. The POTFIT approach is used to express the potential term as the sum of products using the POTFIT approach.



We investigated the quantum T-R dynamics of the encapsulated CO2 molecule on this semiempirical PES checking its quality by direct comparison with experimental X-ray [2] results and computed the specific vibrational states of the CO<sub>2</sub> in both small and large cages of the sI clathate structure in order to compare with FTIR measurements on fundamental and combination stretching modes [3].

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## Does an isolated C<sub>60</sub> molecule have a liquid phase?

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**Synopsis** We present experimental reuslts which suggests that  $C_{60}$  is such a finite system that have liquid phase. The suggestion will provide useful information to understand its formation in interstellar environments.

Recent studies have confirmed the presence of  $C_{60}$  in interstellar environments [1]. However, its formation mechanism in interstellar space is still the subject of significant controversy [2,3]. It is known that carbon is formed by fusion reactions in the cores of stars, and in the late stages of stellar evolution, massive stellar winds expel it into interstellar space. The primary  $C_{60}$  may be formed along with the expeled carbon vapor cools from thousands of degrees Celsius to an appropriate condensation temperature. Studying the Phase Transition (PT) in fragmenting  $C_{60}$ may shed new light on this controversy.

Our previous work has shown that a PT in C<sub>60</sub> multifragmentation induced by nanosecond laser occurs at almost constant temperature covering a wide range of laser fluency [4]. Here, the yields of ionic fragments (IFs) resulting from the multifragmentation are measured within the PT region (see Figure 1). By excluding two small IFs and magic IFs due to their abnormal behavior, the data for residual IFs are used to estimate the distribution behavior of primary IFs. The distributions are found to obey power laws  $n^{-T}$ . Furthermore, the exponent T values have sensitive dependence on lower laser fluency and converge to a constant for larger fluencies. These observations are in good agreement with an explanation based on the Fisher droplet model, offering the tantalizing possibility of a liquid-to-gas PT in C<sub>60</sub> [5]. The physical picture is as follows:

The  $C_{60}$  on irradiation are firstly heated to the melting temperature at certain time during the laser pulse, causing its structural transition from a solid phase to a liquid phase. After a further photo-absorption from later part of the laser pulse, the instability of the melted  $C_{60}$  is encountered when the temperature reaches the fragmentation temperature (about 6000 K), in which various carbon clusters as fragments are formed.

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Such high temperature implies that, in the preliminary stage of fragmentation, each fragment have also a liquid phase.

If it's true, a model of liquid-gas PT can be used to describe the  $C_{60}$  formation in a cooling carbon vapor. The fragmentation temperature proposed by the previous work [4] provide a reference for the starting temperature of  $C_{60}$  formation in the stellar evolution. The two-stage PT proposed by another work [6] provide a picture for  $C_{60}$ formation, i.e. small carbon clusters form initially and then progress into  $C_{60}$  by incorporation of atomic and diatomic carbon.



**Figure 1.** Relative yields of  $C_n^+$  as a function of the size with different laser fluencies.

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## Dynamics of excited clusters of $\beta$ -alanine in the gas phase

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**Synopsis** We present a theoretical study of excited clusters of  $\beta$ -alanine molecules in the gas phase:  $(\beta$ -ala)<sub>n</sub>, n=2-5. Classical molecular dynamics simulations performed for different internal excitation energies showed a thermal decomposition dependence with the cluster size. We also present an assessment study performed with different families of density functionals using the dimer,  $(\beta$ -ala)<sub>2</sub> as a benchmark system. M06-2X provides the best agreement for the relative energies of 20 isomers in comparison with the reference values computed with the MP2 method. The stability and reactivity of several cluster sizes have been investigated with this functional in combination with the 6-311++G(d,p) basis set.

Ionization and excitation of biomolecules and clusters of biomolecules, induced with highly charged ions, is a widely employed technique to study the stability of these species at a molecular level. In these studies, modeling has become а fundamental tool for understanding the fragmentation dynamics [1,2]. We recently studied doubly-positively charged and excited monomers of B-alanine in the gas phase [3]. In a further step, we here present our recent investigations concerning the stability of clusters of this molecule in the gas phase. This is a more complicated system because it presents additional type of interactions between the molecules such as hydrogen bonds, van der Waals forces, etc. When amino acids are embedded in a cluster of molecules, protective effect of а the environment against fragmentation has been observed [4]. Thus, we evaluate which are the main effects behind this behavior.

We have first performed classical molecular dynamics (MD) simulations using the general amber force field including dimer, trimer, tetramer and pentamer clusters of  $\beta$ -alanine. Several trajectories for internal energies in the range T=50-423K were carried out. With these simulations we studied the stability of the neutral clusters upon thermal excitations and we explore the potential energy surface, thus obtaining different structures.

In order to find a suitable computational tool for carrying out reliable electronic structure calculations for clusters of amino acids at a relatively low computational cost, an assessment based on density functional theory was performed. In our study we include different families of functionals, namely B3LYP, B97D, M06, M06-2X and MPWB1K in combination with 6-311++G(d,p) basis set. The MP2 method was taken as a reference for the chosen model system ( $\beta$ -ala)<sub>2</sub>. The M06-2X method is shown to adequately reproduce the relative energies and geometries of 20 isomers of ( $\beta$ -ala)<sub>2</sub>.

Finally, we have used this level of theory to evaluate the relative stability of numerous isomers of different cluster sizes  $(\beta-ala)_n$ , n=2-5. We have also studied ionization potentials and interaction energies. The possibility of inter- and intra-molecular reactions upon ionization and excitation of the clusters will be presented as well.



Figure 1. Stabilization of  $\beta$ -alanine clusters in the gas phase with intermolecular forces.

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## Theoretical Modeling of Mass Spectrometry

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**Synopsis** We present an implementation of the Microcanonical Metropolis Monte Carlo method based on statistical mechanics and electronic structure calculations. The method is designed to study any kind of fragmentation process. Here we show its capabilities to predict mass spectra of simple molecules.

When a highly energetic particle hits a neutral molecule, part of its energy is transferred to the molecule. If this energy exceeds the ionization energy, ejection of one electron occurs, which generates a molecular ion in an excited state. Then, the molecule breaks leading to a characteristic fragmentation pattern. As the excitation energy increases, the number of channels, abundance and variety of the ionized species also increase. The main hypothesis of our method is that the nature and extent of these reactions depend only on the ion's structure and its internal energy, irrespective of the ionization mechanism.

Under this hypothesis, the dynamical evolution of the many-body system is mainly guided by the accessible phase-space. Thus, statistical mechanics provides the appropriate theoretical framework to conduct this kind of simulations. In this context, we have developed the statistical Microcanonical Metropolis Monte Carlo  $(M_3C)$ method [1, 2], which is based on a specific random way to move in the phase-space until a region of maximum entropy is reached, where physical observables are computed by performing a statistical average. The minimum information that  $M_3C$  needs is the electronic energy, molecular geometry and vibrational frequencies for all possible molecules/fragments involved in the fragmentation process, and the main information provided is the breakup-curves (fragmentation probabilities as a function of the excitation energy). The mass spectrum is obtained by a weighted sum of these curves by using the internal energy distribution of the parent ion resulting from the process of electronic ionization.

In this contribution we will show some results for benchmark systems. In particular Fig. 1 shows the capabilities of  $M_3C$  to describe the fragmentation of the diffuoromethane molecule  $(CH_2F_2)$  with their associated breakup-curves.



Figure 1. Fragmentation of  $CH_2F_2$  molecule. Upper panel, breakup-curves. Middle/lower panel, theoretical/experimental [3] mass spectrum.

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## Photoabsorption spectra of Xe atoms encapsulated inside Fullerenes

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**Synopsis** Photoabsorption spectra of Xe atoms encapsulated inside  $C_{180}$  and  $C_{240}$  as well as in  $C_{58}$ ,  $C_{56}$ , and  $C_{54}$  molecules have been investigated using time-dependent density-functional theory (TDDFT) focusing on quantum confinement resonances (CRs). It is concluded that CRs will be destroyed if the shape of the fullerene is deformed significantly from a sphere. When the Xe atom is at the center of the  $C_{240}$  CRs appear, while if it is at 3.2 °A from the center they disappear. Similarly seven peaks can be identified in the spectrum of Xe at the center of the  $C_{180}$ .

Motivated by the recent experiment [1], this paper discusses the confinement resonances of Xe atoms encapsulated inside fullerenes (1)  $C_{180}$  and  $C_{240}$ , which are close to a sphere and (2)  $C_{58}$ ,  $C_{56}$ , and  $C_{54}$ , which are deformed from a sphere. The study of the photoabsorption spectra for the Xe atom inside the  $C_{58}$ ,  $C_{56}$ , and  $C_{54}$  fullerenes may help us to understand the photoionization process of the Xe atom within the deformed fullerenes.

The TDDFT with pseudopotential method [2] was used to calculate the photoabsorption spectra of the Xe atom encapsulated in the fullerenes. This method takes three steps to evaluate the spectrum. Firstly, the structure of the  $C_n$  (n= 54, 56, 58, 60, 180, 240) is optimized. Secondly, the ground state eigenvalues and eigenvectors are created by solving the Kohn-Sham equation selfconsistently. Thirdly the linear response of the system to the perturbation by an external electric field is described by the TDDFT. After the  $C_{n}\xspace$  calculations a Xe atom was then introduced into the  $C_n$ . The photoabsorption spectra of the Xe@C<sub>n</sub> were evaluated using the same procedure as described for the  $C_n$ . Then the photoabsorption spectra of the  $Xe@C_n$  were extracted by subtracting the cross sections of the C<sub>n</sub> from the corresponding cross sections of the Xe@C<sub>n</sub>. Fig. 1 compares the cross sections for the deformed fullerenes with that for the  $C_{60}$  when the Xe atoms are at the center of the fullerenes.



Fig. 1. Photoabsorption spectra, from bottom up, of Xe atoms encapsulated inside the  $C_{60}$ ,  $C_{58}$ ,  $C_{56}$  and  $C_{54}$  molecules, respectively.

We have also calculated the photoionization cross sections of the Xe inside the  $C_{180}$  and  $C_{240}$  using an attractive

short range spherical well potential [3]. In the calculations the Xe atom was described by relaxed orbitals. Intrashell and intershell correlations among the various states were considered in the calculations. The time independent Schrodinger equation was solved using the RPAE method. For the  $C_{180}$  and  $C_{240}$  the results compare very well with those of the TDDFT, demonstrating the significant distortion of the giant resonance, see results in Fig. 2 for  $C_{240}$ ; also, seven peaks are identified for  $C_{180}$ .



Fig. 2. Dashed and solid curves represent, respectively the cross sections of Xe atom encapsulated at the center of the C<sub>240</sub> and 3.2 °A off the center evaluated by the TDDFT method. Dotted and Dash-dotted curves are respectively, the 4d partial cross sections from our model potential calculated with the electron affinity, EA=2.32 eV, V<sub>0</sub> = 7.67 eV and EA=3.81 eV, V<sub>0</sub> = 10.44 eV [3].

From Fig. 2 it is noted the sensitivity of the cross sections to the electron affinity of the  $C_{240}$  and the CRs to the position of the Xe atom from the center.

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## Experimental alternative to investigate the radiation-induced radical chemistry at the molecular level

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**Synopsis** This project aims to develop an original approach to investigate the damage at the molecular level on biomolecules from the indirect irradiation effects. We will construct a new device to put biomolecules in the gas phase, based on the soft laser desorption from microdroplets directly into vacuum, and this source will be coupled with an irradiation platform.

Biologically relevant material is usually associated with considerable amounts of water; e.g. the living cell contains about 70% water. When ionizing radiation interacts with such material one must consider two main modes of energy deposition: the *direct effect* (ionizing radiation is directly absorbed by the biomolecule) and the *indirect effect* (ionizing radiation is absorbed by the surrounding molecules). In the *indirect effect*, radical cations, electrons and slow ions (essentially oxygen ions) are formed. These reactive intermediates interact also with the biomolecules.

The radiation damage, usually obtained from studies where the living cells are directly irradiated with ionizing particles, is consequently the sum of these different effects. In this case, the only contribution of the radical chemistry in the global damage is reasonably impossible to extract. However, the racial species playing an important role in the formation of lesion clustering at the end of the Bragg peak, the understanding of the radical chemistry at the molecular level becomes crucial with the advent of cancer treatments by ionizing radiation [1].

We propose here an alternative to study separately the part of damage due to the radial species. We are currently developing an original source producing biomolecules in gas phase, which is based on the ultra soft laser desorption from liquid microdroplets under vacuum [2]. The desorbed biomolecules, initially present in the liquid, will thus be studied, in the gas phase by mass spectrometry, close to their native forms in solution. Upon irradiation by home-made mid-IR broad band laser pulses (centered on an absorption band of the solvent), analyte ions are ejected directly into high vacuum, with a minimum of perturbations. The possibility to irradiate the droplet with low energy ions gives then a unique access to the damage mechanisms linked with the radical species (see Fig. 1).



Figure 1. Schematic view of the experimental set-up

The low energy ions cannot penetrate the microdroplet and create only water free-radials (OH<sup>-</sup> and solvated electrons) at the droplet surface, which interact later with the biomolecules included into the liquid droplet. This experimental method simulates, close to *real conditions*, the radial chemistry steps occurring during the irradiation.

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## Structural changes in size-selected water and Ar-water clusters under high pressure: the role of the interaction

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**Synopsis** Classical parallel-tempering Monte Carlo simulations in the isothermal-isobaric (NPT) ensemble have been performed for the  $(H_2O)_{20}$  and  $Ar(H_2O)_{20}$  clusters, over a wide range of temperatures (30 - 1000 K)and pressures (3kPa - 10GPa), in order to study their thermodynamical properties and structural changes. We constructed T-P phase diagrams, and special attention has been paid on high pressure regimes, corresponding to solid-to-solid transitions with the argon atom encapsulated in clathrate-like cages. Semiempirical and ab initio-based interactions models were employed to figure out at which conditions such rare-gas hydrates can be formed.

Crystalline hydrates are formed by many hydrophobic gases that do not exhibit strong attractive interactions with water, and in most cases the gas molecules or atoms occupy cages formed by a network of hydrogen bonds. Gas molecules or atoms usually reside inside one of a few cage structures and such structures are called clathrate hydrates. Clathrate hydrates have been extensively studied, a number of spectroscopic and diffraction studies have been conducted to explore under which conditions bulk rare-gas hydrates may be formed or decomposed and what types of them may be obtained under such conditions [1].

Theoretical investigation of these systems is useful for interpreting properly different experimental observations. Since the formation of bulk clathrate hydrates must start from microscopic seeds (clusters), it seems reasonable to start such investigations at this level.

Using isobaric-isothermal parallel tempering Monte Carlo method, we have performed numerical simulations of two finite systems,  $(H_2O)_{20}$ and  $Ar(H_2O)_{20}$  to investigate, in which thermodynamic conditions a water molecules create a stable cage encapsulating the hydrophobic argon atom [2]. If the NPT Monte Carlo method is applied to bulk system, there is no problem with the definition of system volume, which is identified with the volume of the simulation cell. But in the case of finite systems, the situation is much more involved and several model approaches for the evaluation of the system volume are available. In this study, we compare results obtained from simulations of the two systems considered enclosed in a spherical hard-wall container with variable radius with alternative methods described by Baltazar [3].

Full temperature-pressure phase diagrams of those systems have been obtained by the multiple histogram method. The water-water interactions are described empirically by the TIP4P ice pair potential, for the argon-water interaction we have used empirical and ab initio potentials to see how different water-argon models affect the results of simulation.



Figure 1. Phase diagram of the  $Ar(H_2O)_{20}$  cluster. Black dot lines correspond to the maxima of the heat capacity, blue/red dot lines represent the min/max of the Pearson correlation coeffcient, and A, B, and C to different solid-solid transitions.

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## Efficient formation of autoionizing states in nanoplasmas

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**Synopsis** The dynamics of nanoplasmas, which are formed during the ionization of nanometer-scale particles with intense laser pulses, are typically described by quasiclassical approaches, where electron emission is understood to take place via thermal processes. In contrast, we provide evidence here that autoionizing states are formed in significant amounts in nanoplasmas generated by the interaction of intense near-infrared laser pulses with rare-gas and oxygen clusters. Their subsequent decay is directly observed on a ns time scale, whereas the bound-state signatures of electrons emitted from faster autoionization processes are blurred due to energy exchange with the charged cluster environment.

Laser-generated nanoplasmas [1] have been extensively studied during the past 20 years by experimental and theoretical techniques. However, an important mechanism seems to have escaped the observation so far: here we demonstrate that the generation of autoionizing states and their subsequent decay play an important role during the expansion of clusters.

Recently, we reported on the time-resolved observation of electron-ion recombination processes in nanoplasmas, leading to an extensive formation of lowly and highly excited Rydberg states of atoms and ions [2, 3, 4]. Excited states may decay via fluorescence; however, nonradiative decay mechanisms can be more efficient, as they often take place on faster time scales. Evidence for autoionization is found in molecular oxygen clusters interacting with intense nearinfrared (NIR) pulses. In the electron spectrum shown in Fig. 1(a), clear peaks are observed and identified as an electron contribution from well-known doubly-excited autoionizing states of atomic oxygen. We have time-resolved the electron emission following autoionization and show that it takes place on a time scale of 1 ns [5].

In Fig. 1(b), we demonstrate that autoionization is also observed in rare-gas clusters, which have been investigated by a large number of groups in the past. The peak at 0.5 eV in Kr clusters can be attributed to the decay of doublyexcited states, where one electron is spin-excited and the second electron is excited to a higher orbital. A similar result is also found in Xe clusters. The autoionizing states may be formed either by electron-ion recombination or by electron impact excitation in the nanoplasma.

Our results demonstrate that quantum processes – even though largely neglected in the past – play an important role in the dynamics of nanoplasmas. Another recent discovery is intracluster Coulombic decay, where a singly-excited Rydberg atom decays via an energy transfer to a weakly bound cluster electron in the environment that is emitted into the continuum [6].



Figure 1. (a) Electron kinetic energy spectrum from the irradiation of O<sub>2</sub> clusters with  $\langle N \rangle = 2400$ molecules by NIR pulses ( $I = 9 \times 10^{13}$  W/cm<sup>2</sup>). Thermal electron emission is characterized by an exponential contribution, while the peaks are attributed to autoionization of doubly-excited O atoms. (b) Same for Kr clusters with  $\langle N \rangle = 8000$ atoms ( $I = 5 \times 10^{13}$  W/cm<sup>2</sup>). The marked energy at 0.7 eV corresponds to the spin-orbit splitting in Kr, and the peak at 0.5 eV is attributed to autoionization of different doubly-excited Rydberg states.

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## Structure, Ionization and Fragmentation of Neutral and Positively Charged Hydrogenated Carbon Clusters: $C_n H_m^{q+}$ (n = 1 - 5, m = 1 - 4, q = 0 - 3)

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**Synopsis** The  $C_nH_m^{q+}$  family was studied at the DFT-B3LYP//CCSD(T) level of theory. Dissosiation energies, ionization potentials, geometries and frequencies were obtained. Different trends for these properteis have been observed and analyzed. The fragmentation behaviour has been studied within a combinatorial point of view.

Partially hydrogenated carbon clusters have been widely and heterogeneously studied. Theoretical modeling of their properties and their fragmentation behaviour provides valuable information to study the evolution of new molecules and ions detected in the Instersteallar Medium (ISM). It also helps to understand the composition and chemical processes taking place in the ISM[1]. Previously we have only considered bare carbon clusters [2], when hydrogen atoms are added, the complexity of the studied systems increases. In general, only a few works have considered this family of molecules systematically but only on small sequences<sup>[3]</sup>. This work intents to homogenize all the sparse data available in bibliography for the hydrogenated carbon clusters. From this study we obtain trends that they may be extrapolated to bigger and more complex molecules of the same family.

In this work the calculation of several properties for species of the  $C_n H_m^{q+}$ familiy (for n=1-5; m=1-4; q=0-3) are carried out at DFT-B3LYP/6-311++G(3df,2dp)// CCSD(T)/6-311++G(3df,2dp) level of theory. The studied properties are: relative energies between isomers, ionization potentials, dissociation energies, vibrational frequencies and fragmentation reactions.

The results are interpreted in terms of both, energetic and entropic contributions. The energetic contributions are the values obtained for the relative energy of the isomers. For instance, Fig. 1 shows the distribution of all the considered molecules, note the scaling of the problem by increasing the system size on the top panel. The entropic contribution comes from the combinatorial choices of all possible reaction channels. Fig. 2 shows the combinatorial probability density for the dissociation processes leading to 1, 2, 3 and 4 fragments.



**Figure 1.** Bivariate histogram with the number of isomers as a function of the Chemical Formula Index  $CFI[C_nH_m^{q+1}] = (q+1) + 4(m-1) + 4(n-1)$ , and the relative isomer energy (from their ground state).



Figure 2. Combinatorial probability density to break down a  $C_n H_m^{q+}$  molecule(or cation) into different number of fragments as a function of its internal energy

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### **Atom Contains Not Only Electrons and Nucleus**

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Synopsis The space inside an atom is filled with another state of matter.

Present-day atomic theory suggests that, electrons in an atom exist around the nucleus as standing matter-waves (or electron clouds) in inner and outer orbitals [1]. However, because this behavior requires electrons to be constantly moving, and because there is no evidence that electrons display this kind of motion, the present atomic theory may not be accurate. Today we believe that, the charged particles (primarily electrons) in the atoms of a transparent medium play the major role in the transmission of light through that medium [2]. The concept suggests that, the vibrating electromagnetic field of the incident photons induce vibration in the electrons in the atoms of the medium to vibrate at the incident photon frequencies, which cause the electrons to reemit photons in the incident photon frequencies. Light is transmitted as the result of a chain of this kind of interaction of photons with the electrons and the re-emission of photons within the medium (it is assumed as a kind of absorption and emission of photons by the atoms in the medium). It is also believed that, the slowdown of light-speed in a medium is a consequence of this photon-particles interaction. However, there is a problem with this concept. We know that, atoms and molecules in a gas or liquid (or in a solid, above 0K) are in a state of continuous motion. For example, if we consider hydrogen gas (HG), the RMS (root-mean-square) speed of hydrogen molecules in a HG, at a temperature of 300K is 1930 m/s. If a photon with a wavelength, which is not present in the hydrogen spectrum incidents on a HG at an angle perpendicular to the HG interface (HG is contained in a transparent container), which is at lowtemperature and low-pressure, the photon will pass in a straight-line through the HG, at a speed less than the speed of light. (The speed of light with a wavelength of 589.3 nm in HG, at a pressure of 101325 Pa and temperature of 0 °C, v = c/n =

 $\frac{2.99792458 \times 10^8}{1.000132}$  m/s =2.99752891x10<sup>8</sup> m/s, where, n is the refractive index of hydrogen [3] and *c* is the speed of light in a vacuum). Now we see what will happen, if the particles in the hydrogen atoms are involved in the transmission of light through the HG. When a photon incidents on the first hydrogen molecule, the molecule absorbs the photon. However, because the molecule is moving, if the molecule moves away from the path of the incident photon, the time lag that occurs between the absorption and emission of the photon result the photon to change its path. The same thing will happen to the photon, as it interacts with more hydrogen molecule in the HG. Consequently, a photon cannot travel in a straight-line through the HG (If this is the case, then light from a light source cannot reach our eyes in a straight-line through the air molecules in the atmosphere). However, we know that, a photon can travel in a straight-line through a medium, which has a uniform density- if the photon is not absorbed by the medium. This leads to assume that, contrary to the present-day belief, the particles (electrons and nuclei) in the atoms of a transparent medium are not involved in the transmission of light through that medium. Here, even though the photon is not interacting with the particles in the atoms in the medium, the lightspeed is slowed down, leads to the possibility that, the photon is interacting with something else other than the particles in the atoms. This leads to assume that, in addition to the electrons and nucleus, an atom contains another state of matter as well. Because there is no evidence that electrons are in a state of continuous motion around the nucleus, we can conclude that, the electrons in an atom have no role in providing an atom its volume. Therefore, the above-mentioned matter is the probable candidate for providing an atom its volume. Since the space inside an atom is filled with this matter, we can call this matter as space matter.

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## Intercoulombic decay (ICD) resonances in the photoionization of noble gas endofullerene nanomolecules

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**Synopsis** Using the time-dependent local density approximation, we find intercoulombic decay (ICD) of atomic excitations *via* fullerene continua and ICD of fullerene excitations *via* atomic continua for noble gas atoms endohedrally confined in  $C_{60}$ . A novel decay mode from the hybridization of Auger and ICD processes is predicted.

For a binary system A-B of two Coulomb composites, excitation by photon or by chargedparticle impact can form an inner vacancy. This can involve the inner electron of A to move, not only to an excited state of A, but also to that of B, if allowed by the selection rules. Nonradiative ionization from the decay of this vacancy may autoionize an outer electron. If this emitted electron comes from the composite member that held the original vacancy, then the process is a regular Auger decay (AD). In contrast, if the electron emanates from one member while the precursor vacancy belonged to the other, then this exotic decay process is known as the intercoulombic decay (ICD). ICD was observed as an important decay mechanism in metal clusters [1], dimers [2], and predicted for endofullerenes [3], including recent results in the photoionization of  $Ar@C_{60}[4]$ .

On the other hand, if the vacancy decays, resulting in the emission from a level hybridized between A and B, then the process will entail a coherent superposition of AD and ICD [4]. It is likely that this decay mode is abundant for atom-cluster or atom-nanostructure compound systems. Results that evidence some of these effects are presented here for the photoionization of noble gas endofullerene molecules.

A jellium based time-dependent local density approximation (TDLDA) formulation [5], with the Leeuwen-Baerends exchange-correlation functional [6] to produce accurate asymptotic behavior for ground and continuum states, is employed to calculate the dynamical response of the system to the incident photon.

The free Ar 3p cross section in Figure 1 shows three lowest energy ADs from Ar 3s excitations. The equivalent resonances from 3s@ excitations of confined Ar are identified in the Ar 3p@ cross section. Since ground-state hybridization of Ar 3p with C<sub>60</sub> 3p produces hybridization by hybridization of Ar 3p with C<sub>60</sub> 3p produces hybridization hybridization by hybridization hybridization by hyb

brid orbitals, these resonances arise from the Auger-ICD hybrid process.

We also present the total contribution (@ $C_{60}$ ) of  $C_{60}$  levels in the full Ar@ $C_{60}$  cross section which displays structures at energies where Ar 3s@ resonances occur. These are Ar-to- $C_{60}$ forward ICDs, denoted as F-RICD. The Ar 3p@ result also shows other resonances which coincide with the regular ADs in empty  $C_{60}$  cross section (shown) and exist in the @ $C_{60}$  curve. They correspond to the decay of  $C_{60}$  vacancies through Ar continua, the *backward* ICDs (B-RICD in the figure).



**Figure 1.** 3p and 3p@ cross sections for free and confined Ar, and the total cross section of empty  $C_{60}$ . The contribution (@ $C_{60}$ ) of  $C_{60}$  to the total cross section of Ar@ $C_{60}$  is also displayed.

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## Preliminary study of gas phase ion-molecule reactions via tunable synchrotron radiation

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**Synopsis.** The goal of this work is to perform ion-molecule reactions with the incident ion formed by photoionization and to investigate the effect of photon energy on the reaction efficiency. The study is relevant to different fields of chemistry spanning from atmospheric chemistry to hydrocarbon and water activation chemistry (i.e. methane activation).

It is well known that ion processes play a fundamental role in atmospheric chemistry. The link between the ionic and neutral chemistry is of crucial importance. Ions can be produced in vibrationally or electronically excited states and could take part to non-equilibrium processes. The study of the reactivity of ions and neutrals in the gas phase can also provide information on the mechanism of more complex systems and processes such as the activation of the hydrocarbons and water. The models of ion-molecule reactions are investigated in the laboratories with mass spectrometric techniques. More often the effectiveness of the ion processes is obtained with a triple quadrupole mass spectrometer where ions are produced with electron impact (EI) ion sources, mass-selected in the first quadrupole (Q1) and then driven to the second RFonly hexapole where the neutrals are introduced. The reactivity is investigated at the nominal "thermal" collision energy and the charged products are analysed with the third quadrupole (Q3). An example of an ion-molecule reaction [1] is presented in scheme 1:

$${}^{13}\text{CO}_2^+ + \text{CO} \rightarrow \text{CO}_2^+ + {}^{13}\text{CO}$$
 Scheme 1

Ions produced with EI source at electron energy between 30-70 eV are thermalized by collision using high pressure (about 0.1 Torr) in the source. However non-thermal or excited ions are also of interest in many processes that occur especially in the space where electrons or photons at different energies ionize the molecules. The goal of the present preliminary study is to produce ions with controlled internal energy to investigate how this affects the formation of ion products from ion-molecule reactions. The instrument used for these types of experiments is shown in Fig.1.

Figure 1. Home-made instrument for the study of ion-molecule reactions.

The preliminary results obtained studying the model efficient reaction  $SO_2^{+} + CH_4$  [2] are shown in Fig. 2.



**Figure 2.** Reagent  $(SO_2^{+})$  and product  $(HSO_2^{+})$  ion yields vs photon energy (hv).

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Acceleration Lens Octupole

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## Scattering of alpha particle by lithium atom with electron exchange

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**Synopsis** We present formalism of time-dependent exchange perturbation theory (TDEPT) built to all orders of perturbation, for arbitrary time dependency of perturbation and apply it to the problem of alpha particle scattering on lithium atom where we calculate the differential and the total cross-sections.

Time-dependent perturbation theory (TDPT) has been developed and is widely used in nonrelativistic quantum mechanics. This theory describes a wide class of phenomena such as collisions of composite particles, atoms, and molecules that result in a change in the composition of the particles. These processes are not adiabatic; however, a certain range of interatomic distances (distances between composite particles), which can be interpreted as intermediate distances, plays an important role even in these processes. This is a domain of interaction in which a permutation of composite particles associated with the redistribution of electrons occurs. Exchange forces, which are related to the permutation symmetry of the wave function of a system of particles, decay rather rapidly, exponentially, as the distance between the interacting atoms increases. Invariant perturbation theory and the diagram technique, in spite of the fact that they cover both nonrelativistic and relativistic scales, do not directly take into account the processes that are related to interatomic and intermolecular overlapping of electron shells of multicenter systems and occur at these intermediate distances. The problem of consistent description in terms of Feynman diagrams lies in the fact that the general formalism is based on the orthogonal basis of electron states, whereas electron states belonging to different atomic (molecular) centers are not orthogonal.

In this work, the exchange perturbation theory (EPT) formalism is developed for the case of nonstationary perturbations for which a formula for the *n*th term of arbitrary time functions of perturbation is obtained in any order of perturbation theory, and the formalism is reduced to the standard form of invariant perturbation theory. General expressions are obtained for the scattering (*S*) matrix and the transfer (*T*) matrix for arbitrary types of interaction in which intercenter electron permutations between overlapping nonorthogonal states are consistently taken into account [1]. The formalism obtained is applied to the description of the collision of a double-charged helium ion (the alpha particle) with a lithium atom followed by charge exchange.

From the point of view of scientific novelty, the result in this case is consistent allowance exchange deposits associated with centerpermutations of electrons between atomic centers in collisions with the change in the composition of the particles at a constant saving anti-symmetry of the total wave function of the system with respect to the center to center permutations. Another important result is the consideration of the effect of the total spin of the value of the amplitude of the process. Possible uniform description of scattering processes of complex spin systems based on fundamental analysis of the permutation symmetry of identical particles systems, looks very attractive from the point of view of the general theory, and in the sense of solving applied problems.

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## Radiative cooling of hot $C_n^-$ and $C_nH^-$ molecules

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Synopsis We have measured the rates of neutrals produced from 10 keV  $C_n^-$  or  $C_nH^-$  (n=2, 4, 6, 8, and 10) ion beams stored in one of DESIREE's 14 K storage rings. For n=4, 6, and 8 we observe marked differences between  $C_n^-$  and  $C_nH^-$  cooling rates as inverse internal conversion [cf. S. Martin *et al* (2013) *Phys. Rev. Lett.* **110**, 063003] processes are effective for the  $C_n^-$  ions only. Knowledge of the cooling rates of these ions are important for estimates of their formation and destruction rates in cold interstellar environments.

We investigate the cooling of internally hot  $C_n^-$  and  $C_nH^-$  ions with n=2, 4, 6, 8, and 10 stored in the electrostatic ion storage ring DE-SIREE [1, 2] operating at 14 K. We record the signal of neutrals detected after a straight section of the ring as a function of time, t, after producing internally hot  $C_n^-$  or  $C_nH^-$  ions in a sputter ion source. This production method gives wide internal temperature distributions. If the ions do not stabilize radiatively very fast, the hottest ones will decay first giving overall rates of neutrals following  $t^{-p}$  power laws [3].

In Fig. 1 we show data for n=4 (the results for n=6 and n=8 are qualitatively similar). While the  $C_4^-$ -signal is small and disappears rapidly (sub-milliseconds), the  $C_4H^-$ - signal follows a power law for tens of milliseconds. Similar to  $C_6^-$  [4, 5],  $C_4^-$  and  $C_8^-$  are open-shell systems that cool very rapidly as they can convert (part of) their internal vibrational energies to low-lying electronically excited states, which decay through fast radiative transitions. The  $C_nH^-$  ions, on the other hand, are closed shell systems and have much higher HOMO-LUMO This means that inverse internal congaps. versions to electronically excited states become highly unlikely [4, 5] and internal cooling must proceed through much slower vibrational transitions. While  $C_2H^-$  and  $C_{10}H^-$  have similar decay behaviors as  $C_4H^-$ ,  $C_6H^-$  and  $C_8H^-$ , the decays for  $C_2^-$  and  $C_{10}^-$  are much slower than those for  $C_4^-$ ,  $C_6^-$  and  $C_8^-$ . The  $C_{10}^-$  decay is also more complex possibly reflecting the presence of linear and ring isomers in the stored beam. For  $C_n^-$  and  $C_n H^-$  anions, knowledge of their cooling rates are considered to be very important for estimates of their interstellar abundances [6].



Figure 1. Rates of detected neutral particles normalized to the injected ion currents for the two molecular ions  $C_4^-$  and  $C_4H^-$ . The rapid disappearance of the signal for  $C_4^-$  is due to fast cooling through inverse internal conversion [4, 5, 7].

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## Ab-initio modeling of an anion $C_{60}^-$ pseudopotential for fullerene-based compounds

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**Synopsis** A pseudopotential of  $C_{60}^-$  has been constructed from ab-initio quantum-mechanical calculations.

Fullerene-based compounds are often used as an acceptor [1, 2] in donor-acceptor composite with polymers in order to obtain volumetric heterojunction that is very effective for realization of organic solar photoelectric sells (OSPS). To search new promising compounds it is necessary to develop effective method of specification of geometry and stability of composite system. As far as  $C_{60}$  acts as an acceptor in such systems, it is important to determine the pseudopotential of anion  $C_{60}^{-}$ . The shape of pseudopotential near the fullerene radius depends significantly on electron density profile, therefore, it should be estimated with sufficient accuracy. The recent calculations [3] showed that the application of widely used jellium model doesn't bring data into accordance with results of more sophisticated calculations. Therefore in this work we use ab-initio approach to determine electron density profile and the pseudopotential of  $C_{60}^{-}$  anion.

The ab-initio calculatons of the total electron density of  $C_{60}^-$  has been performed by the FireFly QC package [4] within the Hartree-Fock approximation. To extract the values of electron density from the FireFly QC package result and to calculate a corresponding electrostatic potential on a specifed grid of the position vector  $\mathbf{r}$  we used a Multifunctional Wavefunction Analyzer (Multiwfn) [5]. To construct the radial dependence of  $C_{60}^-$  pseudopotential we averaged the electrostatic potential obtained from Multiwfn software over the directions of the position vector  $\mathbf{r}$ .

The results of the  $C_{60}^-$  pseudopotential calculations are presented in Figure 1. The pseudopotential has the correct asymptotic behavior at the large distances as 1/r, which is typical for a single negative ion. Beside there are two different types of interaction between the fullerene's anion and external electron: strong attraction close to a radius of fullerene's anion and weak repulsion outside and inside of fullerene cage.

Since the obtained pseudopotential can be easy fitted by Lorentz functions it can be effectively used both in classical and quantum molecular dynamics of fullerene-based compounds.



**Figure 1**. Pseudopotential of  $C_{60}^-$  obtained from ab-initio calculations (black solid line), an 1/r asymptotic behavior (red dashed line)

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## Variational and Path Integral Monte Carlo calculations on Helium Clusters Doped with Metastable Anions He\*<sup>-</sup> and He<sub>2</sub>\*<sup>-</sup>

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**Synopsis** Variational calculations (T=0 K) on small  $He_N...He^*$  and  $He_N...He_2^*$  metastable clusters (N[] 4), as well as Path Integral Monte Carlo (PIMC) simulations (T=0.4 K) on larger species are presented and discussed.

The calculations[1] have been carried out assuming additive pairwise-like potential surfaces. The underlying He(<sup>1</sup>S)-He\*<sup>-(4</sup>P) potential curve and the He(<sup>1</sup>S)-He<sub>2</sub>\*<sup>-(4</sup>[ $_g$ ) anisotropic interaction have been recently estimated through accurate CCSD(T) calculations[2]. The He-He interaction is described by a semi-empirical potential[3].



**Figure 1**. He-He\*<sup>-</sup> potential curve supporting 15 bound states, the last two ones being depicted in the inset (upper panel), and He-He<sub>2</sub>\*<sup>-</sup> anisotropic interaction (lower panel).



**Figure 2.** Left panel: snapshot from the PIMC simulation for the  $He_{32}$ - $He^{\Box}$ - cluster at T = 0.4 K showing a bi-pyramid anionic structure surrounded by the rest of He atoms. Right panel: the simulation for the  $He_8$ - $He_2^{\Box}$ - cluster shows instead the impurity far away the helium cluster.

For the atomic anion case, the interaction with helium presents a deep well near 1  $\Box$  followed by a small barrier and then a shallow minimum, see upper panel at **Figure 1**. Accordingly, as He atoms are added, a marked preference to form a bi-pyramid charged core He<sub>7</sub><sup>-</sup>, with the rest of He atoms surrounding it, is obtained through PIMC simulations, see **Figure 2** (left panel).

In turn, the molecular anion He<sub>2</sub>\*<sup>-</sup>, considered as a rigid rotor, tends to point towards a set of packed helium atoms which are placed at long distance from the anion, see **Figure 2** (right panel).

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MA	MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD	DINNER	A. Msezane	N. Aguirre	A. Verkhovtsev	J .M. Rost	D. Qian Coffee Break	A. Valdés	I. Braud	M.E. Sanz	Lunch	D. Arismendi-Arrieta	E. Noya	K. Coutinho	A. Domaracka	Coffee Break	P. Bolognesi	M. Ruiz-López	S. Canuto	E. Suraud	Monday, 20 July				ולעננ 201ל	
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