

# Book of Abstracts









# **IMAMPC 2013**

IMAMPC aims at bringing together young scientists in emerging fields of Atomic and Molecular Physics and Chemistry. It is intended to have an interdisciplinary nature, expecting to bring together theoreticians and experimentalists from diverse fields. IMAMPC is intended to promote high-quality research carried out by young scientists, in order to highlight their contributions to these fields. The IMAMPC meetings have grown in popularity due to the original format, bringing together younger researchers to stimulate exchange of ideas, strengthening of existing collaborations or the creation of new ones.

IMAMPC 2013 is organized around the following topics:

- Physics and Chemistry of the Atmospheres
- Astrochemistry
- Physics at the interfaces: Biophysics
- Theoretical and computational chemistry
- Cold Atoms and Molecules

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## **CONFERENCE** PROGRAM

## **Tuesday, July 2**

## *Physics and Chemistry of the Atmospheres I. Chair Bertrand Chazallon*

## 1 14:30

*Thorsten Bartels-Rausch* Chemistry in Ice and Snow: From the Atmosphere to the Molecular Scale

## 2 15:10

*Florent Louis, Katarina Sulkova, Martin Sulka, Maria Sudolska, Josef Federic, Ivan Cernusak* Atmospheric reactivity of iodoalkanes towards OH radicals

## **3** 15:30

*Aude Simon, Fernand Spiegelman* Conformational Dynamics and Finite-Temperature Infrared Spectra of Water Clusters adsorbed on Polycyclic Aromatic Hydrocarbons

## 15:50 - 16:20: Coffee break

## **4 16:20**

*Petr Slavíček* Atmospheric Photochemistry from a Perspective of Ab Initio Simulations

## 5 17:00

Markus Lampimäki, Sepp Schreiber, Veronika Zelenay, Adéla Křepelová, Mario Birrer, Stephanus Axnanda, Baohua Mao, Rui Chang, Hendrik Bluhm, Zhi Liu, Markus Ammann Influence of nitrogen oxides and UV-radiation on metal oxide surfaces: XPS investigation

**6** 17:20

*González-Lezana Tomas, Scribano Yohann, Honvault Pascal* The reaction dynamics of  $H_3^+$  at low energy regimes

#### 18:30: Welcome reception

## Wednesday, July 3

## Astrochemistry Chair Rita Prosmiti

7 09:00

*Fraser, Helen J.* The Physical Nature of Amorphous Solid Water

8 09:40

*Florent Mispelaer, Patrice Theulé, Fabrice Duvernay, Thierry Chiavassa, Pascale Roubin* Diffusion in Amorphous Solid Water Ice : implications in the interstellar ice chemistry

9 10:00

Barbara M. Giuliano, Antonio Jiménez-Escobar, Guillermo M. Muñoz Caro, José Cernicharo Laboratory investigation of formation and isomerization processes of HNCO in interstellar ice analogues

10:20 - 10:50: Coffee break

### 10 10:50

### François Lique

Collisional and reactive processes of astrophysical interest: On the importance of having accurate molecular data

#### 11 11:30

*Elena Moreno , Guzmán Tejeda, José María Fernández, Salvador Montero* Collisional process of  $H_2O + He$  supersonic jets by Raman spectroscopy

## **12 11:50**

*Mario Hernández Vera, François Lique, Fabien Dumouchel, J. Kłos, Jesus Rubayo* Cyanide/isocyanide abundances in the interstellar medium. Inelastic rate coefficients of Al and Mg compounds.

#### **13** 12:10

*Gómez-Carrasco Susana*, *González-Sánchez Lola*, *Aguado Alfredo*, *Sanz-Sanz Cristina*, *Zanchet Alexandre*, *Roncero Octavio* The  $H_2 + H_3^+$  reaction: dynamically biased statistical model for the ortho/para conversion

12:30-14:30: Lunch break

# *Physics at the interfaces: Biophysics Chair Marc Lefranc*

## **14 14:30**

Damien Baigl

Bottom-up designed, triggerable soft matter systems: from DNA and protein regulation to responsive membranes and light-driven microfluidics

### 15 15:10

*François Anquez, Stéphane Randoux, Pierre Suret, Ikram El Yazidi-Belkoura, Emmanuel Courtade* Oxidative stress in biological cells by direct optical excitation of singlet oxygen : towards new strategies for photodynamic cancer therapy

### **16 15:30**

*Ondřej Svoboda, Daniel Hollas, Milan Ončak, Petr Slavíček* Enhanced Biological Damage through Water Ionization

15:50 - 16:20: Coffee break

### 17 16:20

Maxime Dahan

Exploring the dynamic properties of molecular assemblies in live cells with single molecule imaging and manipulation

### **18** 17:00

Daniel J. Arismendi-Arrieta, George S. Fanourgakis , Juan S. Medina, Rita Prosmiti, Gerardo Delgado-Barrio

Investigating the effect of dipole moment on structural and transport properties in liquid water: The NCC(Q) model

### **19** 17:20

Michel Sliwa, Mateusz Rebarz, Cyril Ruckebusch, Avisek Ghose, Pascal Didier, Oleg Maltsev, Lukas Hintermann, Boris-Marko Kukovec, Pance Naumov

Ultrafast spectroscopy and advanced data analysis of Oxyluciferin and its synthetic derivatives to understand the molecular mechanism of Bioluminescence

## 17:40: Information

## 18:30: Poster session

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## Theoretical and computational chemistry Chair Valérie Vallet

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## **21 09:40**

Fadel Bassal, Mahamadou Seydou, Julie Champion, Andréa Sabatie-Gogova, Jean-Yves Le Questel, Gilles Montavon, Nicolas Galland

Highlighting metallic behaviors of astatine in solution with O, S and N model ligands

## 22 10:00

*Romain Vandeputte, Florent Louis, Laurent Cantrel* A theoretical study of cesium borates compounds

10:20 - 10:50: Coffee break

## 23 10:50

*Giacomo Giorgi, Maurizia Palummo, Angel Rubio, Hiroshi Segawa, Koichi Yamashita* Minority surfaces of anatase & derived layered structures: optical signatures and functionalization in photovoltaics oriented applications

## **24** 11:10

*Rivero-Santamaria Alejandro, Rubayo-Soneira Jesus, Dayou Fabrice, Monnerville Maurice* Classical and quantum theoretical studies of the Si + OH  $\rightarrow$  SiO + H reactive collision

## 25 11:30

*Aliezer Martinez Mesa, Gotthard Seifert* Adsorption of molecular hydrogen on nanostructered surfaces

## 26 11:50

*Llinersy Uranga Pina, Jean Christophe Tremblay* Relaxation and quantum diffusion of CO on metallic surfaces

## 27 12:10

Manuel Goubet

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## 12:30-14:30: Lunch break

## Cold Atoms and Molecules Chair Philippe Verkerk

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Michael Mark, Albert Frisch, Aikawa Kiyotaka, Grimm Rudolf, Ferlaino Francesca Ultracold dipolar quantum gases with atomic erbium

**29 15:10** 

Romain Vexiau, Dimitri Borsalino, Nadia Bouloufa-Maasa, Mireille Aymar, Olivier Dulieu Optical trapping wavelengths of bialkali molecules in an optical lattice

30 15:30

*Julia Diaz-Luque, Daniel Hennequin, Philippe Verkerk* Synchronization in a conservative optical lattice

*Hans Lignier, Mehdi Hamamda, Isam Manaï, Pierre Pillet, Daniel Comparat* Ro-vibrational cooling of molecules. Towards Sisyphus cooling of molecules.

#### 32 17:00

*Maxence Lepers, Romain Vexiau, Mireille Aymar, Nadia Bouloufa, Olivier Dulieu* Mutual orientation of ultracold polar molecules

### **33** 17:20

*Manuel Lara Garrido, Pablo Garca Janbrina, Jean-Michel Launay, Francisco Javier Aoiz Moleres* Cold and ultracold dynamics of the barrierless reaction  $D^+ + H_2$ 

#### **34 17:40**

Simon Chefdeville, Thierry Stoecklin, Astrid Bergeat, Kevin Hickson, Christian Naulin, Michel Costes

Low Energy Resonances in CO - para-H<sub>2</sub> Inelastic Collisions

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Graham Worth

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### **36 09:40**

*Iftner Christophe, Korchagina Xenia, Simon Aude, Spiegelman Fernand* Theoretical studies of  $(PAH)_m(H_2O)_n^+/_0$  in Ar matrices : model and benchmark.

## **37** 10:00

*David A. Bonhommeau, Mark A. Miller, Marie-Pierre Gaigeot* Stability of multiply-charged clusters: Applications to droplets produced in ESI-MS experiments

## 10:20 - 10:50: Coffee break

**38** 10:50

Bertrand Chazallon  $CO_2$  capture from binary gas mixture via clathrate hydrates formation: investigation by Raman scattering

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Mitchio Okumura, Leah Dodson, Linhan Shen, Nathan Eddingsaas, Stanley Sander, John Savee, Oliver Welz, David Osborn, Craig Taatjes

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### **40 11:50**

*Pauline Delcroix, Benjamin Hanoune, Bertrand Chazallon, Denis Duflot* Ab initio calculations of the  $H_2CO + H_2O$  reaction

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## 12:30-14:15: Lunch break

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*Lola Gonzalez-Sanchez, Jesús Aldegunde, Pablo G. Jambrina, F. Javier Aoiz* Quantum Mechanical Study of the Cl + HD(v=1) Reaction

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#### Chemistry in Ice and Snow: From the Atmosphere to the Molecular Scale

#### THORSTEN BARTELS-RAUSCH<sup>1</sup>

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The cryosphere and ice clouds strongly interact with the atmosphere and play an active role in Earth's geochemical cycles and in the climate system. For example, snow and ice play a major role in driving the near-surface atmospheric chemistry in Polar Regions. In addition they serve to accumulate and 'amplify' organic pollutants and mercury. Ice and snow further affect the transport of greenhouse gases. The specific consequences of these processes are potential negative health effects. Such outcomes have been well documented for the Arctic population and for consumers of Arctic fish in Europe and also discussed for populations in vicinity of alpine glaciers. Further, a powerful impact not only on the local climate in the Arctic and Antarctica, but also on the larger scale in Europe and globally is recognised.

That those large-scale effects within the Earth system can be assigned to chemical activity in ice and snow on a microscopic level, is one crucial result of the most recent research. However, we are far from a detailed understanding of this emerging field. I will start with highlighting results from laboratory studies that investigated how the structure and composition of ice and snow impacts its reactivity. Examples include

- The transport of trace gases through the porous surface snow cover
- The photo-reactivity in surface snow

Results of these studies are briefly discussed focusing on our ability to parameterise and model processes in snow and ice. Differences and similarities of chemistry in snow to chemistry in liquid water will be shown.

A fundamental understating of above processes can be gained by directly observing how the water molecule network at ice surfaces interacts with atmospheric trace gases upon adsorption. Near ambient pressure XPS and NEXAFS have been successfully used to obtain micro-chemical information of contaminants on ice under environmental conditions. Examples include acetic acid, bromide, acetone, nitrate and chloride. The molecular interaction of water molecules with chemical traces in the topmost, disordered layer on ice is of significant debate. Based on ellipsometry measurements a feedback mechanism was described were adsorption of the acidic trace gas HCl induces disorder along the whole ice surface which in turn leads to an enormous increase in the uptake of this trace gas to the ice. Recent results from surface sensitive near edge X-ray absorption fine structure spectroscopy of nitrate and acetic acid on ice surfaces indicate a more complex picture where changes to the hydrogen-bonding network may be most pronounced to the vicinity of the ionic impurity. Results of these surface sensitive studies will be the main focus of this talk, highlighting the differences between ice surfaces and liquid films.

# Atmospheric reactivity of iodoalkanes towards OH radicals

<u>FLORENT LOUIS</u><sup>1</sup>, KATARÍNA ŠULKOVÁ<sup>2</sup>, MARTIN ŠULKA<sup>2</sup>, MÁRIA SUDOLSKÁ<sup>2</sup>, JOZEF FEDERIČ<sup>2</sup>, IVAN ČERNUŠÁK<sup>2</sup>

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The importance of iodine in the atmosphere is known for more than two decades. Among the frequently discussed effects of atmospheric iodine are: *i*) the ozone depletion in the lower stratosphere due to the presence of IO and OIO species, *ii*) the role of iodine compounds in new particle formation in marine environments, *iii*) chemistry of halogens in troposphere through the interaction of iodine compounds with bromides and chlorides. Besides iodomethane (CH<sub>3</sub>I), several other organic iodine-containing compounds have been detected in marine boundary layer in the coastal water or in open ocean. Iodomethane and diiodomethane are produced by microalgae and phytoplankton in marine boundary layer and belong to the most abundant and reactive alkyl iodides in the troposphere. They participate in the generation of aerosols in coastal zones. While the former can persist from several hours to several days, the latter has shorter lifetime – from minutes to hours. In both cases, these time windows represent a potential for long distance atmospheric transport of iodine and the potential for chemical reactivity that can affect various atmospheric cycles, including ozone cycle.

Iodoalkanes can undergo several decomposition pathways. For instance,  $CH_{3}I$  is easily photolyzed producing iodine atoms that enter ozone cycle or can react with NO, HO<sub>2</sub>, ClO, BrO, or IO.  $CH_{3}I$  can abstract either H or I under attack of OH radicals, or Cl atoms, provided the concentration of the reactant radicals is high enough to compete with the photolysis.

High-level ab *initio* molecular orbital studies offer a viable alternative to provide reliable thermodynamic and kinetic data for the gas-phase chemical reactions. Modelling H- or I-abstraction from alkyl iodides is rather demanding task because for predicting the kinetic parameters one has to reach at least the chemical accuracy of the underlying thermodynamic data (better than  $\pm 4$  kJ mol<sup>-1</sup>). This implies to choose the computational chemistry tools that include all necessary and accurate corrections to molecular energies (basis set saturation, valence and core-valence electron correlation, relativistic effects, spin-adaptation, vibration contributions, and tunnelling corrections).

In this talk, we will report the results of *ab initio* calculations obtained for the reactivity of a series of iodoalkanes towards OH radicals.

## Conformational Dynamics and Finite-Temperature Infrared Spectra of Water Clusters adsorbed on Polycyclic Aromatic Hydrocarbons

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Polycyclic Aromatic Hydrocarbons (PAHs) have raised growing interest since the discovery in the mid-eighties of the Aromatic Infrared Bands, a set of mid-IR emission bands observed in many regions of the interstellar medium, and assigned to a population of PAHs [1]. Despite many experimental and theoretical studies, no specific PAH molecule has been identified yet.

Most published theoretical spectra of PAH-derived species are computed in the harmonic approximation. However, interstellar spectra are emission spectra from species heated by UV-photons. Describing the effect of internal energy on the IR spectra is a current theoretical challenge. In our group, we study PAHs with adsorbed cations, molecules and clusters of astrophysical interest such as  $Si^+$  [2],  $Fe^+$ [3] and  $(H_2O)_n$ (n>1) [4]. Studies with water clusters are also relevant for the chemistry of the atmosphere as PAHs are precursors of soot.

In order to describe the effect of internal energy on the structures and IR spectra of these large and floppy species, a method of choice is to perform on-the-fly Born-Oppenheimer Molecular Dynamics simulations with an electronic structure described with Density Functional Tight Binding (DFTB) in its Self-Consistent-Charge (SCC) form. Finite-temperature IR spectra are obtained computing the dipole moment autocorrelation function. We will present the analysis of conformational dynamics for several  $(H_2O)_nC_{24}H_{12}$  (n=2-8) complexes in the temperature range 10-300 K. The temperature dependence of the IR spectra will be discussed, and the signatures for finite-size effects, such as the edge-coordination of the water clusters on the PAH, will be shown in particular.

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- [4] (a) A. Simon, M. Rapacioli, J. Mascetti and F. Spiegelman, Phys. Chem. Chem. Phys. 14, 6771 (2012); (b) A. Simon and F. Spiegelman, J. Chem. Phys. (submitted)

## Atmospheric Photochemistry from a Perspective of Ab Initio Simulations

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In my talk, I will summarize the work of our laboratory on theoretical modeling of atmospheric photochemical processes. The atmosphere of the Earth can be viewed as a chemical reactor exhibiting a rich chemistry. Many of the chemical processes in the atmosphere are initiated by light. The atmospheric models therefore need data describing the interaction between light and matter (absorption cross sections, quantum yields). While laboratory measurements are able to provide high-quality data, the assistance of theoretical chemistry is often needed. This is the case of unstable radicals or processes taking place on the interfaces as well as in the case of finite size particles

In the first part, I will focus on modeling of UV absorption spectra for floppy molecules using reflection principle method combined with path-integral molecular dynamics or quantum thermostat sampling [1]. The approach will be demonstrated on the atmospherically important nitrate anion on the ice surfaces.

Non-adiabatic photodynamical simulations using techniques of Full Multiple Spawning or Surface Hopping will be demonstrated in a second part of the talk. Special emphasis will be put on the photochemical processes following the excitation of halogen halides on the surfaces of ice particles [2].

In the final part of the talk, I will briefly show how photochemical methods can be used for a characterization of water particles with tens to hundreds of water units, allowing for a direct identification of water nanocrystallization [3].

*Acknowledgement:* P.S. acknowledges project number 208/10/1724 by the Grant Agency of The Czech Republic and project Barrande 7AMB12FR016 by the Ministry of Education of the Czech Republic.

#### References

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[3] C. C. Pradzynski, R. M. Forck, T. Zeuch, P. Slavíček, U. Buck Science 337, 1529

(2012).

# Influence of nitrogen oxides and UV-radiation on metal oxide surfaces: XPS investigation

M. LAMPIMÄKI<sup>1</sup>, S. Schreiber<sup>1</sup>, V. Zelenay<sup>1</sup>, A. Křepelová<sup>1</sup>, M. Birrer<sup>1</sup>, S. Axnanda<sup>2</sup>, B. Mao<sup>2</sup>, R. Chang<sup>2</sup>, H. Bluhm<sup>2</sup>, Z. Liu<sup>2</sup> and M. Ammann<sup>1</sup>

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Catalytic and photocatalytic processes of atmospheric trace gases on the surface of Fe- and Ti-oxide containing mineral dusts may play an important role in atmospheric chemistry. On TiO<sub>2</sub>, UV-radiation induced electron/hole pairs can directly or indirectly via photogenerated reactive oxygen species affect environmental processes through the redox chemistry of atmospheric gases, volatile organic compounds, H<sub>2</sub>O and O<sub>2</sub> [1,2,3]. Photoelectron spectroscopy provides a valuable tool to study adsorption of nitrogen oxide species and the effect of UV-radiation on metal oxide surfaces [4,5]. Here, we have employed near-ambient-pressure x-ray photoelectron spectroscopy for measurements of nitrogen oxide chemistry on well defined Fe- and Ti-oxide surfaces.

The photoelectron spectroscopy measurements were performed at the beamline 9.3.2 at the Advanced Light Source. Core-level metal cation, O and N XPS-transitions, as well as valence band regions were measured at elevated pressures of NOx,  $O_2$ ,  $O_3$  and  $H_2O$ . Phases of surface nitrite and nitrate formation were observed after exposure to NO an  $O_3$ . Furthermore, photochemical experiments were conducted on TiO<sub>2</sub> surfaces in situ by using a UV diode laser.

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- [3] M. Shiraiwa et al., Nat. Chem. **3** 291 (2011)
- [4] J. Haubrich et al., Langmuir, **26** 2445 (2010)
- [5] O. Rosseler et al., J. Phys. Chem. Lett. 4 536 (2013)

# The reaction dynamics of H<sub>3</sub><sup>+</sup>at low energy regimes

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Given its importance in the Astrophysical context the  $H_3^+$  reactive collision has been the subject of numerous studies [1]. Besides the interest to calculate the bound state spectra of the molecule as accurately as possible to describe the corresponding spectra, the collisions of  $H_2$  with  $H^+$  are considered as one of the most effective way to induce ortho/para transitions [2]. Recent studies have provided useful information regarding the dynamics of the process [3-5]. In this contribution I will present a review of the present knowledge we have about the precise mechanisms which seem to govern the  $H^+ + H_2$  reaction and its isotopic analogues, with a special emphasis in the newest results reported for this process.

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#### The Physical Nature of Amorphous Solid Water

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Water is a critical molecule in molecular astrophysics; it controls much of the gasgrain chemical interplay and is vital to the formation of more complex molecules and their recycling to the interstellar gas as star-formation progresses. Yet it has been a perennial question in Astrochemistry, how and where interstellar ices form, and what the structure of this ice is when it is formed. The key outstanding question is whether or not interstellar ASW forms in a 'porous' or 'compact' structure, since desorption processes, reaction kinetics, diffusion rates and physical properties such as frictional aggregation and electrostatics all change between the porous (p-ASW) and compact (c-ASW) form. The second related question is then how the 'phase-change' between p-ASW and c-ASW occurs; changing the surface structure, surface area, chemical binding sites, and the kinetics of the pore collapse.

We have recently undertaken the first neutron scattering experiments on p-ASW (D2O) and c-ASW (D2O) to study the porosity of such materials and investigate the kinetics of this pore collapse [Loerting et al (2012)]. Our results show that pores clearly still exist in ices formed at 80 – 90 K by vapor deposition, the regime commonly referred to as c-ASW, and pores can be maintained to the onset of the phase transition to cubic ice (at around 142 K in our system). The most rapid pore changes occur first at around 120 K (where the water ice is thought to be able to diffuse across the surface), 136 K where liquid A forms, and finally as the ice crystalizes. The pore sizes are not randomly distributed, nor do they increase in size when more material is grown, therefore describing ASW as a fractal solid is incorrect. In fact the pore sizes are limited, and the data show the pore shapes also undergo specific changes around 120 K. Pores clearly start collapsing as soon as the ice is heated, but contrary to literature models [Collings et al (2003a,b)] the process is not autocatalytic, and can be halted if the energy source is removed. These data clearly challenge the image of p-ASW and c- ASW built to date. I will show both how these laboratory data and our recent molecular dynamics simulations of p-ASW [Elkind & Fraser (2012)] paint a very similar picture of the porosity and pore evolution of ASW. Finally with reference to recent observations showing ice formation at the very edges of molecular clouds [Banhidi et al (2012)], I will tie the whole story together to postulate how interstellar ices may form with high porosity, but loose this porosity as they evolve, prior to the protostellar phase. This laboratory approach will provide a new template for future laboratory Astrochemistry experiments and methods of modeling the solid-state chemistry of star-forming regions.

# Diffusion in Amorphous Solid Water Ice : implications in the interstellar ice chemistry

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To explain the observed molecular abundancies in the interstellar medium, we need the kinetic parameters of relevant reactions in the gas and solid phases and a formalism for the relevant dynamical processes. In the ice mantle of the interstellar grains, essentially composed of water, the bulk reactivity is limited by the diffusion of the molecules wich have to migrate to encounter each other. In order to derive a formalism to combine reactivity and diffusion in models of interstellar ices, we first need to perform an extensive experimental study on both processes.

We concentrate on the formation of the ion OCN<sup>-</sup> trough the reaction HNCO +  $NH_3 \rightarrow OCN^-NH_4^+$ . This ion has been observed in solid phase with various abundances in protostar infrared spectra but it is missing in the spectra of starless molecular clouds [1]. This reaction has the advantage to exhibit a low activation barrier so that it may be distinguishable from the slower diffusion process [2] [3].

First, we performe a kinetic study of the solid-phase thermal reaction HNCO + NH<sub>3</sub>  $\rightarrow$  OCN<sup>-</sup>NH<sub>4</sub><sup>+</sup> in a water-free HNCO:NH<sub>3</sub> ice mixture. The ice is formed by growing a film on a cold surface, brought to a fixed temperature between 8 K and 60 K and monitored by Fourier Transform Infrared Spectroscopy.

Then we characterize the diffusion of HNCO,  $NH_3$ ,  $H_2CO$  and CO in amorphous solid water ice. The ice is formed on a cold surface by deposing a mixture of  $H_2O$  and one of the selected molecules. The temperature is raised to allow the molecule to diffuse and desorb. The diffusion coefficients are extracted from the decreasing abundance of the diffusing molecule.

Finally, we study the kinetic behavior of the  $HNCO + NH_3$  reaction when the two molecules are diluted in amorphous water ice.

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## Laboratory investigation of formation and isomerization processes of HNCO in interstellar ice analogues

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The detection of isocyanic acid (HNCO) and its isomers in different astrophysical environments is difficult to explain with current gas phase models. New models suggest that these species could be formed in ice mantles and desorb. In ice processing experiments the formation of HNCO-isomers by thermal processing was reported recently by Theule et al. [1] The formation of HNCO has been observed in UV-irradiation experiments of a H2O:NH3:CO ice mixture by van Broekhuizen et al. [2]

We attempted to study the formation of HNCO and its isomerization by vacuum-UV photoprocessing of interstellar ice analogues containing different mixture of H<sub>2</sub>O; CO; CH<sub>3</sub>OH; NH<sub>3</sub>; and HCN followed by warm-up, under astrophysically relevant conditions. The ice photo- and thermal chemistry has been monitored by Fourier transform infrared using the ISAC set-up at CAB. HNCO is the most stable form of four possible isomers, being the more energetic species cyanic acid (HOCN), fulminic acid (HCNO) and isofulminic acid (HONC). The possible isomerization of HNCO to its tautomers due to ice warm-up has been scrutinized. The molecular products arising from the thermal desorption have been monitored by quadrupole mass spectrometry.

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# Collisional and reactive processes of astrophysical interest: On the importance of having accurate molecular data

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The Herschel telescope and the ALMA interferometer open new windows of observation for wavelengths ranging from far infrared to sub-millimeter with spatial and spectral resolutions previously unmatched. To make the most of these observations, an accurate knowledge of the physical and chemical processes occuring in the interstellar medium (ISM) is essential. In this presentation, I will show what are the current needs in astrophysics in terms on molecular data and how accurate data are a crucial parameters for the determination of physical conditions in molecular clouds.

In particular, I will show how new collisional data for the HCN/HNC isomers, two of the most abundant molecules in the ISM, have allowed to revise the abundance of the two isomers in cold molecular clouds and how collisional data for the  $CN^-$  anion have allowed to confirm the presence of this negative ion in the ISM. I will also show how accurate rate constants for the F+H<sub>2</sub> reaction have allowed a more accurate determination of the gas density in diffuse ISM. Finally, I will show how first principles calculations can predict the existence of new molecular anions and how we predict the existence of the N<sub>2</sub>H<sup>-</sup> anion.



Figure 1: Microwave and far-infrared spectra of the N<sub>2</sub>H<sup>-</sup> complex.

## Collisional process of H<sub>2</sub>O + He supersonic jets by Raman spectroscopy

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Supersonic jets of pure gases and gas mixtures are relevant for different areas of physics, chemistry, and engineering [1]. The properties of these systems can differ markedly from those of a gas at thermodynamic equilibrium, since they are conditioned by the collisional dynamics.

In this work we report the diagnostic of several  $H_2O$  + He supersonic jets, with  $H_2O$  mole fractions from 1.4% to 33%, particularly their fluid dynamic properties. With  $H_2O$  partial pressures around 12 mbar, all these jets were checked to be free from  $H_2O$  condensation, a must for the quantitative analysis of the collisional kinetics. The jets have been probed by Raman spectroscopy, a non-intrusive technique with a spatial resolution of a few microns.

The primary experimental data obtained are number densities and rotational populations along the flow lines. It is found that the distribution function of the lowest rotational energy levels very nearly obeys a Boltzmann distribution for all our stagnation conditions. This enables accurate determination of rotational temperatures by means of the Raman spectra of Q branch of the symmetric stretching mode ( $v_1 \sim 3657 \text{ cm}^{-1}$ ) and the simulation of its profile using literature reference data [2]. Translational temperatures ( $T_t$ ) have been obtained from number densities and rotational temperatures by conservation of mass, momentum, and enthalpy along the jet [3].

Employing a Kinetic Master Equation that describes the time evolution of the rotational populations we have determined the average rate coefficients, both for H<sub>2</sub>O:He and H<sub>2</sub>O:H<sub>2</sub>O collisions, for the 6 lowest of ortho-H<sub>2</sub>O between  $T_t$ = 40 and 100K. Our results for H<sub>2</sub>O:He inelastic collisions will be compared with calculated [4,5] state-to-state rate coefficients.

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## Cyanide/isocyanide abundances in the interstellar medium. Inelastic rate coefficients of AI and Mg compounds.

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Modelling molecular abundances in the interstellar medium requires accurate molecular data. Hence, accurate determination of collisional rate coefficients is an essential step in order to estimate molecular abundances in interstellar clouds. Cyanide/isocyanide species are the most common metal-containing molecules in circumstellar gas [1,2]. It is crucial to provide collisional data for the cyanide/isocyanide molecules .

In this work, we have carried out calculations of rate coefficients for the rotational excitation of aluminum cyanide (AlCN), aluminum isocyanide (AlNC), magnesium cyanide (MgCN) and magnesium isocyanide (MgNC) molecules in their ground vibrational state in collision with He. The calculations are based on new two-dimensional potential energy surfaces obtained from highly correlated *ab initio* calculations. Coupled states quantum approximation was used to obtain pure rotational (de-)excitation cross-sections of AlCN, AlNC, MgCN and MgNC by He. Rates coefficients for transitions among the 26 first rotational levels of AlCN and AlNC and among the first 41 fine structure levels of MgCN and MgNC were calculated for the temperature range between 5 and 100 K. Significant differences between the rate coefficients of both isomers were observed. These differences confirm that specific calculations have to be performed for each isomer in order to obtain the necessary level of detail. The new rate coefficients should induce important consequences on the determination of metal abundance in the ISM. In particular, our work confirms<sup>3</sup> that the AlCN molecule is significantly less abundant than AlNC in the ISM.

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## THE H<sub>2</sub> + H<sub>3</sub><sup>+</sup> REACTION: DYNAMICALLY BIASED STATISTICAL MODEL FOR THE ORTHO/PARA CONVERSION

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A treatment combining statistical and quasiclassical trajectories methods is here presented[1] to describe the evolution of the title reaction. The work can be considered as a further extension of the previous statistical method by Park and Light[2]. While the nuclear spin selection rules are properly taken into account by the statistical method, the dynamical contribution is introduced in the so-called scrambling probability. The scrambling matrix, which depends on the collision energy, is generated by means of quasiclassical trajectories and determines the probability for the identity/hop/exchange mechanisms to occur.

It is also found that in the quasiclassical calculations the high zero-point energy (ZPE) of the fragments, which is randomly distributed among all the degrees of freedom, shortens the lifetime of the  $H_5^+$  complex. Since reactants and the  $H_5^+$  complex have similar zero-point energies, a new ZPE-biased scrambling matrix is obtained by reducing "artificially" the ZPE in the QCT calculations. This new matrix yields a good agreement with the recent experiments by Crabtree et al.[3] for the hop/exchange ratio at room temperature. At lower temperatures, however, the present simulations predict too high ratios because the biased scrambling matrix is not statistical enough. This demonstrates the importance of applying quantum methods to simulate this reaction at low the temperatures of astrophysical interest.

All the calculations in the present work have been performed on a recent global potential energy surface[4], instead of the long-range ion-induced dipole interaction previously used[2].

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## Bottom-up designed, triggerable soft matter systems: from DNA and protein regulation to responsive membranes and light-driven microfluidics

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We follow a bottom-up approach to design various kinds of triggerable soft matter systems allowing the control of a large variety of properties and functions in response to an external stimulus, such as light. At the molecular scale, the photocontrol of nucleic acid (DNA, RNA) higher-order structure [1,2] enables the photocontrol of gene expression at both transcription and translation levels, in a sequence-independent and reversible manner [3,4], with applications for the photocontrol of enzymatic reactions [5]. Enzymatic activity can also be controlled through regulated higher-order structural changes of giant DNA-protein star-shaped conjugates [6]. At the supramolecular level, we are engineering well-defined cell models in the form of giant liposomes, which can be i) photo-stimulated to analyze the membrane mechanical properties [7] or ii) functionalized with triggerable membrane proteins by using a synthetic biological approach. Finally, at the micro- to macro-scales, we develop laser-free methods where a simple light illumination stimulus (e.g., from a LED device) is used to manipulate [8], divide [9], mix [10] or merge continuous micro-scale flows (light-driven microfluidics) or discrete nL- to µLsized droplets (digital optofluidics), with high spatio-temporal resolution, in a costeffective, portable and robust manner.

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#### Oxidative stress in biological cells by direct optical excitation of singlet oxygen : towards new strategies for photodynamic cancer therapy

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Singlet oxygen ( ${}^{1}O_{2}$ ) is an electronic state of molecular oxygen which plays a major role in many chemical and biological photo-oxidation processes. It has a high chemical reactivity which is commonly harnessed for therapeutic issues. Indeed,  ${}^{1}O_{2}$ is believed to be the major cytotoxic agent in photodynamic therapy. In this treatment of cancer,  ${}^{1}O_{2}$  is created, among other reactive species, by an indirect transfer of energy from light to molecular oxygen *via* excitation of a photosensitizer (PS). This PS is believed to be necessary to obtain an efficient  ${}^{1}O_{2}$  production.

We will present results demonstrating that production of  ${}^{1}O_{2}$  can be achieved in living cells from PS-*free* 1270 nm laser excitation of molecular oxygen. The quantity of  ${}^{1}O_{2}$  produced in this way is sufficient to induce an oxidative stress leading to cell death. Other effects such as thermal stress are discriminated and we conclude that cell death is only due to  ${}^{1}O_{2}$  creation. This new simplified scheme of  ${}^{1}O_{2}$  activation can be seen as a breakthrough for phototherapies of malignant diseases and/or as a noninvasive possibility to generate reactive oxygen species in a tightly controlled manner.

## Enhanced Biological Damage through Water Ionization

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The radiative damage to living cells can proceed either directly or indirectly through the interaction with water. It is generally agreed that indirect damage is more harmful to the living cells. However, its mechanism is still only partially understood. The simulations we have performed [1] on the water dimer system provide further insight into the mechanism in question.

The valence photoelectron spectrum of water comprises four characteristic peaks centered at approximately 12 eV ( $1b_1$ ), 15 eV ( $3a_1$ ), 18 eV ( $1b_2$ ) and 32 eV ( $2a_1$ ). We have carried out molecular dynamics simulations following the electron ejection from the first three molecular orbitals (so called inner-valence MOs). Moreover water dimer being constituted of hydrogen bond donor and hydrogen bond acceptor moieties, we have investigated the donor and acceptor sites separately. In our molecular dynamics simulations we have been using the semiclassical surface-hopping algorithm together with the complete active space self consistent field (CASSCF) method for the description of electronic structure.

The molecular dynamics simulations suggest the final products are statedependent. The ionization from the highest occupied molecular orbital leads unequivocally to the formation of  $H_3O^+$  and  $OH^\bullet$  species. When higher energy is available, we have observed also the dissociation into  $H_2O^{\bullet+}$  and  $H_2O$  fragments. Finally if an electron is ejected from the  $1b_2$  molecular orbital the atomic hydrogen (H<sup>•</sup>) is formed together with  $H_2O^{\bullet+}$  and  $OH^\bullet$  radicals. In an environment containing multiple water molecules, the  $H_2O^{\bullet+}$  radical-cation would immediately react with another water molecule yielding  $H_3O^+$  and  $OH^\bullet$  species. Such a formation of double the amount of reactive  $OH^\bullet$  radicals could have severe biological consequences.

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## Exploring the dynamic properties of molecular assemblies in live cells with single molecule imaging and manipulation.

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Single molecule techniques are becoming ubiquitous tools in *in vitro* and *in vivo* assays. In cell biology, they now can be used to count molecules, image with sub-diffraction resolution and track individual molecules as they move in their natural habitat. Thus, single molecule imaging is a tool of choice to address the dynamics, composition and structural properties of supramolecular assemblies in live cells. In this talk, I will present our effort to develop and apply ultrasensitive fluorescence methods. I will in particular present novel optical methods based on adaptive optics or multifocal imaging to enable the 3D localization and tracking of individual molecules in live cells. All these techniques will be illustrated by experiments made on a variety of biological systems, such as post-synaptic membrane receptors, molecular motors or transcription factors. Finally, I will describe recent experiments in which we used magnetic nanoparticles for locally controlling signaling activity inside cells, demonstrating the interest of using perturbative approach in cell biology.

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#### Recent publications:

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## Investigating the effect of dipole moment on structural and transport properties in liquid water: The NCC(Q) model

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Equilibrium molecular dynamic simulations are carried out to compute structural properties, while within the Green-Kubo formalism single and collective transport coefficients, such as self-diffusion, shear and bulk viscosities, are also determined. In order to investigate the role of the electrostatic contribution and improve previous results from semi-empirical models [1, 2], we employed reparameterized versions of the ab initio NCC water potential [3]. We considered dipole moment values previously employed in several commonly used empirical water models, by appropriately modifying the point charges of the H-atom and M-site of the NCC model. A detailed analysis and discussion is presented at various temperatures between 273 and 373 K, along with some guidelines for the proper parametrization of water models in order to predict accurately such properties. We found that the predictions of the NCC(Q), are in much better agreement with the experiment than its predecessor [3]. By analyzing radial distribution functions we show that the repulsive part of the potential needs to be adjusted. Also one can see that the self-diffusion results follow similar trends with the ones for the viscosity (see figure 1), thus we propose the inclusion of the self-diffusion coefficient as a target property in the developing water models.



Figure 1: Self-diffusion coefficients and shear viscosity values for the indicated water models.

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## Ultrafast spectroscopy and advanced data analysis of Oxyluciferin and its synthetic derivatives to understand the molecular mechanism of Bioluminescence

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The research interest in the amazing natural phenomenon bioluminescence – light emission from chemically produced excited states observed with bacteria, fungi and invertebrates, has been revived recently due to its immense potentials for application to novel ultrasensitive bioanalytical techniques, including in vivo bioluminescence imaging, gene expression and trace ATP analysis. One of the most studied bioluminescent reaction systems currently are bioluminescence beetles, particularly fireflies. Fireflies utilize the ground state of the heterocyclic acid D-luciferin as a substrate for enzymatic (protein luciferase) multistep oxidation to generate oxyluciferin (OxyLH<sub>2</sub>) in its first excited state. Subsequent deexcitation produces visible photon, which is observed as bioluminescence. Due to alleged instability and lifetime about few nanoseconds, the spectrochemistry and structure of OxyLH<sub>2</sub> within luciferase in its exited state have still remained unexplored.

To understand dynamics of the emitter we undertook thoroughly stationary and ultrafast time resolved (fluorescence, absorption, infrared) studies of oxyluciferin and its derivatives in different environment and different state (solution and crystals). We also developed a strategy based on a powerful mathematical procedure (combining careful selection of model compounds with multiset data analysis) to disentangle individual spectra of the components of different chemical forms of oxyluciferin. For the first time, the different species (ground state and excited state) of the oxyluciferin system in aqueous solution were mathematically extracted from an extensive set of pH-dependent measurements [1]. Obtained results open also the perspective for purposefully designed emitters exhibiting optimized performance of the polaritydependent emission and being applied as fluorescence probe in vitro and in cells.

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#### Abstract for IMAMPC - oral communication on 4 July 2013

#### Applications of theoretical chemistry tools to nuclear safety issues

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The IRSN (Institut de Radioproctection et de Sûreté Nucléaire) is a French institute in charge of research and expertise on nuclear safety and radioprotection. Fukushima situations reinforced the need to develop capabilities of predicting evolution and consequences of all possible accidental situations whatever are their postulated probability of occurrence. Of particular importance are the situations that can lead to the release of radionuclides produced by the fission of the nuclear fuel to the environment and thus to possible radiological consequences. Predicting the evolution of the chemical speciation and isotopic inventory of all radionuclides during the accident progress is essential not only to prepare the accidental and post-accidental situation management but also to define new devices to mitigate the environmental releases.

During the last decades, IRSN implemented among with French and foreign partners experimental research programs to develop the knowledge on radionuclides chemistry. But radionuclides that can mostly contribute to radiological consequences (iodine, ruthenium ...) are extremely reactive and conditions of an accident in a nuclear installation can hardly reproduced experimentally to derive directly from pure empirical models that can be used to simulate radionuclides behaviour in such a broad range of severe accidental conditions. So a few years ago, IRSN decided to complement experimental approaches with theoretical chemistry one either to complete/interpret results of some experimental programmes and thus increase the value of their results or to get piece of information useful to decline/check some potential nuclear safety issues and bring data not available in literature and hardly reachable experimentally. To illustrate implementation of this mixed experimental/theoretical strategy quite new in the nuclear safety context, three examples will be presented:

- The behaviour of fission products in degraded fuel;
- The chemistry of iodine in the reactor coolant system ;
- The chemistry of Plutonium in the fuel reprocessing cycle in case of accidental fires.

All these researches are led in close collaboration with some academic laboratories to associate all the specific skills needed to cover all the involved phenomena.

# Highlighting metallic behaviors of astatine in solution with O, S and N model ligands

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Astatine (At, Z=85: [Xe]4f<sup>14</sup>5d<sup>10</sup>6s<sup>2</sup>6p<sup>5</sup>) is the last known halogen in the periodic table. One of its longest-lived isotopes, <sup>211</sup>At, is of considerable interest as a potential radiotherapeutic agent for alpha-therapy<sup>[1]</sup>, due to the energy and nature of the emitted particles. Since there is no stable isotope of astatine, many of the basic chemical studies with this chemical element have unfortunately been set aside<sup>[2]</sup>. Although located below iodine, the chemical similarities of At with the halogen group are not always obvious. Indeed, it is clear that the development of targeted radiotherapy agents based on At needs to gain a better understanding of its basic chemistry in aqueous solution. Recent studies showed that astatine presents a metal-like behavior when existing under the oxidation states +I and +III as At<sup>+</sup> and AtO<sup>+</sup> species<sup>[3]</sup>. However, at the present time, the number of studies dealing with the complexation properties of the cationic forms of astatine remains limited<sup>[4]</sup>, owing to its low availability.

This work, based on an approach combining theoretical and experimental studies<sup>[5]</sup>, aims at studying the complexation of the AtO<sup>+</sup> cationic form with different heteroatomic (N, S, O) model ligands. As astatine is a heavy element, the quantum calculations used a two-component relativistic approach (SO-DFT) to reproduce the influence of spin-orbit coupling on At properties. Solvent effects are simulated through an implicit solvation model (UAHF) completed with specific parameters for At cavities. The computed equilibrium constants have been confronted with the experimental ones. The comparison reveals an outstanding coherence between both sets of values. This allowed us identifying the nature of the AtO<sup>+</sup> binding with heteroatomic ligands, which could not be obtained experimentally from spectroscopic tools. A large variety of interactions have been evidenced together with a specific reactivity against carbon atoms in case of aromatic ligands. Finally, the key role of the solvent on the elemental chemistry of astatine has been highlighted.

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#### A theoretical study of cesium borates compounds

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As part of a major nuclear accident, products resulting from the degradation of the control rods are likely to influence the transport of iodine in the reactor coolant system (RCS) of a pressurized water reactor (PWR). An international program PHEBUS-PF (replica at a 1/5000<sup>th</sup> scale of a PWR) was launched by the "Institut de Radioprotection et de Sûreté Nucléaire" (IRSN) to help the understanding of the phenomenology that can lead to releases of fission products to the environment in case of accident. A test PHEBUS-FP (FPT3) was performed in 2003 with control rods made of boron carbide (B<sub>4</sub>C) and showed some unexpected results concerning iodine, with a high gaseous fraction at the break instead of a dominant aerosol fraction as observed in other tests. The boron may promote the gaseous iodine fraction at low temperature by preventing the CsI aerosol formation due to the possible formation of  $Cs_x B_y O_z$  compounds (especially cesium metaborate CsBO<sub>2</sub>). The behaviour of fission products in the RCS is modelled by the IRSN severe accident software ASTEC (accidental source term evaluation code). This modelling integrates some thermochemical equilibrium calculations whose data ( $\Delta_{\rm f} H^{\circ}_{298K}$ ,  $S^{\circ}_{298K}$ ,  $C_{p,T}$ ,  $G^{\circ}_{298K}$ ) have to be re-assessed in some cases resulting from large uncertainties. A valuable solution to estimate these data is to use the combination of quantum chemistry tools with statistical thermodynamics.

For the thermochemical study, structural parameters (geometries and vibrational frequencies) for  $CsB_yO_z$ ,  $Cs(B_yO_z)_2$  and  $Cs_2(B_yO_z)_2$  compounds were determined using the B3LYP method associated with the cc-pVTZ and aug-cc-pVTZ basis sets for boron and oxygen atoms while the B3LYP/aug-cc-pVDZ level of theory was used to obtain the structural parameters in the case of the microsolvation of CsBO<sub>2</sub>. In both cases, the caesium atom was described by the pseudopotential ECP46MDF developed by Lim et al.<sup>[1]</sup>. The potential energies were then computed using Dual-Level methodologies:

- (i) for the thermochemistry of  $Cs_xB_yO_z$ : B3LYP/aug-cc-pVnZ//B3LYP/ccpVTZ, B3LYP/aug-cc-pVnZ//B3LYP/aug-cc-pVTZ (n = T, Q, 5) levels of theory;
- (ii) for the microsolvation: B3LYP/aug-cc-pVnZ//B3LYP/aug-cc-pVDZ (n = D, T, Q).

The results will be presented and compared with available literature data.

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## Minority surfaces of anatase & derived layered structures: optical signatures and functionalization in photovoltaics oriented applications

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The revolutionary discovery of splitting water by irradiating  $TiO_2$  nanoparticles with sunlight [1] has boosted the interest of the scientific community towards the very appealing properties of titania. Nowadays, many industrial and technological applications, in catalysis, in sun-to-energy conversion (organic-inorganic solar cells, dye sensitized SCs), in photocatalysis, in gas sensing, and in many other fields, take advantage of this manifold material, as witnessed by the ever increasing number of published scientific reports and patents focusing on its relevant device oriented properties. Not secondarily, the prompt availability of more accurate and sensitive experimental techniques has lead to the synthesis of nanostructured  $TiO_2$ -based materials: their surface area enhancement and the inherent improvement of their photochemical activity make them subject of further deep analysis. Among all the possible morphological shapes, the study of (001)-oriented nanosheets (NSs) is of wide interest for the enhanced optical activity of systems with such facet exposure [2].

Here, moving from the analysis of electronic and optical properties of different reconstructions of the parental minority (001) surface of anatase, we shed light, by using first-principles simulations, on the unambiguous relation among atomic structure, electronic bandstructure and optical properties of several derived nanosheets. The last part of this work focuses on the possibility of using such NSs in DSSC. We report results about the anchoring mechanism on top of them with molecules characterized by functionality of interest. A common theoretical scheme for the study of both surface and bilayer electronic/optical properties and based on a combined Density Functional plus Many Body Perturbation Theory is used [3].

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# Classical and quantum theoretical studies of the Si + OH $\rightarrow$ SiO + H reactive collision.

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The SiO molecule is the most widespread silicon-bearing molecule in the interstellar medium. The largest abundances of SiO are found in shocked layers of molecular outflows associated with regions of star formation. The model currently adopted to explain the production of SiO invokes the erosion of interstellar dust grains made of silicates by shock waves [1]. The subsequent release of silicon atoms or SiO molecules into the gas phase can lead to the formation of SiO through Si + OH  $\rightarrow$  SiO + OH reaction.

This work presents the first theoretical dynamics calculations on the reactive collision between Si and OH using a recently developed 3D potential energy surface. For this purpose, three theoretical methods have been used (QCT, MPPST, TDWP). The results show that the barrierless studied reaction occurs with a probability less than 0.6 for collision energies between 1-1000 meV. The reaction proceeds through an indirect mechanism involving a long life complex. The products energy distributions show a mix between statistical and not statistical behaviour. The computed thermal rate constant show strong temperature dependence for temperatures between 10-1000 K. This feature is quite different from the constant value of 10<sup>-10</sup> cm<sup>3</sup>.s<sup>-1</sup> which is currently adopted by the astrophysical chemical reaction network [2].

This work is the first contribution to the understanding of the mechanism of the SiO production via  $Si + OH \rightarrow SiO + OH$  reaction. In the absence of experimental results, our findings can serve as a basis for future works in this area of study. Also, the thermal rate constants reported for a large range of temperatures could be introduced in the astrophysical models currently in use.

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#### Adsorption of molecular hydrogen on nanostructered surfaces

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We investigate the effect of the structural characteristics of idealized nanoporous environments on the adsorption of molecular hydrogen. The adsorption properties of the target nanostructures (graphene and ZnO sheets, carbon foams [1,2], metal-organic frameworks) are evaluated in a broad range of thermodynamic conditions. The study is carried out within the density functional theory for quantum fluids at finite temperature (QLDFT) [3], which allows to account for the many-body and quantum delocalization effects in a single theoretical framework. The exchange-correlation (excess) functional is derived from the empirical equation of state of the homogeneous system. We focus on the evaluation of hydrogen storage capacities of the substrates and on the emergence of quantum effects triggered by the confinement imposed by the host structure. The relation between the microscopic structure of the hydrogen fluid and the calculated adsorption properties is also addressed.



Gravimetric storage capacities of carbon foams at p=5 bar (left panel) and p=100 bar (right panel).



Spatial distribution of  $H_2$  molecules inside the unit cell of (3,3) armchair (left panel) and (4,4) armchair (right panel) carbon foams.

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#### Relaxation and quantum diffusion of CO on metallic surfaces

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We investigate the excitation and relaxation dynamics of diatomic molecules adsorbed on metallic surfaces using a model Hamiltonian which resembles that of CO on Cu(100) [1]. The model accounts both for diffusion and desorption of the molecular adsorbate. The dissipative dynamics is simulated using the reduced density matrix in its Lindblad form. An explicit expression for the evaluation of position-dependent transition rates in an optimized DVR is introduced. A wide range of coupling strengths between the different degrees of freedom is considered. The influence of the dimensionality on the energy redistribution among the vibrational and translational modes is explored.

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#### Supporting electronic structure calculations for high resolution spectroscopy: internal rotors and PAHs as examples

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The combination of high resolution spectroscopy with quantum chemistry calculations has nowadays become a standard. Theoretical molecular parameters are an invaluable help to start the spectral analysis. In turn, the experimental data permit to calibrate the calculations which provide relevant properties of the studied systems as well as reliable estimations about systems of the same class when experiments are missing. Such a complementary is emphasized by some peculiar cases at the edge of both approaches. Indeed, when the limits of the experimental capabilities are reached, the most accurate results may come from previously calibrated calculations and contrarily, the limits of what could be expected from calculations may be evidenced by the experiments. Two recent studies, although having quite different objectives, are good examples of the theory-experiment duality.

Four isomers of the dimethylbenzaldehyde molecule have been analyzed by Fourier transform microwave spectroscopy supplemented by quantum chemical calculations. These isomers represent benchmark species for the development of the theoretical model of asymmetric top molecules containing two nonequivalent methyl tops, exhibiting different barrier heights and coupling terms to methyl internal rotation (the BELGI-Cs-2Tops program).

High resolution spectroscopic data of 16 Polycyclic Aromatic Hydrocarbons (PAHs) and aza-derivatives have been used to calibrate density functional theory (DFT) calculations at the anharmonic level. Unconventionally, the rotational parameters, rather than the vibrational frequencies, are used as reference data to validate the theoretical approach. As consequences, excellent equilibrium geometries for the PAHs family of compounds may be estimated and the accurate rotational parameters will permit to strongly support the rather complicated spectroscopic analysis in the IR/Far-IR region or to account for the rotational structures of the IR bands (e.g. in the AIBs models) when experiments are not possible.

# Ultracold dipolar quantum gases with atomic erbium

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In the field of ultracold quantum gases, only recently non-alkali-metal atoms have become of central interest thanks to their special properties that open novel fascitating frontiers in quantum physics. Species with multiple unpaired valence electrons, such as lanthanides, have a very rich atomic energy spectrum and provide exceptionally large magnetic moments. The interaction between strongly magnetic lanthanides is dominated by long-range magnetic dipole-dipole forces and the study of unexplored dipolar phenomena, e.g. crystal phase, super-solid phase or p-wave pairing, is accessible.

In our experiment in Innsbruck we have produced the first Bose-Einstein condensate (BEC) of <sup>168</sup>Er and could demonstrate the dipolar-induced d-wave collapse of the superfluid. One of the key ingredients for this experiment is the magnetic tunability of the contact interaction exploiting so-called Feshbach resonances. In quantum gas experiments the contact interaction can easily be controlled by changing an external magnetic field.

For various Erbium isotopes we found a much richer resonant interaction spectrum as compared to alkali quantum gases. Taking advantage, these resonances allow to magnetically associate atoms and to form dipolar  $Er_2$  molecules at ultralow temperatures of around 100nK. The molecules have large magnetic dipole moments of up to  $12\mu$ B - almost two times larger than for atoms. In molecule-molecule collisions the effect of the dipolar interaction is already comparable to the interaction of heteronuclear systems such as ground state RbK molecules. With erbium molecules a collisionally stable system can be realized.

# Optical trapping wavelengths of bialkali molecules in an optical lattice

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The last few years have seen spectacular advances in the field of atomic quantum gases. More recently the goal of many physicists is to perform similar experiments on cold molecular species which will allow a series of fundamental studies in physics and chemistry [1,2]. An important prerequisite for all proposed molecular quantum gas experiments is the control of the internal and external degrees of freedom of the molecules. This is done by loading and manipulating the molecules in the presence of an optical lattice which provides full control over the motional wavefunction and prevents collisional loss [3,4].

In this work our motivation is to find optimal parameters for trapping of bialkali molecules in an optical lattice. We have calculated dynamic polarizabilities of bialkali molecules subject to an oscillating electric field, using accurate potential curves and electronic transition dipole moments from advanced quantum chemistry computations [5].

The creation of the sample of ground-state molecules relies on an adiabatic population transfer from weakly-bound molecules created on a Feshbach resonance towards the lowest rovibrational level a their ground state. We show that for particular wavelengths of the optical lattice, called "magic wavelength", the polarizability of the ground-state molecule is equal to the one of the Feshbach molecule. Such a coincidence ensures that both the initial and final states are favorably trapped by the lattice light, allowing optimal transfer in agreement with experimental observation. A systematic investigation of those magic wavelength for the ten heteronuclear bialkali molecules will be presented.

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#### Synchronization in a conservative optical lattice

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In a conservative optical lattice, it is possible to trap cold atoms thanks to the external potential created by the reactive effects of the atom-light interaction. We study the behaviour of an atom trapped in a conservative square lattice in 2D, where the potential leads to non-linear movement equations that make chaos likely to appear. The parameters of the lattice, like the laser detuning [1] or the phase between the orthogonal standing waves that form it, allow to modify the dynamics of the atom and, in particular, to control the presence of chaos.

I will present some results of a deterministic approach on the behaviour of the atom inside the potential wells, which include simulations of the real potential and some calculations of an approximated situation. In particular, I will show how certain configurations of the square lattice lead to a synchronization [2] phenomenon between the movements of the atom in the two directions of space. This synchronization inhibits chaos and makes possible the existence of periodic and quasi-periodic solutions.

Finally, I will also present some of the preliminary results of a quantum approach on an atom trapped in a conservative square lattice.

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# Ro-vibrational cooling of molecules. Towards Sisyphus cooling of molecules.

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Laser techniques applied to precision spectroscopy or to the control of chemical reactions have improved considerably our knowledge of molecular physics. One of the greatest challenges of modern physical chemistry is to push forward the limits of electromagnetic or laser techniques to probe or manipulate molecules at low temperatures where molecular interactions are dominated by pure quantum phenomena.

In this context, we have developed an original technique that enables us to manipulate the internal degrees of freedom of diatomic molecules. Basically, the principle consists in using a broadband laser to pump all the internal levels towards a target level. We performed various experiments demonstrating the feasibility of the process: vibrational cooling [1] and rotational cooling [2] were successful on the cesium dimer formed by photoassociation of cold atoms.

In our recent project, we project to apply this method to rovibrationally cool a molecule (barium monofluoride) produced in a supersonic beam. Barium monofluoride is somehow particular as it has the property to stand about twenty optical cycles without escaping to another vibrational level. Once this species is prepared in a single rovibrationnal state, it will be possible to implement a Sisyphus cooling scheme, a well-known effect/method in the realm of cold atoms that potentially removes a huge quantity of kinetic energy per photon. In other words, Sisyphus cooling applied to molecules might be a solution to slown down and thoroughly cool a supersonic molecular beam. We will discuss the various difficulties and the possible solutions.

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#### Mutual orientation of ultracold polar molecules

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Due to their large permanent electric dipole moment, heteronuclear bialkali molecules offer the possibility of an exceptional level of control of their quantum properties by external electric fields in the ultracold regime. To that end, a detailed modeling of the molecule-molecule long-range interactions and molecule-field interactions is requested [1].

We have computed the long-range interactions between two identical heteronuclear bialkali molecules in their ground state. In free space, their interaction is characterized by a huge van der Waals coefficient, larger by three orders of magnitude than the one for alkali atoms. In an external electric field this huge isotropic van der Waals interaction competes with the expected anisotropic dipole-dipole interaction, induced by the alignment of the molecules with the electric field.

Moreover below a critical intermolecular distance which is independent of the electric field magnitude, we predict the mutual orientation of the two molecules but with no preferential direction in the lab frame. This effect occurs for all bialkali molecules, with the noticeable exceptions of LiNa and KRb [2]. In its own frame, the tetramer possesses a strong dipole moment along the intermolecular axis. This opens the possibility of realizing a stimulated-emission photo-association of tetramers, by inducing a photon transition from two colliding molecules to a bound rovibrational level of the tetramer in its electronic ground state.

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#### Cold and ultracold dynamics of the barrierless reaction D<sup>+</sup> + H<sub>2</sub>

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The  $H_3^+$  system is considered the prototype of barrierless ion-molecule reaction. It has been extensively studied theoretically and experimentally due to its importance in astrochemistry [1]. Below 1.7 eV, the only reactive process that can take place on the ground adiabatic potential energy surface (PES) is the non-charge transfer proton exchange process. We have calculated quantum reactive cross-sections for the collision D<sup>+</sup>+*para*-H<sub>2</sub> $\rightarrow$ H<sup>+</sup>+HD using the hyperspherical quantum reactive scattering method[2]. Considered kinetic energies range from the ultracold regime, where only one partial wave is open, up to the Langevin regime, where many of them contribute. At very low kinetic energies, long-range (LR) interactions (usually neglected in both PES and dynamics calculations) determine the amount of incoming flux which reaches the short range region where rearrangement may occur, and are thus essential. Both accurate descriptions of the LR region in the PES, and long dynamical propagations, up to distances of hundreds of a.u., are required. Accordingly, the hyperspherical methodology was recently modified in order to allow considering LR interactions while minimizing the computational expense[3]. The method is suitable for systems involving ions, as the R<sup>4</sup> behaviour largely extends the range of the potential. Besides, very simple ideas stemming from Multi-Quantum Defect Theory allow methodological tricks which may further reduce the expense[4]. In order to show the significance of the LR effects, calculations are carried out on two different published PES[5], which result from two different fittings of similar *ab initio* points: one fitting does not pay special attention to the LR interactions while the correct LR behaviour is explicitly included in the other.

Emerging experimental techniques are making possible quick advances in the analysis of cold and ultracold reaction dynamics, and the title system appears as a good candidate for such experimental studies. The range of energies where the Wigner regime should be found is discussed.

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#### Low Energy Resonances in CO - *para*-H<sub>2</sub> Inelastic Collisions

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In this presentation we will present results on the study of inelastic collisions between CO and *para*-H<sub>2</sub>, at collision energies approaching the cold regime. These results will be compared with quantum mechanical calculations.

The CO  $(j = 0) + H_2$   $(j = 0) \rightarrow$  CO  $(j = 1) + H_2$  (j = 0) process is of particular importance in astrophysics. Theoretical calculations predict that this system is dominated by quantum effects called resonances [1]. These resonances can only be revealed at very low energies, and their experimental observation provides a test for the theoretical models.

Experiments were performed using a crossed molecular beam apparatus, combining a variable beam intersection angle and cryogenically cooled fast-pulsed valves [2]. The CO and H<sub>2</sub> beams were characterized using resonance-enhanced multiphoton ionization time-of-flight spectrometry. The lowest collision energy reached was 3.3 cm<sup>-1</sup>, which is below the threshold of the ( $j = 0 \rightarrow 1$ ) rotational transition in CO at 3.85 cm<sup>-1</sup>. The experimental excitation function shows a sharp rise at threshold followed by successive waves, evidencing the underlying resonance structures. This is the first observation of scattering resonances in an inelastic process [3].

In parallel, quantum mechanical scattering calculations were performed using the  $CO-H_2$  *ab initio* potential energy surface determined by Jankowski and Szalewicz [4]. Comparison between the experimental and theoretical excitation function shows that agreement depends critically on the details of the surface that is used to perform the scattering calculations.

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# Accurate studies of ultrafast photoexcited processes in polyatomic molecules: the MCTDH method.

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What occurs within the first few hundred femtoseconds after a molecule absorbs a photon is an interesting and challenging topic for computer simulations. Interesting, as often processes occue that dominate the subsequent photochemistry and photophysics os a molecule, as is observed in time-resolved laser spectroscopy experiments. Challenging, as an accurate simulation requires solution of the timedependent Schrödinger equation (TDSE) to account for the coupling of nuclear and electronic motion (non-adiabatic effects) that lead to a breakdown of the Born-Oppenheimer Approximation.

The numerical solution of the TDSE has become an essential tool for the study of fundamental molecular processes, and the Multi-configuration time-dependent Hartree (MCTDH) method [1, 2] is a powerful quantum dynamics algorithm, able to include more degrees of freedom than other methods. This is particularly useful in photochemistry, where it is often difficult to isolate a few important degrees of freedom leading to the need to simulate a multi-dimensional problem [3]. A benchmark example was a study of the pyrazine molecule including explicitely all 24 vibrational modes [4]. In a more recent example that demonstrates the utility of the approach, simulations on benzene combined with experiments made by the Fielding group at UCL, have uncovered a channel with ultrafast inter-system crossing that plays a role in the classic channel 3 problem [5].

MCTDH is, however, a grid-based method. And like all grid-based quantum dynamics methods is restricted to small molecules. To extend it to more general systems, we are developing a direct dynamics version, in which the potential surfaces are calculated on-the-fly using quantum chemistry calculations only when required. The DD-vMCG method is fully quantum mechanical, and promises to have good convergence properties, essential for these expensive calculations [6].

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# Theoretical studies of $(PAH)_m(H2O)_n^{+/0}$ in Ar matrices : model and benchmark.

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Interest regarding Polycyclic Aromatic Hydrocarbons (PAH) systems has grown during the last decades, since the discovery in the mid-eighties of the Aromatic Infrared Bands, a set of mid-IR emission bands that was assigned to a population of PAHs<sup>1</sup>. Despite many experimental and theoretical studies, no specific PAH molecule has been identified yet. Among experimental studies, cryogenic matrix experiments have been performed<sup>2</sup>. To our knowledge, theoretical studies to quantify the influence of the Argon matrix on the IR spectra are scarce<sup>3</sup>.

In this poster, we present and benchmark a theoretical approach for the description of  $(PAH^{+/0})Ar_n$  clusters. This approach is based on a QM (quantum mechanical)/MM (molecular mechanics) scheme. The QM part is computed with the Density Functional based Tight-Binding DFTB) method in its Self-Consistent Charge (SCC)version<sup>4</sup>. The interaction between PAH<sup>+/0</sup> and the Ar atoms is determined by adding to the diagonal elements of the SCC-DFTB Hamiltonian a perturbation term ( $u_{x-Ar}$ , x refering to an atomic orbital of C or H) obtained from the fits of diatomic C-Ar and H-Ar CCSD(T) potentials. In order to benchmark this approach, we determined the influence of the number of Ar atoms on the ionization potential of benzene, and compared our results to DFT and CCSD(T) data, and also with experimental and theoretical results available in the literature.

The objectives of our future work is to obtain dynamical and spectroscopic properties for  $(XPAH^{+/0})Ar_n$  systems  $(PAH=C_{24}H_{12}, X=H_2O)$  in relation with cryogenic matrix experiments, in particular those conducted by J. Mascetti<sup>5</sup>. Our ultimate goal is to improve our understanding of the thermal, dynamical and spectral properties induced by the matrix.

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# Stability of multiply-charged clusters: Applications to droplets produced in ESI-MS experiments

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Charged droplets are entities of interest in many research fields from the study of aerosols in atmospheric physics to biomolecules in electrospray ionisation (ESI) experiments. Recently, we developed a set of parallel programs, a classical Monte-Carlo code, called MCMC<sup>2</sup>[1], and a molecular dynamics code, called MDMC<sup>2</sup>[2], that aim to help determining the structural, thermodynamic, and dynamic properties of multiply-charged clusters, model systems for charged droplets in a coarse-grained representation. The interaction between particles that composed the clusters are based on Lennard-Jones and electrostatic interactions with possible inclusion of polarisation. We will first focus our discussion on the structure and thermodynamics of charged clusters in the size range  $55 \le N \le 1169$ . In particular, we will discuss the influence of temperature, charge values, and number of charged particles on the energy landscape explored during the Monte Carlo simulations and on the distribution of charged particles within the cluster (interior or surface of the cluster)[3]. To shed some light on stability conditions[4] and fragmentation mechanisms of these clusters (Coulomb explosion or fission), heat capacity curves from Monte Carlo simulations will be discussed in conjunction with cluster distortion coefficients and mass spectra derived from dynamics simulations. Some of these structural and dynamic results will be compared to force fields molecular dynamics simulations performed by other groups to model ESI droplets.

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#### CO<sub>2</sub> CAPTURE FROM BINARY GAS MIXTURE VIA CLATHRATE HYDRATES FORMATION: INVESTIGATION BY RAMAN SCATTERING

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#### ABSTRACT

The global greenhouse effect of CO2 has attracted increased attention as a worldwide problem. CO<sub>2</sub> capture and sequestration (CCS) for industry is a great challenge that is susceptible to reduce carbon emission. Exhausting gases from industry contains CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> in localized areas: steelmaking plants, gas or coal power plants, chemical plants, etc. In post combustion capture, CO2 concentration is generally low; typically 5-10% for power plants, but it can be higher: up to 40% in steelmaking plants, or also in some cases of natural gas production. Different strategies and technologies of capture need to be developed to decrease the cost of the process, in respect to the specific compositions and operative conditions, especially pressure. Gas hydrates are currently getting a significant attention as a potential CO<sub>2</sub> storage technology. The equilibrium properties of CO<sub>2</sub>-N<sub>2</sub> gas hydrates are investigated by p-T and in-situ Raman spectroscopy. sI and sII structures are identified depending on the loading or equilibrium composition [1]. The equilibrium properties of CO2xTBAB-H<sub>2</sub>O (with x = 40 wt%, 5 wt%) hydrates and N<sub>2</sub>-xTBAB-H<sub>2</sub>O (with x =5wt%) are determined and the structure (type A or B) is found to depend on the equilibrium (or loading) pressure of CO2 or N2. It is the first time that an inversion of the stable phase of tetra-n-butyl ammonium bromide (TBAB) is observed when a gas ( $CO_2$  or  $N_2$ ) is trapped in the water cages [2].

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#### Multiplexed Photo-Ionization Mass Spectrometry Investigation of the Acetyl Peroxy + HO<sub>2</sub> Reaction

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Peroxy radicals are important intermediates in the oxidation of Volatile Organic Compounds(VOCs) in the troposphere, and play a crucial role in air pollution, the formation of photochemical smog and organic aerosols. The acetyl peroxy radical,  $CH_3C(O)O_2$  is generated from free radical reactions of carbonyl compounds. It can subsequent chemistry can lead to formation of formic acid, acetic acid, and acetyl nitrate (PAN). A key loss process is the radical-radical reaction with hydroperoxy radical,  $HO_2$ , particularly when nitrogen oxides are low.

The reaction of the acetyl peroxy radical with HO<sub>2</sub> has three product channels:

 $\begin{array}{rl} CH_3C(O)O_2 + HO_2 & CH_3C(O)OH + O_3 \\ \rightarrow CH_3C(O)OOH + O_2 \\ CH_3C(O)O + O_2 + OH \end{array}$ 

The third channel was discovered recently, and it may be important in resolving discrepancies between the concentrations of hydroxyl radicals OH observed in the atmosphere and that predicted by models. However, there remains significant disagreement concerning the OH yield among recent laboratory kinetics studies.

Time-resolved photoionization mass spectrometry (PIMS) provides a powerful approach for studying the product branching ratios and reaction rates, by selective time-resolved detection of most of the reactants, intermediates, and primary products. We report our studies of this reaction in a laser-photolysis low-pressure flow cell experiment which utilizes tunable VUV radiation generated at the Advanced Light Source synchrotron at the Lawrence Berkeley Laboratory, coupled to the Sandia multiplexed PIMS apparatus. We are able to determine relative product yields based on measurements of absolute radical concentrations, coupled with kinetic modeling of the time-dependence of the observed species. We have also investigated the acetyl +  $O_2$  reaction

 $\begin{array}{rcl} CH_{3}C(O) + O_{2} & \rightarrow & CH_{2}C(O)O\left(\alpha\text{-lactone}\right) + OH \\ & & CH_{3}C(O)O_{2} \end{array}$ 

and find significantly different OH yields when compared to the literature.

#### *Ab initio* calculations of the H<sub>2</sub>CO+H<sub>2</sub>O reaction

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Interactions of formaldehyde ( $H_2CO$ ) with water are of a fundamental interest to understand the origin and fate of formaldehyde in the atmosphere as well as in astrochemistry. In order to understand these interactions between formaldehyde and water in the gas phase and the liquid phase, we performed *ab initio* and DFT calculations with the Gaussian03 and Gaussian09 software packages.

We studied the hydration mechanism of formaldehyde with water to form methanediol  $(CH_2(OH)_2)$  catalysed by up to 5 water molecules. Reactants, molecular complexes, products and transition state structures were fully optimized at DFT (B3LYP), MP2 and wB97XD levels of theory using the Pople-style 6-311++G<sup>\*\*</sup> and the larger 6-311++G(3df,2p) basis sets. Two mechanisms have been investigated, in the gas phase and with an implicit solvent, which allows to simulate long range interactions, in order to determine the influence of the presence of the solvent on the reaction.

These *ab initio* calculations will allow us to calculate the rate constants using the bimolecular transition state theory. These rate constants will be compared with experimental data.

*Ab initio* molecular dynamics simulations have also been performed in the NVE ensemble with Car-Parrinello Moldecular Dynamics (CPMD) software package on systems mimicking 0.01 and 0.05 mol. Frac. formaldehyde solutions at 300 K, for which we have experimental data. These dynamical calculations will provide further information about solvation shell of water around the solute  $(CH_2(OH)_2 \text{ and } H(CH_2O)_2OH)$ .

#### Collisional excitation of HCl in the interstellar medium

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Our knowledge of astrophysical media rely mainly on absorption and emission spectra. The analysis of such spectra allows us to derive the physical conditions ( temperature, gas density, molecular abundance) of molecular clouds. In order to model these spectra, we need to determine the collisional rate coefficients of molecules in collision with the most abundant interstellar species which are H, He and H<sub>2</sub>. Indeed collisional process compete with radiative process for the populating of excited rovibrational levels of interstellar species.

The first spectra from HERSCHEL space observatory show, quite unexpectedly, a large number of hydride lines (CH, NH, OH<sup>+</sup>, OH, H<sub>2</sub>O, etc.). Unfortunately, there are only few reliable data set to perform the analysis of the hydrides spectra. Among the molecular hydrides, the HCl molecule has a special interest since it is a tracer of dense region [1]. Then we are studying collisions involving chlorine hydride and He and H<sub>2</sub> in order to provide collisional data for interpreting HCl observations.

We present here a new study of the rotational excitation of HCl by He and by  $H_2$ . For both systems a new accurate potential energy surface was calculated at the CCSD(T) level, using large atomic basis set. Inelastic cross sections for the rotational excitation have been performed using a close coupling method. Then, collisional rates coefficients have been obtain from a maxwellian average of the cross section. For HCl-He, the hyperfine structure have been take into account using a recoupling method. For HCl-H<sub>2</sub>, we have notice near-resonance effect, due to energetically close rotational level. This effect is responsible for larger cross sections than expected. Surprisingly the data for HCl-He and HCl-H<sub>2</sub> are quite different.

For the HCl-He system the new collisional data have been compared with the one previously published by Neufeld & Green [2] and we found significant differences between the two sets of data. The new collisional data are expected to have a strong influence on astrophysical modelling. In particular, HCl abundance derived from the emission spectra will have to be reviewed using the new data and we expect that the data will allow us to have a better knowledge of Cl chemistry in the interstellar medium.

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#### Quantum vibrational ground state properties of H<sub>7</sub><sup>+</sup>

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Diffusion Monte Carlo (DMC) and path-integral Monte Carlo (PIMC) computations of the vibrational ground state and thermal equilibrium state properties of the  $H_7^+/D_7^+$  cations are presented, [1] using an *ab initio* full-dimensional potential energy surface (PES). [2] Quantum anharmonic effects and structural fluctuations of the  $H_7^+$ and  $D_7^+$  at a temperature of T=10 K are also investigated. Anharmonic zero-point energies and dissociation energy values are determined for first time for both clusters, and compared with previous theoretical estimates from electronic structure calculations by standard harmonic analysis, and experimental measurements available. Probability density distributions are also computed for the ground vibrational/thermal equilibrium states of the  $H_7^+$  and  $D_7^+$  cations. We found that these complexes are best described as a central  $H_3^+/D_3^+$  core surrounded by solvent  $H_2/D_2$  molecules rotating around the  $C_2$  axes (see Figure 1). The classical approximation overestimates the rigidity of the  $H_7^+$ , and quantum fluctuations affect predominantly the rotational degrees of the solvating hydrogen molecules. Such fluxional nature of the  $H_7^+$  is in qualitative agreement with a previous theoretical studies and recent experimental measurements. [3] The existence of large-amplitude motions, and their implication in vibrational spectra are also discussed.



Figure 1: Isosurfaces of the vibrational ground state wavefunction for the  $H_7^+$  (left panel) and  $D_7^+$  (middle panel) from the DMC simulations. The three lowest stationary points on *ab initio* PES are shown in right panel.

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#### Theoretical investigation of the vibrational dymanics and spectroscopy of H/D<sub>5</sub><sup>+</sup> cations

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The recent increased interest on research studies of the H<sub>5</sub><sup>+</sup> cation, and its isotopologues, is due to the postulation for their presence, although still not detected, in the interstellar medium. There is no doubt, particularly in the light of the recent laboratory observations, [1] that the spectroscopy of these systems is also a great challenge for the theorists. We report full-dimensional (9D) time-dependent and time-independent calculations within the MCTDH method on vibrational dynamics these highly fluxional cations, providing important information on their spectroscopy in a rigorous manner. For the spectroscopic characterization of the  $H_5^+$  and its deuterated isotopologues we employed recent ab initio-based potential energy surfaces [2] It is found that these systems are highly delocalized, interconverting between equivalent minima through rotation and internal proton transfer motions even at their vibrational ground state (see figure). Isotopic substitution affects the zero-point energy and structure, showing preference in the arrangements of the H and D within the mixed clusters, and the most stable conformers of each isotopomer are the ones with the H in the central position. The computed infrared absorption spectra [3] for both cations are in very good agreement with the recent experimental measurements available from multiple- and singlephoton photodissociation spectroscopy [1] The predominant features in the spectra are assigned to the excitations of the shared-proton stretch mode (see figure), while above dissociation the symmetric and antisymmetric stretching of the two  $H_2$  and the breathing mode of the  $H_3^+$  are also involved. [3]



Figure 1: Probability density distribution of the  $H_5^+$  ground state (left panel). Comparison of the theoretical simulations and experimental measurements (right panel).

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#### Experimental test of universality of the Anderson transition

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In the presence of a disordered potential, the classical diffusive transport of a particle can be inhibited by quantum interference between the various paths where the particle is multiply scattered by disorder, a puzzling phenomenon known as Anderson localization [1]. The dimensionality of the system plays a major role, which can be understood qualitatively from the scaling theory of localization [2, 3]. In dimension d = 3, there is delocalized-localized (or metal-insulator in solid state physics language) transition — known as the Anderson transition — with a mobility edge  $E_c$  separating localized motion at low energy (strong disorder) from diffusive motion at high energy (low disorder).

A key prediction of the scaling theory is that the critical exponents are **universal**, that is do not depend on the microscopic details of the model used, such as the correlation functions of the disorder, the dispersion relation of the particles, etc.

We experimentally test the universality of the Anderson three dimensional metalinsulator transition, using a quasiperiodic atomic kicked rotor [4]. Nine sets of parameters controlling the microscopic details have been tested. Our observation indicates that the transition is of second order, with a critical exponent independent of the microscopic details. We thus demonstrate that the value of the critical exponent is universal. the average value  $1.63 \pm 0.05$  agrees very well with the numerically predicted value  $\nu = 1.58$  [5].

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# Photodynamic processes upon Rydberg excitation of Nitrogen Monoxide in Ne solid matrix

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Rydberg excitation of chromophores trapped in rare gases matrices have been subject of experimental and theoretical works during several years [1,2]. The structural rearrangements induced in these matrices after this kind of electronic excitation explains the existence of Stoke's shifts between absorption and emission bands. These structural rearrangements can be analyzed from their temporal behavior using Classical Molecular Dynamics simulations.

On the other hand, different behaviors, after electronic excitation, can be found in the matrix when the nature of the rare gas solid is changed. In that sense lighter rare gas atoms like Ne expresses predominantly quantum characteristics, while atoms like Ar could be treated as classical particles [2,3]. This effect can strongly influence the photodynamical processes in the system. In addition, new Potential Energy Surfaces (PES) have been developed to account a better description of NO-Ne interaction in the ground and first Rydberg states [4,5].

Classical Molecular Dynamics with a new value of temperature from the Temperature Quantum Correction [6] calculations and a new Potential Energy Surface for NO-Ne interaction [5], in a solid Ne system, when, a NO molecule placed in a substitutional site, is excited upon it's first Rydberg state, are presented.

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#### Environmental Scanning Electron Microscopy of Ice Doped with Uranyl

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Ice is a solid state of water that covers large areas of our planet. Chemical compounds present in the environment as pollution can also be found in natural ice and snow. These substances can be either adsorbed on the surface of ice crystals from atmosphere or they can already be present in water prior to freezing. Impurities are expelled from the growing ice lattice to the boundaries of ice grains during freezing [1] Thus, concentration of impurities in remaining brine layer is increasing in the process. The reactivity of chemical compounds in ice differs from their reactivity in aqueous solution. Potentially harmful substances can be formed and eventually released to the environment [2, 3]. It is important to gain better knowledge of the distribution of impurities in ice and the nature of their microenvironment.

Low Temperature Scanning Electron Microscopy (LTSEM) is a valuable tool for observation of ice and snow samples. However, this technique requires very low pressure and low temperature [4].

We employed Environmental Scanning Electron Microscopy (ESEM) for the observation of artificial ice with impurities at temperatures above 250 K and pressures in several hundreds of Pascals. Uranyl nitrate was used as a model impurity in our study. We obtained images of ice samples using both secondary electrons detector and back-scattered electrons detector. Our experiments yielded information about surface morphology and distribution of impurities on ice. Luminescence analysis of the samples was done in order to discover the nature of local microenvironment surrounding the impurities (uranyl).

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#### Processes Accompanying Freezing of Aqueous Solutions

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When aqueous solution freezes, most of the compounds initially dissolved in the solution are expelled from the ice lattice and tend to accumulate in the remaining solution. Subsequently, after the solution is completely frozen, impurities are mostly located on the boundaries of ice grains [1].

In case of solutions of salts, the ability of the cations and the anions to incorporate into the ice lattice may differ. This unequal distribution of ions results in generation of electric potential across the ice-solution interface. This phenomenon is called freezing potential [2, 3]. The freezing potential effect is eventually neutralized via flow of  $H^+/OH^-$  ions from the solution to the ice lattice and the acidity of the unfrozen portion of solution changes significantly [3]. It affects the stability of compounds frozen in presence of common salts [3, 4].

We applied UV-Vis absorption spectroscopy to measure the acidities of frozen aqueous solutions [5]. A low amount of an acid-base indicator was used as an internal probe. The effects of type and concentration of salt and the method of freezing were examined. Freezing potentials of selected solutions were also measured. Results of these experiments were correlated with the abilities of ions to incorporate into the lattice of ice.

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# Path integral Monte Carlo calculations of Ca impurity in helium droplets

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Helium clusters have been successfully employed as an ideal environment to spectroscopically investigate an ample list of impurities. For the case of atoms, the question of establishing solvation or surface location for the impurity in the helium droplet is an issue of great importance to further understand its behavior and the spectroscopic observations.

A crutial aspect which needs to be taken into consideration for these systems is the dopant-solvent interaction. In particular, in the case of the Ca atoms, the He-Ca potential energy curve (PEC) has been studied and reported through various publications in recent years: The modeling of it via simple empirical formulae was put forward by Kleinekathöfer in the year 2000 [1], where he found a well depth of 10.3 cm<sup>-1</sup> at a distance of 5.1 Å. Earlier calculations of Stienkemeier et al. [2] had provided a well depth of 11.6 cm<sup>-1</sup> at a distance of 5.45 Å, similarly to recent Tang's predictions [3] of 12.42 cm<sup>-1</sup> and 4.9 Å, respectively. On the other hand, *ab initio* quantum chemical calculations indicate a very different scenario: the work of Lovallo and Klobukowski [4] found an equilibrium distance of 6.02 Å and a well depth of 3.32 cm<sup>-1</sup> in line with calculations carried out by Czuchaj et al. [5], K. Partridge et al. [6], and the very accurate quantum chemical studie of Hinde [7].

In this work we present path integral Monte Carlo (PIMC) [8] calculations of  ${}^{4}\text{He}_{N}$  nanodroplets doped with a single calcium atom at low-temperature range. Simulations have been carried out using different He-Ca interactions, revealing substantial discrepancies regarding the precise location of the Ca impurity with respect to the helium droplet and the binding energy of the system.

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# Formation of paramagnetic polar molecules from open-shell and closed-shell atoms

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Molecules with non-zero magnetic and electric dipole moments are extremely interesting for their novel applications in quantum information theory [1] or experimental physics probing the fundamental theories [2]. Obvious candidates for such molecules are the mixtures of laser-coolable closed-shell atoms (eg. Yb) with open-shell atoms (alkali-metal atoms, Cr, lanthanides) – and significant experimental progress toward this direction has been initiated very recently [3,4,5].

Recently [6], a new mechanism which drives Feshbach resonances in systems like RbSr. However, such Feshbach resonances are extremely narrow: predicted widths of such resonances are very small compared to fields at which they occur – the crucial ratio  $B_{res}/B_{res}$  is at best 10<sup>-5</sup> for such systems, which is prohibitive for their practical use. The molecules such as RbSr can be formed, however, with optical methods, and we discuss the prospects for formation of such molecules.

We also discuss a mechanisms which might be much more promising for formation of paramagnetic, polar molecules. First we focus on mixture of ultracold Cr and Yb atoms which could form molecules with huge magnetic moment of  $_{\rm B}$  and dipole moment of 0.1-0.2 D. If both atoms approach each other, anisotropic spin-spin interaction appears in interaction-distorted Cr atom. Such effect can be as large as 0.5 cm<sup>-1</sup> near R<sub>e</sub>=3.4 Å. This is enough to produce the Feshbach resonances at magnetic fields below 150 G, typically as broad as 0.1-1G for magnetically ground states of Cr atoms. In lanthanides the spin-spin interaction, hence the resonances can be even broader. We examine also the YbEr system in which the spin-spin effect competes with the anisotropy of the interaction potential related to non-zero atomic angular momentum [7]. Such anisotropy, is small, of order of 1500-2000 cm<sup>-1</sup>. In this example system we also find very broad magnetic Feschbach resonances (1G) induced by such effect, also, at very low fields.

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#### Development and application of a polarizable force-field for halides counter anions and lanthanides cations in aqueous solution

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The hydration of transition metals, lanthanides (Ln) and actinides (An) in aqueous solution is a topic that attracts the attention of many scientists as this process is of relevance to environmental problems and medicinal applications. Actinides have an environmental and toxicological interest since they are nuclear fuel wastes with both chemical and radiochemical toxicity, becoming extremely difficult to handle it from experimental point of view. In this context, a more quantitative use of the Ln/An analogy is desirable to develop theoretical approaches capable of reproduce the experimental data existing for the former and capable of predict macroscopic properties in the solvation of the later.

In order to investigate hydration of lanthanide/actinide and halides counter ions[1], one of our goal is to develop a polarizable force-field model adjusted on state-of-the art ab initio calculations[1, 2, 3]. Another goal is to discuss the accuracy of the model by investigating the impact of the parametrization uncertainties in the bulk water model and in the metal-water interaction model on the molecular simulation results.

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# Accurate global potentials for the interaction between rare gases and graphene-based surfaces. A joint atom-bond and computational approach

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The interaction between atoms and molecules with graphene type surfaces is a topic of great interest given the potential new applications of these materials. For example it is in principle possible to detect with high resolution the presence of a single atom adsorbed on these surfaces[1]; also its porous sheets synthesized with atomic precision[2] have been proposed as a nano-scale membrane which could be used as an atmospheric nanofilter[3]. Thus in this kind of studies it is necessary not only a reliable and accurate description of the interaction potential but it is also fundamental to obtain a convenient parametrization of the involved non-covalent interactions to support dynamical studies on the physisorption of atoms and molecules.

We report reliable global potentials for the physisorption of rare gases with graphene and graphite surfaces amenable for a variety of dynamics simulations.

An atom-bond pairwise additive form[4] of the potential is used, where the interaction pairs, represented by proper analytical functions, are constituted by the Rg atom (Rg= He, Ne, Ar, Kr) and the C-C bonds of the graphene sheet(s). The parameters of the atom-bond pair potential, derived from the polarizability of the interacting partners, are fine-tuned exploiting calculations of the prototypical Rg--coronene system(see Fig. 1) using high level electronic structure methods, such as DFT-SAPT[5] and MP2C[6], and large basis sets. The atom-graphene/graphite potential is further expanded in a Fourier series and it is found that, for an accurate representation of the interaction, only a small number of corrugation terms need to be added to the laterally averaged potential. Furthermore, this corrugation part of the potential is identical for both Rg--graphene and Rg--graphite; in other words, inner layers of graphite only play a role in the laterally averaged Rg-graphite potential. For all systems, the hollow at the center of the carbon ring is preferred over the bridge and top adsorption sites (see Fig. 1), although diffusion barriers are low. Present results[7] are found to compare well with previous data[8] regarding well depths and equilibrium distances at different adsorption sites and, for graphite, the long-range dispersion coefficient C<sub>3</sub>. Moreover for Rg-graphene an estimation of the long-range dispersion coefficient C<sub>4</sub> is provided for the first time.

In addition, the interaction between Rg and porous graphene is modeled and barriers for penetration through the pores have been obtained; a potential use for lighter gases separation from the heavier ones is proposed.

#### **Quantum Mechanical Study of the Cl + HD**(*v*=1) **Reaction**

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Time-independent quantum mechanical calculations, at two different total energy values and for various initial states, have been performed in order to to characterize the dynamics and stereodynamics of Cl + HD reactive collisions [1], using the adiabatic potential energy surface by Bian and Werner [2]. For reaction with HD(v=1), integral and differential cross sections have been calculated and the effect of vibrational *vs.* translational energy on the reactivity has been examined. From these results, the spatial preferences of the reaction and the extent of the control of the cross sections achievable through a suitable preparation of the reactants have been also studied. The directional requirements are tighter for the HCl channel than for the DCl one. Formation of the products takes place preferentially when the rotational angular momentum of the HD molecule is perpendicular to the reactants approach direction.

Computed cross sections and polarization moments have been compared with experimental results by Kandel *et al.* [3] for the reaction with HD(v=1) produced by stimulated Raman pumping. The agreement so obtained is good and it improves the accordance found in previous calculations with other methodologies and potential energy surfaces.

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#### MILLIMETER AND SUBMILLIMETER WAVE SPECTRA OF THE HCOO<sup>13</sup>CH<sub>3</sub> ISOTOPOLOG OF METHYLFORMATE IN THE GROUND STATE AND IN THE FIRST EXCITED TORSIONAL STATE

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The detection of nineteen new rotational transitions of the parent molecule of methylformate (HCOOCH<sub>3</sub>) in the second lowest excited torsional mode ( $v_t = 2$ ) was recently reported in Orion-KL[1], as well as the detection of eighty new lines corresponding to the two <sup>18</sup>O isotopologs of methylformate in their ground states[2]. The laboratory work on HCOO<sup>13</sup>CH<sub>3</sub> was continued[3]. A wide spectral range from 50 to 940 GHz was recorded in Lille with the submillimeter-wave spectrometer based on harmonic generation of a microwave synthesizer source, using a multiplication chain of solid state sources (50-100 and 150-940 GHz) and a backward wave oscillator (100-150 GHz), and coupled to a 2.2 m cell. The absolute accuracy of the line positions is better than 30 kHz up to 630 GHz and 50 kHz above. The two states ( $v_t = 0$  and 1) were fitted together using the RAM Hamiltonian of the BELGI[4] program and a new set of 45 parameters was accurately determined. The fit contains 7050 lines corresponding to the ground state up to J = 78 and  $K_a = 34$  and 1907 lines related to  $v_t = 1$  up to J = 59 and  $K_a = 24$ . The detection of new  $v_t = 1$  lines in Orion KL will be reported and discussed. *This work is supported by the French Programme National de Physico-Chimie du Milieu* 

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#### Recent advances in the understanding of the reaction Mu+H<sub>2</sub>(v=0-1)

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Our aim is to shed light on the importance of quantum effects such as tunneling, the preservation of the zero point energy and the vibrational adiabaticity in the reaction Mu+H<sub>2</sub> [1]. In addition to accurate QM calculations, quasiclassical trajectories (QCT) have been run in order to check the reliability of this method for this isotopic variant. It has been found [2, 3] that the reaction with H<sub>2</sub>(v=0) is dominated by the high ZPE of the products and that tunneling is largely irrelevant. Accordingly, QCT calculations that preserve the product's ZPE succeed in reproducing the QM rate coefficients. However, when the hydrogen molecule is vibrationally excited [3, 4], QCT calculations fail completely in the prediction of the huge vibrational enhancement of the reactivity. This failure is attributed to tunneling, which plays a decisive role breaking the vibrational adiabaticity when v=1. By means of the analysis of the results, it can be concluded that the tunneling takes place through the v=1 collinear barrier. Somehow, the tunneling that is missing in theMu+H<sub>2</sub>(v=0) reaction is found in Mu+H<sub>2</sub>(v=1).

- [1] D. G. Fleming *et al.*, Science **331**, 448 (2011)
- [2] P. G. Jambrina et al., J. Chem. Phys. 135, 034310 (2011)
- [3] J. Aldegunde *et al.*, submitted to Mol. Phys.
- [4] P. G. Jambrina et al., Phys. Chem. Chem. Phys. 14, 14596 (2012)

# Adsorption of polycyclic aromatic hydrocarbons on soot particles

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Polycyclic Aromatic Hydrocarbons (PAHs) play an important role in the formation of soot particles during combustion processes. Moreover, they have a proven impact on health and environmental concerns. However, studies to characterize quantitatively PAH adsorption on soot particles are difficult to perform and do not allow to detect the ability of these molecules to bind to soot particles during their growth in flames. One reason is that these investigations require a calibration method, which involves standard particles with known PAH content.

The project CAHAPS (online Characterization of Adsorption of Polycyclic Aromatic Hydrocarbons in Soot), a collaboration between the CORIA (INSA Rouen) and CIMAP (Caen), aims to demonstrate the feasibility of a bottom-up approach to characterize the adsorption rate of PAHs on well defined soot particles.

The first stage of this project consists of implementing a system to quantify the adsorption rate of PAHs on soot aggregates with a controlled amount of soot particles of a given size and PAHs molecules. The PAH particles are produced within a gas aggregation source [1] in which size selected soot nanoparticles are injected, allowing to condensate a controlled vapor of PAH molecules on soot particles. The resulting particles produced will be analyzed by time-of-flight mass spectrometry (TOF-MS) [2]. We will study the dependence of the PAH adsorption yield as a function of the size and morphology of the soot particles as well as on the type of PAH molecules.

- 1. Zimmermann, U., et al., *Producing And Detecting Very Large Clusters*. Zeitschrift für Physik D-Atoms Molecules And Clusters, 1994. **31**(1-2): p. 85-93.
- Chandezon, F., B. Huber, and C. Ristori, A New-Regime Wiley-Mclaren Time-Of-Flight Mass-Spectrometer. Review Of Scientific Instruments, 1994. 65(11): p. 3344-3353.

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## **Conference Schedule**

	Tuesday, July 2 <sup>nd</sup>	Wednesday, July 3 <sup>rd</sup>	Thursday, July 4 <sup>th</sup>	Friday, July 5 <sup>th</sup>
00.00		Astrochemistry	Theoretical and computational chemistry	Physics and Chemistry of the Atmospheres II
09:00		Helen J. Fraser 09:00 - 09:40	Laurent Cantrel 09:00 - 09:40	Graham Worth 09:00 - 09:40
10:00		Florent Mispelaer 09:40 - 10:00	Fadel Bassal 09:40 - 10:00	Christophe Iftner 09:40 - 10:00
		Barbara Michela Giuliano 10:00 - 10:20	Romain Vandeputte 10:00 - 10:20	David A. Bonhommeau 10:00 - 10:20
		Coffee break 10:20 - 10:50	Coffee break 10:20 - 10:50	Coffee break 10:20 - 10:50
11:00		François Lique 10:50 - 11:30	Giacomo Giorgi 10:50 - 11:10	Bertrand Chazallon 10:50 - 11:30
			Alejandro Rivero-Santamaria	
		M <sup>a</sup> Elena Moreno Atahonero 11:30 - 11:50	Aliezer Martinez Mesa 11:30 - 11:50	Mitchio Okumura 11:30 - 11:50
12:00		Mario Alejandro Hernández Vera 11:50 - 12:10	Llinersy Uranga Pina 11:50 - 12:10	Pauline Delcroix 11:50 - 12:10
		Susana Gómez Carrasco 12:10 - 12:30	Manuel Goubet 12:10 - 12:30	Concluding remarks 12:10 - 12:30
		Lunch break 12:30 - 14:30	Lunch break 12:30 - 14:30	Lunch break 12:30 - 14:15
13:00				
14.00				
14.00	Opening : 14:00 - 14:30			
	Atmospheres I	Physics at the interfaces: Biophysics	Cold Atoms and Molecules	
15:00	Inorsten Bartels-Rausch 14:30 - 15:10	Damen Baigi 14:30 - 15:10	Michael Mark 14:30 - 15:10	
10.00	Florent Louis 15:10 - 15:30	Emmanuel Courtade 15:10 - 15:30	Romain Vexiau 15:10 - 15:30	
	Aude Simon 15:30 - 15:50	Ondrej Svoboda 15:30 - 15:50	Julia Diaz-Luque 15:30 - 15:50	
16:00	Coffee break 15:50 - 16:20	Coffee break 15:50 - 16:20	Coffee break 15:50 - 16:20	
	Petr Slavíček 16:20 - 17:00	Maxime Dahan 16:20 - 17:00	Hans Lignier 16:20 - 17:00	
17:00	Markus Lampimaki 17:00 - 17:20	Daniel J. Arismendi Arrieta 17:00 - 17:20	Maxence Lepers 17:00 - 17:20	
	González-Lezana Tomas 17:20 - 17:40	Michel Sliwa 17:20 - 17:40	Manuel Lara Garrido 17:20 - 17:40	
		Information 17:40 - 18:00	Simon Chefdeville 17:40 - 18:00	
18:00				

Welcome reception 18:30	Poster session - Wine and cheese.	Conference dinner - 20:00