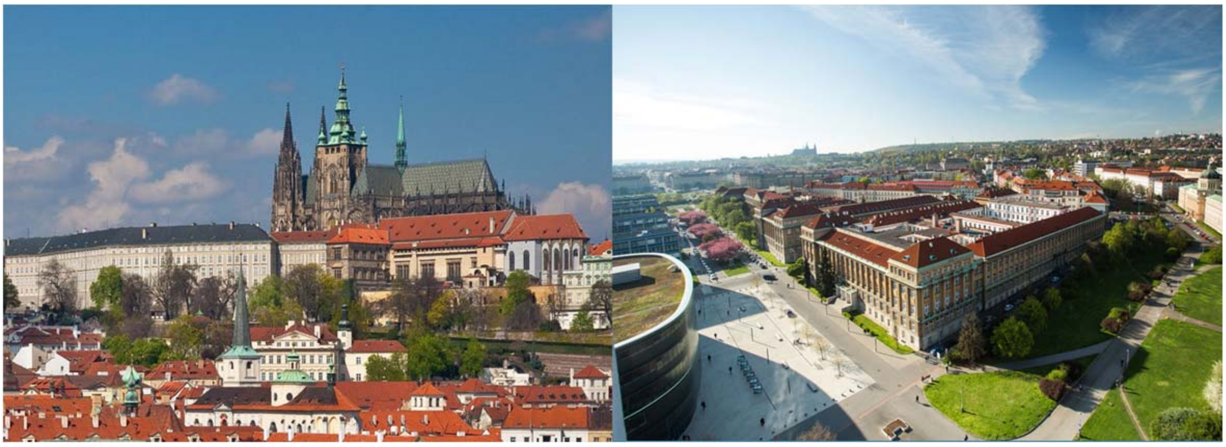
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

Our Astrochemical History CM1401

Book of abstracts



First General Meeting in Prague

May 25-29, 2015

ÚFCH JH

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

COST Action Our Astrochemical History CM1401

May, 25-29, 2015

Prague, Czech Republic

University of Chemistry and Technology Prague

J. Heyrovský Institute of Physical Chemistry AS CR, v.v.i

Local Organizers: Petr Slavíček, Eva Muchová, Laurent Wiesenfeld, Vladimíra Bergerová

Action managing: Laurent Wiesenfeld (Chair), Inga Kamp (Vice-Chair), Helen Fraser (Grant Manager), Lauri Halonen (STSM Manager)

Local Team: Daniel Hollas, Jan Chalabala, Jakub Med, Martina Rubešová, Daria Galaktionová, Jakub Kubečka, Veronika Jurásková

Conference Venue

The meeting will be hosted by the Jaroslav Heyrovský Institute of Physical Chemistry, AS CR, v.v.i., all program will be held in the institute. J. Heyrovský Institute of Physical Chemistry is situated in the northern part of Prague, in a small campus together with other research institutes. The address of the Institute is **Dolejškova 2155/3**, 182 23 Prague 8, Czech Republic.

The institute is easily reachable via metro line **C** (station Ládví), via tram **10** (station Ládví), or via bus **103**, **177**, **183** (station Ládví)

Walk to the Institute from tram-stop or subway station Ládví, line C is depicted in red. Note that you cannot drive to the Institute via this route - use Davídkova and Pod Vodarenskou věží streets when driving.

Registration

The registration will take place on **Monday, May 25** at the Jaroslav Heyrovský Institute of Physical Chemistry, AS CR, v.v.i. between **16.00-19.00**. The registration is also possible on Tuesday morning.

Poster Sessions

Posters sessions will be divided into 2 groups.

Group A – will be held on **Tuesday, May 26**.

P1 João Brandão

P2 Niyazi Bulut

P3 + P4 Andrea Cernuto

P5 Henda Chaabouni

P6 Carla Coppola

P7 Alexandre Faure

P8 Enrique Garcia

P9 Robin Giereth

P10

P11 Benjamin Irving

P12 Baptiste Joalland

P13 Stanislav Kedžuch

P14 Jacob Laas

P15 Lei Song

P16

P17 Savino Longo

P18 Ioan Schneider

P19 Yves Ellinger

Group B - will be held on **Wednesday, May 27**.

P1 Jan Chalabala

P2 Daniel Hollas

P3 Jan Meisner

P4 Jakub Kubečka

P5 Christian Meíja

P6 Milan Milovanovic

P7 Marta Pasquini

P8 Françoise Pauzat

P9 Ramya Kormath Madam Raghupathy

P10 Matt Redman

P11 Johannes Kaestner

P12 Maria Luisa Senent Diez

P13 Ana Lopez Sepulcre

P14 Péter Szabó

P15 Isabel Tanarro

P16 Ionut Topala

P17 Céline Toubin

P18 Tomaz Urbic

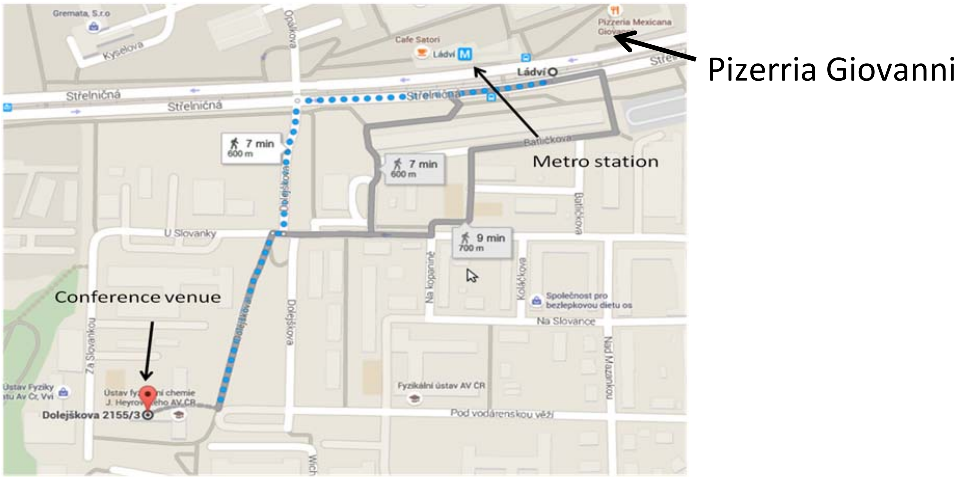
P19 Ján Žabka

P20 Jean Louis Lemaire

P21 Sergio Ioppolo

Food and Drinks

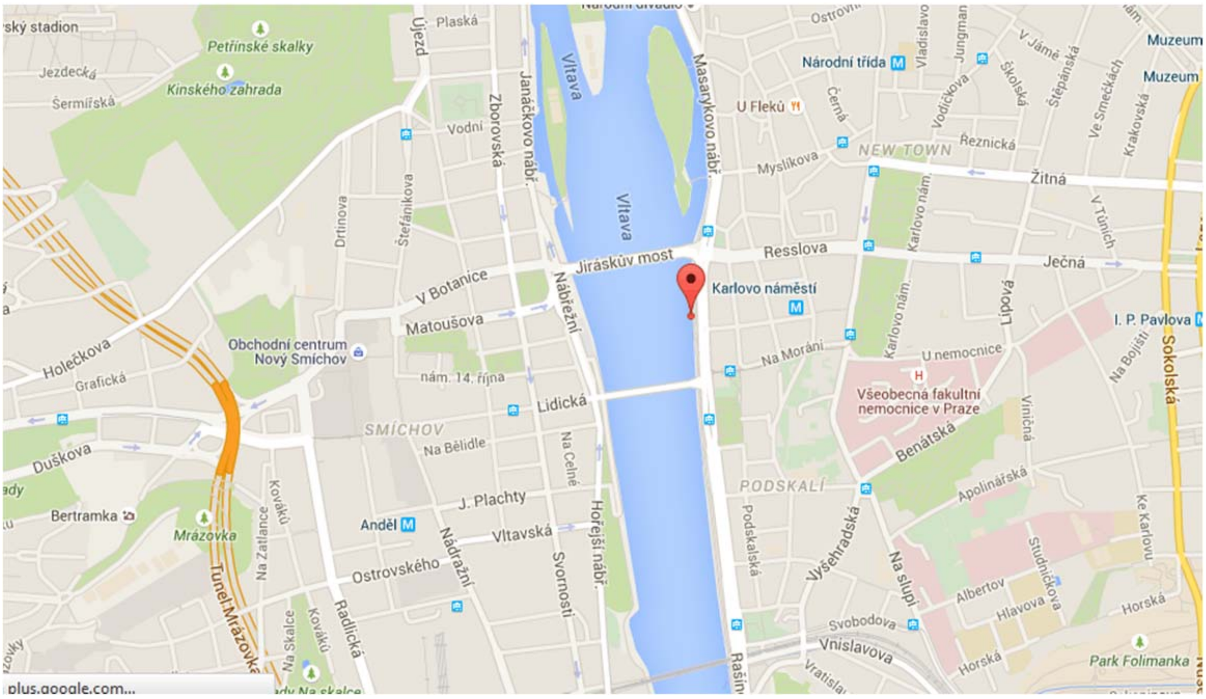
Coffee breaks will be taken in the room adjacent to the meeting room. Lunch will be served at the restaurant Pizzeria Giovanni (Střelničná 1826/35, 182 00, Praha 8).



Conference Banquet

The conference banquet will take place on **Thursday, May 28 at 19.30** and will be held on the Labe boat (http://www.praguesteamboats.com/) at Rašín Embankment - between the Palacký and Jirásek Bridge. All participants are welcome to join; the banquet is fully covered by the fee.

Meeting point: **Conference Venue, 18.45** or at Rašín Embankment at 19.30.



Excursions

The excursions will take place on **Wednesday afternoon, May 27**. The excursions are fully covered by the fee.

1. guided tour in Prague castle + Mala Strana - the tour is scheduled for app. 2.5 hours.

- Meeting point: **metro station Ladví at 14.30**

2. guided tour in Klementinum (http://www.klementinum.com/en/) - the tour is scheduled for app. 1 hour.

- Meeting point: **metro station Ladví at TBA**

SCIENTIFIC PROGRAM

Tuesday May 26

Session 0: Introduction

9:00 - 9:30	Laurent Wiesenfeld	*Our Astrochemical History: A Short Overview of the COST Action CM1401*
9:30 - 10:00	Lauri Halonen	COST STSM

Session 1 : Overviews

chairman	*Petr Slavíček*	
10:00 - 10:40	Xander Tielens	Invited
Coffee		
11:10 - 11:50	Naoki Watanabe	*Experimental Approach to Chemistry of Cosmic Dust*
11:50 - 12:30	Claire Vallance	*Scattering Dynamics in Astrochemistry*
Lunch		

Session 2: WG1 Gas Phase Chemistry

chairman	*Alexandre Faure*	
14:00 - 14:40	Nadia Balucani (IT) /Jes Jorgensen (DK)	Introduction
14:40 - 15:20	Cristina Puzzarini	*Astrophysics and Astrochemistry: The Role of Rotational Spectroscopy*
15:20 - 15:40	Dimitrios Skouteris	*Cyanomethanimine and Formamide Formation Routes in the InterStellar Medium from Electronic Structure and Kinetics Calculations*
15:40 - 16:00	Roland Wester	*Reactive and Rotational State-Changing Collisions of Negative Ions at Low Temperature*
Coffee		
16:30 - 16:50	Ludovic Biennier	*Cosmic Anions in the Laboratory*
16:50 - 16:30	Daniel Zaleski	*Using the Tools of Next-Generation Radio Astronomy to Understand Chemistry in the Universe*
17:30 - 19:30	Posters Group A	

Wednesday May 27

Session 3: WG2 Surface Chemistry

chairman	*Stephan Schlemmer*	
9:30 - 10:10	Herma Cuppen (NL) / D. Semenov (DE)	Introduction
10:10 - 10:50	Kjartan Thor Wickfeldt	Invited
Coffee		
11:10 - 10:30	Monfardini Penteado	*Constraints on CH_3OH Formation from the 4.67 um Solid CO Band towards Young Stellar Objects*
11:30 - 11:50	Albert Rimola	*Quantum Mechanical Contributions in the Study of Ice-Based Astrochemical Problems*
11:50 - 12:10	Jennifer Noble	*Matrix Isolation Photochemical Studies of Coronene/Water Complexes: New Insights into the Astrochemistry of Neutral Pahs*
12:20 - 12:40	Yasuhiro Oba	*Glycine Becomes Chiral by Grain-Surface Reactions at Low Temperatures*
Lunch		
14.30	Excursion A - guided tour Prague castle	meeting point - metro Ladvi
14.00	Excursion B - guided tour Klementinum	meeting point - metro Ladvi
In parallel 14:00-17:00	Management Committee Meeting	
17:30 - 19:30	Posters Group B	

Thursday May 28

Session 4: WG3 Photo-Chemistry

chairman	*Gunnar Nyman*	
9:30 - 10:10	P. Slavíček (CZ) / JH Fillion (FR)	Introduction
10:10 - 10:50	Guillermo Muñoz-Caro	*Photodesorption and Photochemidesorption of Astrophysical Ices*
Coffee		
11:20 - 10:40	Marie-Claire Gazeau	*Vacuum Ultraviolet Spectroscopy and Photochemistry of Interstellar and Prebiotic Molecules*
11:40 - 12:00	Robert Kolos	*Experimental and Theoretical Research on Selected Families of Astrochemically Significant Isomeric Molecules*
12:00 - 12:20	Wing-Fai Thi	*The Interplay Between Dust Grain Charging and Gas-Phase Ionization Fraction*
12:20 - 12:40	Lisseth Gavilan	*Hard X-Rays Irradiation of Interstellar Silicate Analogs*
Lunch		

Session 5: WG4 Isotopes chemistry

chairman	*Maria Luisa Senent Diez*	
14:30 - 15:10	C. Vastel (FR)/ O. Roncero (ES)	Introduction
15:10 - 15:50	Evelyne Roueff	*Isotopes and Isotopic Chemistry in the InterStellar Medium*
15:50 - 16:10	Luca Bizzocchi	*Nitrogen Fractionation in the Cold Pre-Stellar Gas*
Coffee		
16:40 - 17:00	Audrey Coutens	*Water Deuterium Fractionation in the Warm Inner Regions of Solar-type Protostars*
17:00 - 17:20	Thanja Lamberts	*Experimental constraints on HDO formation: High- and Low-Temperature Studies*
17:20 - 17:40	Emanuele Congiu	*Laboratory Evidence for Isotope Effects of Surface Processes*
19.30 - 22.30	**Conference Banquet**	

Friday May 29

Session 6: Hot topics

chairman	*Johannes Kaestner*	
9:30 - 9:40	Inga Kamp (NL)	Introduction
9:40 - 10:20	Martin Rubin	*Mass Spectrometry at 67P/Churyumov-Gerasimenko with Rosetta/ROSINA*
10:20 - 11:00	Bertrand Lefloch	*Exploring our Astrochemical History with Spectral Line Surveys*
11:00 - 11:20	Juraj Fedor	*Lack of Aggregation of Guest Molecules on Ice Nanoparticles*
11:20 -11:40	Martin Ferus	*High–Energy Chemistry of Formamide: A Unified Mechanism of Nucleobase Formation*
Refreshment		
	Farewell, questions, open problems,…	

Invited Speakers

Our Astrochemical History

A short overview of the COST action CM1401

Laurent Wiesenfeld

Institut de Planétologie et d'Astrophysique de Grenoble (IPAG)

CNRS and Université Joseph-Fourier-Grenoble, France

A large variety of chemical compounds, from hydrides to complex organic species, are observed in star and planet forming regions. These complex species are also detected in present-day comets and meteorites, possibly as witnesses of the early stages of Solar System formation. An active chemistry proceeds in the harsh environments of pre-stellar cores and proto-planetary disks, where UV photons or X-rays irradiate cold diluted gases and ices, and radicals are copiously produced. The aim of this Action is to bring together laboratory and theoretical gas phase and surface chemistry as well as large facilities based experiments with the aim of rationalizing the molecular evolution. Specific markers, such as isotopic fractionation, ices composition, and abundance ratios of isomers, must be used and understood, in order to draw a coherent picture of our chemical origins.

Chemistry is present in many harsh environments of our Universe. Molecules, and in particular organic molecules, have been observed in low temperature interstellar media, in star forming regions, in gases expelled by dying stars, and on the various types of grains that exist throughout our Galaxy. Also, in galaxies, local and in the early Universe, large reservoirs of molecules are observed. All these molecules were and are routinely observed mainly by the large infra-red, radio-telescopes and interferometric arrays.

The Action aims at tackling the various problems of chemical evolution with methods of physical chemistry. Due to the unusual physical conditions prevailing in interstellar medium, new methods have to be developed in addition to existing ones. This is true for all areas of physical chemistry, in the laboratory, in chemical theory and also in modelling of the chemical networks kinetics. The areas identified as challenging are: (1) Low densities and temperatures; (2) Interplay between surface and gas phase chemistry; (3) Presence of high energy irradiation ; (4) Large variations of isotopic contents ; (5) Observables quantities of cations, anions, and open shell species.

We wish to treat these problems by dividing our Action in four working groups, described below:(1) Gas phase chemistry;(2) surface chemistry ;(3) photochemistry; (4) isotopic chemistry.

As an introduction to the meeting, the overall rationale and the main aims will be presented, with illustration from laboratories of the various working groups.

Experimental approach to chemistry of cosmic dust

Naoki Watanabe
Institute of Low Temperature Science, Hokkaido University, Sapporo, Hokkaido 060-0819, Japan
watanabe@lowtem.hokudai.ac.jp

Recent significant progress of astronomical observations has elucidated a rich variety of physical and chemical properties of the Universe. In association with the progress of observations, it is of increasing importance to understand the physical and chemical processes of interstellar matters on a molecular/atomic scale. Furthermore, phenomena occurring in extreme conditions under interstellar clouds fascinate scientists in not only astronomy but also pure physics and chemistry. In this context, astrochemistry (and its society) is now growing as one of important interdisciplinary sciences. Experimental approach certainly plays an essential role in understanding astrochemistry. In my talk, I would like to overview experiments regarding physicochemical processes of cosmic dust, especially ice dust, which have started in 1980s. Topics will include photolysis, photodesorption, surface reaction, diffusion, thermal desorption and nuclear conversion.

Scattering Dynamics in Astrochemistry

Claire Vallance, Department of Chemistry, University of Oxford

Historically, laboratory astrochemistry measurements have focused on spectroscopic and kinetic studies, aimed at identifying molecules detected in space and determining the rate constants needed for kinetic modelling of interstellar gas clouds. However, there is increasing interest in obtaining additional information on astrochemically relevant processes through collision dynamics studies. Such investigations yield product speed and angular distributions, product quantum-state distributions and information on energy and angular momentum partitioning, all of which can provide detailed mechanistic insights into the process under study. This talk will provide an overview of the information available from scattering studies, an introduction to some of the most widely used experimental methods, and wide-ranging examples of scattering studies on processes such as photodissociation and photoionization, dissociative electron attachment, ion-molecule and radical-radical reactions, and surface-catalysed reactions.

Astrophysics and Astrochemistry:
The role of Rotational Spectroscopy

Cristina Puzzarini

Dipartimento di Chimica “Giacomo Ciamician”, University of Bologna, Via F. Selmi 2,
Bologna, I-40126, Italy. Email: cristina.puzzarini@unibo.it

The identification of a large variety of chemical compounds in space as well as planetary atmospheres has been made possible through the spectral signatures of astronomical bodies. For their interpretation, laboratory measurements are essential and rotational spectroscopy plays a leading role. In fact, astronomical observations require the knowledge of either the spectroscopic parameters or the transition frequencies involved. Furthermore, the knowledge of very accurate rest frequencies is important for astrophysical purposes: precise transition frequencies are essential, for instance, in studies of molecular excitation, radiative transfer, systematic velocity gradients, ambipolar diffusion in star-forming regions, and also for the identification of new species.

Rotational spectroscopy, thanks to its intrinsic high resolution, is a powerful tool for providing most of the information mentioned above: accurate or even very accurate rotational transition frequencies, accurate spectroscopic as well as hyperfine parameters, accurate pressure-broadening coefficients and their temperature dependence. For instance, by exploiting the Lamb-dip technique it is possible to further improve the intrinsic high resolution of rotational spectroscopy and then to resolve hyperfine structures and/or measure very accurate rest frequencies. With respect to collisional phenomena and line shape analysis studies, rotational spectroscopy may provide very good results: not only this technique does not produce uncontrollable instrumental distortions or broadenings, but also, having a high sensitivity, it is particularly suitable for this kind of investigations.

Finally, quantum-chemical calculations have nowadays reached such an accuracy that they not only can be used to guide and support experiment in the field of rotational spectroscopy, but also can directly support astrochemical investigations.

A number of examples will be presented to illustrate the role of rotational spectroscopy in the field of astrophysical and astrochemical investigations with particular emphasis on the work carried out at the Laboratory of Mm-/submm-wave Spectroscopy of Bologna (LMSB) and on the fruitful interplay of experiment and theory.

Dr. Kjartan Thor Wikfeldt
University of Iceland

Amorphous ice plays a key role in the surface chemistry of interstellar molecular clouds by catalyzing chemical reactions, absorbing energy from exothermic reactions and providing a substrate where reactants can coexist. However, many fundamental aspects regarding the physicochemical properties of ice surfaces remain poorly understood. While experiments have provided a wealth of information on the properties of ice and its surface reactivity, molecular-level detail is often difficult to obtain. Computer simulations at the molecular scale can provide unique complementary information in this regard.

This talk will present a series of efforts devoted to elucidating molecular processes on both amorphous and crystalline ice surfaces using state-of-the-art simulation methods. First, the development of a novel *ab initio*-based polarizable interaction potential for water, the single-center multipole expansion (SCME) model, will be outlined. SCME accurately describes cooperative effects in intermolecular hydrogen bonds and is thus transferable between different environments, such as clusters, bulk ice and ice surfaces, yet the computational cost is a fraction of pure *ab initio* methods. An application of SCME to hexagonal ice surfaces generated from long-timescale adaptive kinetic Monte Carlo (AKMC) simulations will be discussed, where novel insights into molecular reordering processes at low temperature were obtained.

Preliminary results from two additional projects will also be presented. In the first project, a computational approach based on density functional theory (DFT) calculations has been applied to the adsorption and diffusion of H and O atoms on ice surfaces. Periodic structure models representing crystalline hexagonal ice as well as both high-density and low-density amorphous ices were compared to obtain insights into the sensitivity to the ice surface structure. Adsorption energies and diffusion barriers that have been corrected for nuclear quantum effects were fed into kinetic Monte Carlo simulations to obtain diffusion rates at temperatures characteristic of cold molecular clouds.

The same structure models for hexagonal and amorphous ice surfaces were also used in the second project, which focuses on the hydrogenation of CO using DFT calculations. A screening of density functionals was performed for the gas phase H+CO reaction. While standard functionals were found to severely underpredict the reaction barrier, the HCTH functional provided a fair agreement with benchmark quantum chemistry calculations. Systematic DFT calculations were subsequently performed to locate possible adsorption sites for CO and reaction pathways for HCO formation, again focusing on the sensitivity to the structure of the ice surface. The relevance of these theoretical results to astrochemical modeling will be discussed.

Photodesorption and Photochemidesorption of Astrophysical Ices

G. M. Muñoz Caro[1], R. Martín-Doménech[1], G. A. Cruz Diaz[1], Y.-J. Chen[2]

[1] Centro de Astrobiología, INTA-CSIC, Torrejón de Ardoz, 28850 Madrid, Spain
[2] Department of Physics, National Central University, Jhongli City, Taoyuan County 32054, Taiwan

Photodesorption of molecules from ice mantles, induced by vacuum-UV radiation, was invoked as a non-thermal mechanism that might explain the observed gas phase abundances of molecules in cold dense cloud interiors. The case of pure CO ice has been extensively studied because CO ice is not efficiently dissociated at photon energies below 11 eV, and therefore photodesorption becomes important. In addition, CO ice has a clear infrared absorption band that allows monitoring of the photodesorption. But most molecules present in ice mantles are, either efficiently photodissociated like methanol, or not active in the infrared like molecular oxygen/nitrogen. In these cases, the study of photodesorption implies the detection of the desorbed molecules or their photoproducts directly in the gas phase. We use IR spectroscopy in transmittance of the ice and QMS of the desorbed molecules to provide a quantification of these processes; this was done for CO_2 ice. In addition, the VUV-photoabsorption of the molecular ice components was also measured, allowing the determination of their absorption cross sections, and the estimation of the photodesorption rates as the number of photodesorbed molecules per absorbed photon in the ice.

We introduce *photochemidesorption* as the formation of a new molecule on the ice surface during irradiation, which desorbs when the excess energy overcomes the binding energy of the molecule in the ice. Certain ice molecules, like methane, were not found to photodesorb significantly in the pure ice form, but their photochemidesorption was observed during irradiation of pure methanol ice. This mechanism could be relevant for the release of some species from ice mantles in cold regions, since the photodesorption rate of the same species seems to be negligible.

Isotopes and isotopic chemistry in the InterStellar Medium

Evelyne Roueff

LERMA, Observatoire de Paris, PSL Research University, CNRS, UMR8112, Place Janssen,
92190 Meudon Cedex, France

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The increased sensitivity and high spectral resolution of millimeter telescopes allow the detection of an increasing number of isotopically substituted molecules in the interstellar medium.

We overview and revisit the basic isotopic fractionation reactions involving D, ^{13}C and ^{15}N at the light of recent experiments and ab-initio quantum chemistry studies [1, 2, 3]. As possible consequences, we will emphasize the pathways of deuteration in moderately warm environments [4, 5] and the uncertainties in the ^{14}N/^{15}N ratio derivation of carbon and nitrogen containing molecules [3].

References

[1] Roueff E., Gerin, M., Lis D.C., Wootten A., Marcelino N., Cernicharo J., Tercero B. 2013, JPCA 117, 9959
[2] Mladenovic M., Roueff E. 2014, A&A 566, A144
[3] Roueff E., Loison J.C., Hickson K.M. 2015, A&A 576, A99
[4] Parise B., Leurini S., Schilke P., Roueff E., Thorwirth S. and Lis D.C. A&A 508, 737
[5] Favre C., Bergin E.A., Cleeves, L., Hersant F., Qi C., Aikawa Y. 2015, ApJ 802, L23

The impact of chemical networks and ice adsorption energies on protoplanetary disk models and the interpretation of their observations

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Detailed observations of protoplanetary disks provide key constraints on the initial stages of planet formation. The wealth of data collected through recent space missions (e.g. Spitzer and Herschel) and ground-based facilities (e.g. VLT and ALMA) for a significant number of disks warrants a concerted effort to interpret these multi-wavelength datasets with a coherent and standardized thermo-chemical disk model. Besides the disk geometry and dust properties such as opacities and grain sizes, chemical networks are key ingredients to such models. Adsorption energies depend on the surface properties of the solids, e.g. Whether these are bare grains, or grains with various levels of water ice coverage. Using the radiation thermo-chemical disk modeling code ProDiMo, we demonstrate the impact of varying the adsorption energies throughout then disk on the resulting 2D chemical structure of the disk and frequently studied emission line diagnostics from optical, near-, mid-IR wavelengths to the sub-mm rotational lines of CO, HCN, HCO^+, N_2H^+. This work is performed in the context of the EU FP7-project DIANA (www.diana-project.com).

Mass spectrometry at 67P/Churyumov-Gerasimenko with Rosetta/ROSINA

Martin Rubin and the ROSINA team

In August 2014 the European Space Agency's Rosetta mission arrived at 67P/Churyumov-Gerasimenko and has since then been conducting an in-depth characterization of the comet's nucleus and its coma.

In this presentation we will give an overview of the Rosetta/ROSINA mass spectrometer suite (Balsiger et al., 2007), which is designed to characterize the volatile inventory of the comet. It consists of the Double Focusing Mass Spectrometer (DFMS), the Reflectron-type Time-Of-Flight mass spectrometer (RTOF), and the COmet Pressure Sensor (COPS). The two mass spectrometers have high dynamic ranges and complement each other with high mass resolution (DFMS) and high time resolution and large mass range (RTOF). The pressure sensor COPS is capable to derive total gas densities, velocities, and temperatures.

We will review some of the key findings from almost one year of observations around the comet. This includes the striking variety in the coma: the major species H_2O, CO, and CO_2 are constantly changing in absolute and relative abundance above regions of different illumination on the comet's surface (Hässig et al., 2015; Bieler et al. 2015). Furthermore, the coma has been shown to be remarkably diverse, even at distances around 3.5 AU. Thanks to ROSINA's high resolving power and sensitivity almost all atomic and molecular species previously detected in cometary comae could already be identified (Le Roy et al., 2015) including sputtered elements of low volatility (Wurz et al., 2015) and ions (Fuselier et al., 2015). Finally, ROSINA has produced some fundamental results regarding the formation of our Solar System including the D/H ratio in the cometary water (~3 Earth's ratio; Altwegg et al., 2015) and the confirmation and quantification of the presence of molecular nitrogen (Rubin et al., 2015) and argon (Balsiger et al., 2015) in Jupiter family comets.

We will finish our presentation with a brief outlook over the coming months and touch on what we can expect following comet 67P/Churyumov-Gerasimenko through perihelion and away from the Sun again.

References

Altwegg, K., et al., 67P/Churyumov-Gerasimenko, a Jupiter family comet with a high D/H ratio, Science, 2014. 347(6220).

Balsiger, H., et al., ROSINA - Rosetta Orbiter Spectrometer for Ion and Neutral Analysis, Space Science Reviews, 2007. 128: p. 745-801.

Balsiger, H., et al., Detection of argon in the coma of comet 67P/Churyumov-Gerasimenko, submitted to Science Advances, 2015.

Bieler, A., et al., 3D kinetic and hydrodynamic modeling of the neutral Coma of Churyumov-Gerasimenko, submitted to A&A, 2015

Fuselier, S. A., et al., ROSINA/DFMS and IES observations at C-G: Ion-neutral chemistry in the coma of a weakly outgassing comet, submitted to A&A, 2015.

Hässig, M., et al., Time variability and heterogeneity in the coma of 67P/Churyumov-Gerasimenko, Science, 2015. 347(6220).

Le Roy, L., et al., Volatile inventory of comet 67P/Churyumov-Gerasimenko, in preparation, 2015.

Rubin, M., et al., Molecular nitrogen in comet 67P/Churyumov-Gerasimenko indicates a low formation temperature, Science, 2015. 348(6231).

Wurz, P., et al., Solar Wind Sputtering of Dust on the Surface of 67P/Churyumov-Gerasimenko, submitted to A&A, 2015.

Exploring our Astrochemical History with Spectral Line Surveys.

Bertrand Lefloch

The conditions for planet formation and the emergence of life is one of the key-questions in modern astrophysics.

Spectral line surveys constitute the most powerful diagnostic tool to study the emergence of molecular complexity in solar-type star forming regions. Thanks to the recent advances in instrumentation, such surveys are now routinely carried out with the major (sub)millimeter facilities on the ground. Such systematic studies have brought a new perspective on the formation of complex organic molecules. I will review the main results recently obtained in the domain. I will discuss the perspectives offered in this context by the advent of ALMA and NOEMA.

Lack of aggregation of guest molecules on ice nanoparticles

Juraj Fedor

It is believed that in outer space molecular ice particles (water ice in particular) represent “sponges” where guest molecules are adsorbed and meet other molecules yielding reactions, often assisted by high energy radiation. One factor will strongly influence efficiency of such ice-assisted synthesis: the mobility and migration of guest molecules on the particle surface itself. The fact whether molecules form aggregates prior to the triggering radiation event, can result in a dramatically different outcome of the subsequent reaction. We have found that multiple molecules adsorbed on a surface of ice nanoparticle prefer to stay isolated and do not form aggregates in spite of their initial proximity. This is in strong contrast with their behavior on the surface of argon nanoparticles, where they coagulate very efficiently. These results follow both from the laboratory experiment where nanoparticles are mimicked by cryogenic clusters, and from molecular dynamics simulations.

High−Energy Chemistry of Formamide: A Unified Mechanism of Nucleobase Formation

Martin Ferus

The coincidence of the late heavy bombardment period and the emergence of terrestrial life about 4 billion years ago suggests that extraterrestrial impacts could contribute to the synthesis of the building blocks of the first life-giving molecules. We simulated the high-energy synthesis of nucleobases from formamide during the impact of an extraterrestrial body. A high-power laser has been used to induce the dielectric breakdown of the plasma produced by the impact. The results demonstrate that initial dissociation of the formamide molecule could produce a large amount of highly reactive CN and NH radicals, which could further react with formamide to produce adenine, guanine, cytosine, and uracil. Based on GC-MS, high-resolution FT-IR spectroscopic results as well as theoretical calculations we present a comprehensive mechanistic model, which accounts for all steps taking place in the studied impact chemistry. Our findings thus demonstrate that extraterrestrial impacts, which were an order of magnitude more abundant during the late heavy bombardment period than before and after, could not only destroy the existing ancient life forms, but they could also contribute to the creation of biogenic molecules.

Contributed Speakers

Cyanomethanimine and formamide formation routes in the interstellar medium from electronic structure and kinetics calculations

Dimitrios Skouteris[1], Fanny Vazart[1], Camille Latouche[1], Vincenzo Barone[1],
Nadia Balucani[2], Cecilia Ceccarelli[3]

[1]Scuola Normale Superiore, 56125 Pisa, Italy
[2]DCBB, Università degli Studi di Perugia, 06123 Perugia, Italy
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In this contribution, new insights into the formation of interstellar cyanomethanimine and formamide, two molecular species of great relevance in prebiotic chemistry, are provided by electronic structure and kinetic calculations for the reactions CN + CH_2=NH and NH_2 + H_2CO.

E-C-cyanomethanimine has been recently identified in Sgr B2(N) in the Green Bank Telescope (GBT) PRIMOS survey by P. Zaleski et al. [1] and no efficient formation routes have been envisaged so far. At the moment, the principal astrochemical databases for molecular formation routes in the interstellar medium (UMIST12, OSU2009 and KIDA) do not include any pathway for this species or its isomers. Because of the lack of gas-phase routes, Zaleski et al. suggested that “a radical chemistry formation route … could occur in interstellar ices”. In this contribution we demonstrate, instead, that the reaction between two widely diffuse species, that is cyano radical and methanimine, can easily account for cyanomethanimine formation under the characteristic conditions of interstellar clouds. According to our calculations [2], indeed, the CN + CH_2=NH reaction is characterized by a rate coefficient in the gas kinetics range, even under the extreme conditions of density and temperature typical of cold interstellar clouds. We recall that cyanomethanimine is an important species in the context of prebiotic chemistry, essentially because of its role as an intermediate toward adenine formation [3]. Since the dimerization of HCN to cyanomethanimine was already proved to be a difficult step in the absence of liquid water [4], the reaction investigated here can be regarded as a potential shortcut toward the formation of adenine in extraterrestrial environments that allows avoiding the bottleneck of HCN dimerization [5].

Formamide has been detected a long time ago in the direction of Sgr B2 [7]. A systematic search of this molecule has been recently achieved with the IRAM 30-m telescope [6]. In that study formamide was detected in five (IRAS 4A, IRAS 16293, SVS13A, Cep E, and OMC-2) objects, while it was not detected in other colder sources devoid of hot corinos [6]. This was explained by invoking that NH_2CHO *(i)* forms in the gas phase at temperatures above $\sim$ 100 K, and/or *(ii)* forms predominantly on the icy mantles of dust grains at low temperatures, and subsequently sublimates into the gas-phase when the temperature in the inner regions rises [6].

The reaction NH_2 + H_2CO has been already considered and disregarded as a possible formamide formation route by Garrod et al. [8] who estimated an entrance barrier of ca. 1000 K. Our calculations at the CBS-QB3 level, instead, demonstrate that this reaction is not characterized by a barrier in the entrance channel. Preliminary results show, rather, that there is an exit barrier in the channel leading to NH_2COH + H slightly above the reactants asymptote. The presence of such a barrier would prevent a significant NH_2COH formation at 10 K, but not at 100 K, thus explaining the observation by Lopez-Sepulcre et al. [6].

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Using the Tools of Next-Generation Radio Astronomy to Understand Chemistry in the Universe

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Chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy is a powerful technique for molecular detection and characterization. One of the strengths of this technique is the ability to analyze complex mixtures quickly and unambiguously. This capability is exploited utilizing a method called broadband reaction screening. Chemical reactions in an electric discharge are monitored with broadband rotational spectroscopy, and the products are studied in the context of astrochemistry. Because of advancements in high-speed digital signal processing with increased data throughput astrochemistry is currently experiencing an emerging synergy between broadband laboratory spectra and broadband radio astronomical survey spectra. The availability of high quality radio astronomy survey spectra is expected to dramatically increase in the coming years, which in turn should provide the impetus for moving beyond the traditional “targeted search” model and instead focus on “reaction product screening”. Since the two techniques characterize molecules in the same fashion, by their rotational spectra, directly comparing both types of broadband spectra may lead to a better understanding of the complex chemistry that occurs in the interstellar medium.

Cosmic anions in the laboratory

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The molecular diversity of cold interstellar space has been recently enriched with the detection of anions, C_4H^-, C_4H^-, C_8H^-, C_3N^-, C_5N^-, and CN^-, all linear carbon chains (*1-7*). The circumstellar envelope of the evolved carbon star IRC +10216 is the only object so far in which all of them have been identified. The anion to neutral abundance ratio derived from astronomical observations of this source ranges from 10^{-4} to 0.5 depending on the species (*8*). Electron attachment onto neutral counterparts is considered as the main formation mechanism of medium-size and large anions whereas the small CN^- anion could be the product of C_x^- + N reaction. However, only a few chemical pathways leading to the formation or to the destruction of anions have been investigated so far. Experimental studies of the kinetics, products and branching ratios of reactions involving these species are required to assess precisely the production and destruction chemical routes. In our laboratory, we have explored the reaction of CN^- and C_3N^- with cyanoacetylene HC_3N over the 50-300 K temperature range in uniform supersonic flows using the CRESU (French acronym standing for Reaction Kinetics in Uniform Supersonic Flow) technique. Cyanopolyynes such as HC_3N are abundant in circumstellar envelopes of carbon rich stars, peaking at 1 ppm. The results show that the CN^- + HC_3N reaction contributes directly to the growth of larger anions (*9*) whereas C_3N^- + HC_3N does not. The investigation is currently extended in the laboratory to other anions through the synthesis of adapted molecular precursors. The development of a versatile selected anion source, which will be combined with the CRESU apparatus, is also presented.

Acknowledgments

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Reactive and rotational state-changing collisions of negative ions at low temperature

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Cryogenic radiofrequency ion traps [1,2] have become important tools to understand the collisional properties of cold molecular ions as they exist in interstellar molecular clouds. There, the recently detected carbon chain anions [3,4] are expected to contribute or even play an important role in the growth of large organic molecules. To gain insight into the abundance of these carbon chain anions, a detailed analysis of absolute photodetachment cross sections [5,6] and possible chemical reaction channels is indispensable. Furthermore, to understand the branching between internal cooling by radioemission, the astronomical observable, and inelastic quenching collisions, information on the elementary collision steps are needed.

Recently, we have investigated reaction rates for reactions between hydrocarbon chain anions and molecular hydrogen [7]. The measurements have been performed in a cryogenic 22-pole radiofrequency ion trap, which allows us to study negative ions for hundreds of seconds and search for very slow ion-molecule reactions. The carbon chain anions C_n^- (n=4,6) and C_nH^- (n=2,4,6) were found not to react with H_2. To test the influence of the measured upper limits on the evolution of anions in dense interstellar clouds an astrochemical model calculation was performed.

We have also studied absolute rate coefficients for the rotationally inelastic collision of hydroxyl anions and their deuterium-containing counterparts upon interaction with cold neutral helium atoms [8]. The OH^- and OD^- anions in the excited rotational state J=1 are selectively depleted by a photodetachment laser tuned below the electron affinity of the neutral. By monitoring the depletion as a function of the detachment laser intensity and the helium density the absolute rate coefficients for rotational inelastic scattering have been determined. The rate coefficients for both isotopologues were found to be very similar. To understand this we have performed ab initio quantum scattering calculations for both anions using the time-independent quantum coupled-channel method. Experiment and quantum scattering theory show excellent agreement without adjustable parameters. The two rates were explained by a thermal average over many quantum scattering resonances that incidentally lead to very similar values at the temperature of the trapped ions in the experiment. This approach may be also extended to carbon chain anions.

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Constraints on CH_3OH formation from the 4.67 um solid CO band towards Young Stellar Objects

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Abstract

CO is the second most abundant molecular species in the Universe, so the study of its bands present in observed astronomical spectra is important to characterize the chemical and physical properties of different astrophysical environments. The prominent CO-stretch band commonly observed in icy sources towards Young Stellar Objects (YSO) consists of three different components (Pontoppidan et al. 2003). This reflects the diversity of molecular environments of CO in the ice mantles. The broad 'red component' (2136 cm^{-1}) is generally attributed to solid CO mixed in a hydrogen-bonded environment. Since water is the dominant molecular species found in ice mantles, a mixture of CO with water was for a long time considered responsible for this component, although methanol is also candidate (Sandford et al. 1988; Tielens et al. 1991). Laboratory experiments showed, however, that it is not possible to reproduce the observed red component with $CO:H_2O$ mixtures without producing a shoulder at 2152 cm^{-1} due to dangling OH bonds, which has never been observed in astronomical spectra. Alternatively, Cuppen et al. (2011) showed that mixtures containing only CO and methanol can reproduce the width and position of the astronomically observed red component without the appearance of the 2152 cm^{-1} band. In order to expand this proposition, the present study compares laboratory spectra of $CO:CH_3OH$ mixtures to high-resolution observed spectra of the massive YSO GL7009S and of the low mass YSO L1489. This allows for accurate band profile fits of both the ^{12}CO and ^{13}CO ice bands. We find that the spectra of both sources can be fitted with CO mixed with methanol, while respecting the profiles and depths of other methanol bands taken as constraints. Our results also suggest the presence of a gradient in $CO:CH_3OH$ concentrations in the grain mantles.

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Quantum Mechanical Contributions in the Study of Ice-Based Astrochemical Problems

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The existence of cosmic molecules is of great relevance due to their connection with the chemical evolution steps occurring in the universe [1,2]. A crucial aspect of this chemical evolution is given by reactions occurring on or in cosmic ices. The current knowledge of the chemical role played by these ices is mostly based on spectroscopic observations, helped by laboratory experiments and astrochemical models. This combination has been fruitful to obtain important information, like the chemical activity of an ice with a given composition [3]. However, this approach cannot provide atomic-scale information such as the precise mechanistic steps and quantitative energetic data of the reactions, or the exact role played by the icy particles. This is a serious limitation to fully understand the basic physical and chemical steps that lead to the chemical complexity in space. This information gap, however, can partly be filled in by using theoretical calculations based on quantum mechanical approaches [4]. In this contribution, examples on how these theoretical calculations can contribute to ice-based cosmochemical studies in both rationalizing puzzling experimental results as well as predicting possible reaction channels will be presented. Here, results obtained from simulations devoted to the formation of H_2CO and CH_3OH through H additions to CO on water ice nanoparticles [5] will be shown, and the fruitful interplay between theory and experiment will be demonstrated showing results focused on the formation of formaldehyde-derivatives in water-dominated interstellar ices [6,7].

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MATRIX ISOLATION PHOTOCHEMICAL STUDIES OF CORONENE/WATER COMPLEXES: NEW INSIGHTS INTO THE ASTROCHEMISTRY OF NEUTRAL PAHS.

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Matrix isolation FTIR and UV-visible spectroscopies have been used to study the photo-reactivity of coronene with water molecules at low temperatures in argon matrices and in solid water ices. Comparison of calculations with experimental results obtained in water-doped argon matrices have allowed the identification of several $(C_{24}H_{12})_x(H_2O)_y$ complexes. Photochemical reactions of coronene with water are observed both in amorphous water ices and in water-doped argon matrices, leading to the formation of oxygenated molecules (quinones and alcohols).

Glycine becomes chiral by grain-surface reactions at low temperatures

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Glycine (NH_2CH_2COOH: d_0-Gly) is a representative achiral amino acid. However, if one of the carbon-bound hydrogen is replaced with deuterium (D), it becomes chiral deuterated glycine ($NH_2CHDCOOH$: d_1-Gly). Since chiral glycine is a possible catalyst for amplifying an enantiomer excess of some chiral molecules [1], it may be related to the origin of homochirality on the Earth. In the present study, we performed laboratory experiments on the formation of chiral d_1-Gly by surface reactions of d_0-Gly with D atoms at low temperatures.

All experiments were performed in an ultra-high vacuum reaction chamber equipped with an atomic source and an organic effusion cell. We continuously codeposited d_0-Gly with D atom onto a reaction substrate (~10 K). After the codeposition, the sample was warmed up to room temperature and extracted from the substrate by H_2O. The extracted sample was analyzed by using a high-resolution mass spectrometer with the mass resolution of ~70,000 at $m/z = 200$.

Figure 1 shows mass spectra (m/z ~ 77) of d_0-Gly in the positive ion mode before and after the reaction with D atoms. After the reaction, the peak intensity of $C_2H_4DNO_2$, which is equivalent to $NH_2CHDCOOH$, significantly increased, while that of $C_2H_5{}^{15}NO_2$ and $^{12}C^{13}CH_5NO_2$ does not. This result indicates that H-D exchange reactions occurr at 10 K. We propose the following reactions for the H-D exchange:

$$NH_2CH_2COOH + D \rightarrow NH_2CHCOOH + HD, \quad (1)$$

$$NH_2CHCOOH + D \rightarrow NH_2CHDCOOH. \quad (2)$$

Since reaction (1) has a large activation barrier of 23.4 kJ mol^{-1} [2], it does not easily proceed thermally at low temperatures. It is therefore reasonably considered that this reaction proceed through quantum tunneling.

Chiral molecules have never been observed toward any sources, and moreover, their formation was not confirmed in laboratory experiments at ~10 K. The present results imply that d_1-Gly is one of the primordial chiral molecules in space.

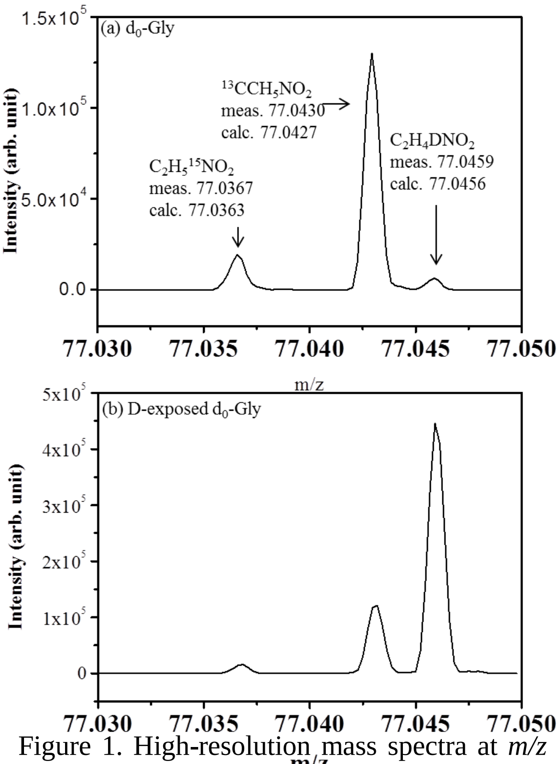

Figure 1. High-resolution mass spectra at *m/z* ~ 77 of (a) d_0-Gly and (b) d_0-Gly exposed to D atoms.

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Vacuum ultraviolet spectroscopy and photochemistry of interstellar and prebiotic molecules

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For many years, our group has been investigating the VUV spectroscopy and photochemistry of medium-sized molecules of astrophysical and prebiotic interest. Synchrotron radiation has been used mainly as photoexcitation light source. References [1-8] give the most significant publications in the last three years in this context. We are measuring absolute absorption cross sections in the VUV at room temperature, and as a function of temperature if necessary for the respective astrophysical application. Furthermore, the elementary processes following photoionization are studied in depth using photoionization mass spectrometry as well as electron/ion coincidence techniques in combination with velocity map imaging. State-of-the-art quantum calculations are performed to interpret the measurements. An aerosol source for reactive and thermo-labile compounds has been developed too since many bigger molecules of astrophysical or biological importance are not easily vaporized [9].

Very recently, we have studied acetyl cyanide ($CH_3C(O)CN$), sometimes called pyruvonitrile [1], and aminoacetonitrile (NH_2CN_2CN) [under review], which are key compounds for the prebiotic chemistry occurring in interstellar space. We present results from our last year's measurement campaigns on these compounds (cf. Fig. 1). NH_2CN_2CN is a direct precursor of glycine and has been detected in Sgr B2(N) in 2008. $CH_3C(O)CN$ has not been detected yet in astrophysical objects but its formation in the ISM is likely. Such medium-sized molecules give us insight into the functioning of astrophysical objects because of the chemical network they constitute. Basic UV and VUV photophysical data are needed in order do understand and model their chemical evolution.

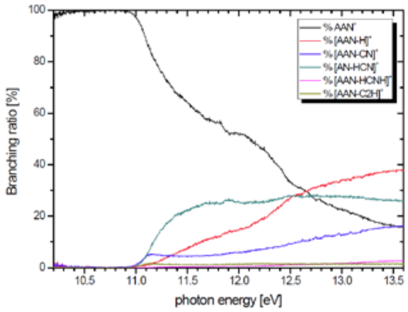

Figure1.
Branching ratios of five different dissociative ionization reactions of aminoacetonitrile (Loss of H, CN, HCN, HCNH and C_2H). Using high level quantum chemical calculations, the chemical structures of formed neutral and ionic fragments have been determined as will be shown.

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Experimental and theoretical research on selected families of astrochemically significant isomeric molecules

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Quite a number of structural isomers, chemical compounds containing identical atoms but connected to one another differently, are already known to be present in the interstellar medium and many more such families are likely to be found. Molecules having the same stoichiometry and very different thermodynamic stabilities may coexist within the same gas cloud, sharing one or more precursors and/or synthetic pathways, as often illustrated by the example of interstellar hydrogen cyanide HCN and hydrogen isocyanide HNC [1], where the dissociative recombination of $HCNH^+$ is an important common source of both species. Investigating families of structural isomers should contribute to our understanding of astrochemical processes, may promote the assignment of thus far unidentified spectral features, and may point to potential astro-molecules.

A brief discussion of selected examples, based on our quantum-chemical predictions and photochemical experiments, will be given.

1) The cyanoacetylene (HC_3N) family. Three isomers of this family have been detected in space. Four have been observed in laboratory experiments [e.g. 2, 3]. However, five are theoretically predicted [4]. The fifth isomer, cyanovinylidene CC(H)CN, a potential interstellar species, remains elusive [5].

2) The cyanodiacetylene family (HC_5N). A total of 26 isomers have been theoretically investigated. Of the seven most stable isomers [6], four are expected to absorb strongly in the infrared and have indeed been found via IR spectroscopy in cryogenic (noble gas matrix) experiments [7, 8]. None of these, apart from HC_5N, have thus far been detected in space. Quantum chemical predictions for rotational and vibrational spectroscopy are available [9].

3) The methylcyanoacetylene family. Quantum-chemical investigations indicate a family rich in structural isomers. Cryogenic, photochemical experiments are under way. To date, two isomers, CH_3C_3N (methylcyanoacetylene) and $H_2C_3(H)CN$ (cyanoallene), have been detected in interstellar gas clouds.

4) The HMgNC / HMgCN pair. Both MgNC and MgCN are known astrochemical molecules. Following our *ab initio* predictions of rotational constants and electric dipole moment [10], hydromagnesium isocyanide (HMgNC) was subsequently detected by Cabezas et al. [11] in the circumstellar shell of IRC +10 216.

5) The H_2NCS^+ family. Both HNCS and NCSH have been found in dense interstellar clouds. Cations of the [H,H,C,N,S] stoichiometry are supposedly their direct precursors. We addressed the problem of the interstellar synthesis of such ions and have provided a set of spectroscopic parameters [12, 13] of value to relevant astronomical searches.

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Wing-Fai Thi

The interplay between dust grain charging and gas-phase ionization fraction.

Dust grains can be important charge carriers in dense molecular regions. The grain charge distribution and the gas-phase ionization fraction are thus intimately linked. The grain charging physics is in itself complex and most gas-phase chemical models assume a limited range in the grain charges: the grains are mostly neutral, single positively-charged or singly-negatively charged. The limits on the charges are not compatible with the presence of large grains (with radii larger than 1 micron) in protoplanetary disks or in the densest parts of molecular clouds where evidences of grain growth have be found. Here I present a new gas-phase chemical model that couples the full grain charging physics and the gas-phase reactions. In this model there is no restriction on the amount of (positive or negative) charges on a grain. At the same time the rates of charge-exchange reactions with gas-phase electrons and ions are computed to be consistent with the actual grain charges. Charge exchange reactions and freeze-out desorption of PAHs have also been incorporated. The new implementation has been included in the ProDiMo code, which is designed to model the physics and chemistry of protoplanetary disks. Ionization fraction is an important disk characteristic, which controls the efficiency of the coupling of the magnetic field to the gas, driving the so-called Magneto-Rotational-Instability possibly at the origin of the large scale turbulence in disks.

WG3 UV and X-ray photochemistry

Hard X-rays irradiation of interstellar silicate analogs

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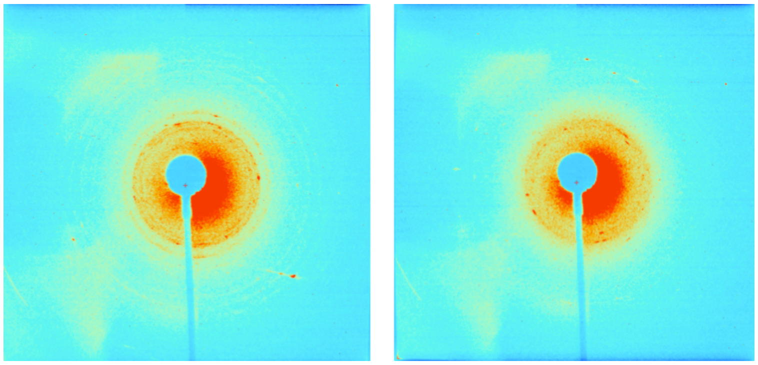
ABSTRACT

We have performed experiments on silicate dust grains using hard X-ray irradiation at the European Synchrotron Radiation Facility. Our goal is to simulate the X-ray photochemistry of dust during their life in diverse inter- and circum- stellar environments. The coherent, high flux X-rays provided by the synchrotron allow us to simulate cosmic fluences in a matter of minutes (a function of the selected energy and spot size) and in-situ tests allow us to examine the morphology and structural changes of dust at room temperature via X-ray diffraction (XRD). These experiments aim to discover possible non-thermal processes in dust grains and preliminary results from this analysis will be presented.



Laboratory evidence for isotope effects of surface processes

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Several processes concern the physics and chemistry at the surface of cosmic dust grains: sticking and accretion, diffusion and reactivity, formation of new species and desorption. Isotope effects turn out to play a role in all those processes. Over the last ten years, using the FORMOLISM set-up [1], our group carried out experiments that shed light on many isotope effects occurring at the surface of dust grain analogues at low temperatures. We showed that the sticking of H, D, HD, H_2, and D_2 on silicate behaves the same as on amorphous water ice. The sticking coefficient decreases with gas temperature, and is dependent on the mass of the impactor. We also performed temperature-programmed desorption (TPD) experiments in various proportions of binary layered CD_3OD-H_2O and CH_3OH-D_2O ices to show the rapid H/D transfer between the two species above 100 K (another group showed the same result by using the FT-RAIRS technique [4]). We then determined the different desorption energies of H_2, HD, and D_2 on compact water ice and emphasized the isotope segregation effect in mixtures of the three isotopologues of molecular hydrogen [5, 6]. The talk ends with some suggestions for future research.

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Water deuterium fractionation in the warm inner regions of solar-type protostars

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Water plays a key role in many astrophysical environments (star-forming regions, outflows, prestellar cores, comets, asteroids, …) as well as for the emergence of life as we know it. Its detection in the inner regions of low-mass protostars raises the question whether this is similar to the water that is incorporated into comets and asteroids that may deliver it to Earth-like planets. The water deuterium fractionation is very helpful to understand how it forms and evolves. For example, Cleeves et al. (2014) recently showed that a contribution of water formed in the primordial cloud is necessary to explain the HDO/H_2O ratio of the terrestrial oceans. Observations of the deuterated and non-deuterated forms of water at an early stage of star formation may therefore potentially be an important tool to describe the origin of water on Earth.

We here present recent interferometric measurements of the distribution and deuteration of water on Solar System scales. During the last few years, a few HDO and $H_2{}^{18}O$ lines were observed in the inner regions of Class 0 protostars with interferometers (Jørgensen & van Dishoeck 2010, Codella et al. 2010, Persson et al. 2012, 2013, 2014, Taquet et al. 2013), which enables estimates of the HDO/H_2O ratios. Our recent detection of D_2O with the Plateau de Bure interferometer towards the low-mass protostar NGC1333 IRAS2A leads to a surprisingly high D_2O/HDO ratio compared with the HDO/H_2O ratio (Coutens et al. 2014). These results contradict the predictions of current grain surface chemical models and indicate that either an ingredient is missing in our understanding of the surface deuteration process or that both sublimation of grain mantles and water formation at high temperature ($T > 230$ K) take place in the inner regions of protostars. We also present the first results of an ALMA Cycle 2 program (PI: A. Coutens) that targets several HDO, $H_2{}^{18}O$ and D_2O lines at a spatial resolution of ~0.3" (40 AU) toward the nearby protostellar binary IRAS 16293-2422. These observations will especially reveal if the high D_2O/HDO ratio derived in NGC1333 IRAS2A is specific to this source or common among low-mass protostars.

Experimental constraints on HDO formation
- High- and low-temperature studies -

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The ratio between singly deuterated water, HDO, and regular water, H_2O, is often used as a tracer in the quest for the origin of water on Earth. Whether the delivery of water to our planet is brought about by celestial bodies or through hydrous minerals in the crust, the origin of water and its isotopologues lies in the interstellar medium. The surface formation of regular water, occuring on dust grains in dense molecular clouds, has been widely studied experimentally and theoretically over the past decades [1, 2, 3, 4, 5, 6]. The current surface reaction network consists of 17 reactions. Upon including not only hydrogen, but also deuterium, this number increases to about 40, since cross reactions between pure hydrogenation and deuteration of O, O_2, and O_3 need to be taken into account. This poses serious restrictions on the experiments that can be performed, be it quantitatively or qualitatively. Therefore, we chose to study two specific processes within the framework of HDO formation.

The first concerns the thermally induced proton/deuteron exchange in mixed amorphous H_2O:D_2O ices [7]. These ices have been monitored through the change in intensity of characteristic vibrational bending modes of H_2O, HDO, and D_2O with time and as function of temperature (90-140 K). With this non-energetic detection method we find a significantly lower activation energy for H/D exchange than previously reported, rendering the process relevant on interstellar timescales. Furthermore, proton/deuteron swapping also occurs in ice mixtures of water with other hydrogen bonded molecules, in particular on the OH and NH moieties.

The second process we studied deals with the low-temperature (15 K) surface reactions between water and hydroxyl radical isotopes. The reactions R1, $H_2O + OD \longrightarrow OH + HDO$, and R2, $D_2O + OH \longrightarrow OD + HDO$, are important cross links between the H- and D-atom addition schemes. Moreover, hydroxyl radicals are known to play role in surface chemistry, not only as intermediate species in the solid state formation of water, but also provoking abstraction reactions in the framework of complex hydrocarbon molecules [8]. We find that reaction R1 is more efficient than reaction R2 by a factor of ~ 5.

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Nitrogen fractionation in the cold pre-stellar gas

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In our Solar System, the $^{14}N/^{15}N$ abundance ratio shows large variations when measured in different materials and N-bearing molecules. Conspicuous nitrogen “isotopic anomalies” have been measured in comets, and the nitrogen isotopic ratio of the Earth atmosphere is itself larger than the recognised pre-solar value by almost a factor of two. Measurements of $^{14}N/^{15}N$ ratio in dense star-forming cores were obtained from abundant N-bearing species such as N_2H^+, NH_3, CN, HCN, and HNC, and the results are still puzzling. In particular, no chemical models have been able so far to reproduce the low ^{15}N fraction found in N_2H^+. Recently, $^{14}N/^{15}N = 1000 \pm 200$ has been measured in N_2H+ toward L1544, a prototypical pre-stellar core which has well constrained density and temperature radial profiles. This conspicuous ^{15}N anti-fractionation was revealed by IRAM 30m observations and resulted from a new determination of the main isotopologue columns density based on non-LTE modelling and revised $N_2H^+/p\text{-}H_2$ collision data.

Posters

Challenges to model gas-phase interstellar chemistry

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In the study of interstellar gas-phase chemistry we face the same problem we found in combustion studies: the energy distribution of the intermediate reactive species is unknown. Since the time interval between collisions is very large, each collision can be treated individually, being the energy of the colliding species the same as they had as products in earlier reactions, taking into account any decay by spontaneous emission or interaction with cosmic radiation.

Recently, we have proposed a new molecular reaction dynamics method [1] which, by using simultaneously all the available Potential Energy Surfaces (PESs) for a complex chemical system, is able to model the dynamics of a reactive system avoiding the assumption of thermal equilibrium between the present molecular species. Applying this method, the program Multiple Reaction Dynamics (MReaDy) has shown to be useful to study the combustion of a hydrogen/oxygen mixture [1], while showing that the vibrational, rotational and translational energies of the intermediate OH present on a bulk mixture are not in thermal equilibrium [2], a result that has been experimentally confirmed [3].

We adapted the MReaDy code in order to study a very dilute system with scarce collisions. Although keeping the simultaneous treatment of all the molecular species present in the bulk system, the code has been modified to propagate in space the different molecules while checking for their next collisions, which are treated separately. By this way, the simulation code has two different time scales: the translation of the molecules between collisions and the rigorous treatment of each collision.

As each molecular collision is treated individually, we can use a semiclassical method to account for quantum tunnelling [4], which can play an important role in reactions at low temperatures. We stress that the intermolecular forces between reactants, that should also play an important role in the dynamics of these reactions at low kinetic energies, are already taken into account.

With the modifications referred above, the MReaDy program would be able to study the dynamics of a very dilute molecular system at low temperatures. A second step will be the additional implementation of the available PESs involving also nitrogen and carbon atoms or ions. The objective is to be able to account for the formation of small organic molecules present in the interstellar space. The MReady code has been built in a modular way so the addition of a new PESs will extend the reaction mechanism contributing to a better simulation of the overall chemical simulation.

In another step, spontaneous or induced emission will be included to account for its effect on the vibrational or rotational excitation or relaxation of the molecules in the translation period and its effect on the dynamics of the overall process. This can be accomplished by using experimental or computed data for the corresponding Einstein coefficients and the interstellar radiation spectra.

With this approach, we also will be able to study the dependence of the enrichment in the heavy isotope deuterium on the reaction conditions.

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THE IMPORTANT EFFECT OF DEUTERIUM ON THE REACTIVITY FOR THE F+HCl COLLISON *

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In this work, we have showed the effect of deuterium on the reaction dynamics and kinetics for the F+HCl reactive collision where the reaction rate decreases when changing from H to D atom. An accurate state-to-state quantum wave packet calculations of integral cross sections for collision energies up to 0.5 eV and different initial rotational and vibrational excitation, DCl(v=0, j=0-1; v=1, j=0), have been calculated. Calculations are carried out on the best available ground $1^2A'$ global adiabatic potential energy surface of Deskevich *et al.* [1]. Initial-state resolved rate constants of the title reaction have been calculated in a temperature range of 100-400 K. It is found that the initial rotational excitation of the DCl molecule does not enhance reactivity, in contrast to the reaction with the isotopologue HCl in which initial rotational excitation produces an important enhancement. These differences between the isotopologue reactions are analysed in detail and attributed to the presence of resonances for HCl(v=0, j) [2], absent in the case of DCl(v=0, j) [3]. A review will be presented for both F+HCl and F+DCl collision processes to show the isotopic effects.

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Internal energy effects in the reaction of CH_3^+ with but-2-yne: an experimental and theoretical study

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The methyl carbocation is ubiquitous in gaseous environments fed by high energy sources, such as terrestrial and planetary ionospheres, cometary comets, the interstellar medium as well as combustion systems and plasma set-ups for technological applications. It has been detected in the ISM, in the atmosphere of Titan [1] and in laboratory plasmas, with special reference to those used for methane conversion into higher hydrocarbons or for plasma-based dry reforming of CO_2/CH_4 mixtures, i.e. their conversion into value-added chemicals.[2] The reactivity of the methyl cation with several hydrocarbon molecules (CH_4 [3], C_2H_6 [4], C_2H_4 and C_2H_2 [5]) has been studied in the past, but relevant for understanding the chemical evolution of Titan's atmosphere is the study of the reactivity of CH_3^+ with methyl substituted acetylenes such as but-2-yne (C_4H_6). In the experiment that we report, the methyl cation is generated via direct photoionization with synchrotron radiation of methyl radical, formed in a supersonic beam by pyrolysis of CH_3NO_2. This generation method allows the production of the methyl cation with a controlled degree of internal excitation, thus opening the possibility to investigate the effect of internal degrees of freedom (vibrational) on its reactivity. The reaction of methyl cation CH_3^+ with but-2-yne has been investigated by using both the home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) at Trento (Italy) and the CERISES-apparatus, a GIB-MS installed on the DESIRS beamline of the synchrotron radiation source SOLEIL (France). With the first set-up preliminary results were obtained by producing the methyl cation in an electron impact ion source, hence with an uncontrolled amount of internal excitation. Conversely, the CERISES set-up permits the production of CH_3^+ from VUV photoionisation (with photon energy tuned between 9.8 and 12.5 eV) of CH_3 radicals. Absolute reaction cross-sections have been measured for this system as a function of collision energy at 10 and 12 eV photon energies. The products formation mechanisms are studied with theoretical method and energies calculated, so as to discuss the reactions pathways and the dependence on the CH_3^+ parent ion vibrational energy. All stationary points on the energy hypersurface were determined within the Density Functional Theory (DFT),[6] making use of the M06-2X functional [7] with the cc-pVTZ basis set.[8] The nature of the critical points was checked by vibrational analysis. The optimizations were followed by Coupled Cluster CCSD(T) single-point energy computations. The calculations were carried out by using the GAUSSIAN 09 system of programs.

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Dissociative Charge Transfer of interstellar Dimethyl ether and Methyl Formate in collisions with He$^+$. Experimental and theoretical study

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Ion-molecule reactions play an important role in the chemistry of planetary ionospheres and interstellar molecular clouds. Helium ions are found in the interplanetary space and have also been detected in Titan's magnetosphere and in the Earth's polar cusp region.[1] For this reason studies on collision of molecules with He$^+$ are of fundamental importance for modeling planetary and cometary atmospheres.[2] They are also important for understanding chemical processes in natural and synthetic plasmas.[2] In the experiment that we report, the dissociative charge transfer reactions are carried out with the smallest organic O-containing molecules: dimethyl ether (CH_3OCH_3), DIM and methyl formate ($HCOOCH_3$), MF. The former molecule (DIM) is particularly important in hot cores [3], while the latter (MF) is another important specie observed by radioastronomy in hot cores and it is very abundant in star forming regions.[3] It is considered to play a key role in understanding the origin of life because it leads to the synthesis of bio-polymers.[4] The reactions of helium cation He$^+$ with dimethyl ether and methyl formate have been investigated by using the home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) apparatus in Trento (Italy). Using this set-up absolute cross sections and branching ratios can be measured as a function of the collision energy in the hyperthermal energy range (i.e. from about 0,5 to 7 eV). In addition both the charge transfer processes and the fragmentation dynamics have been studied with theoretical methods and preliminary results will be discussed at the meeting.

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Interaction of deuterium atoms with ammonia on oxidized graphite surface

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Singly and multiply deuterated ammonia species NH_2D, NHD_2, and ND_3 have been observed in many astrophysical sources, such as cold dense cores (10-20 K, 10^6 cm^{-3}) and cold dense interstellar clouds (10 K, 10^4 cm^{-3}) [1]. The abundances of these species in gas phase were found to be higher than the cosmic elemental D/H ratio (~ 2 10^{-5}).

We have investigated laboratory experiments for the reaction between NH_3 and D atoms on cold surfaces of dust grains analogues, mainly in the sub-monolayer regime [2]. About one monolayer of solid ammonia was pre-deposited on the oxidized graphite surface held at 10 K, and then exposed to D atoms for different exposure doses. The experiments were performed with the FORMOLISM setup using atomic and molecular differentially pumped beam-lines, mass spectroscopy and the temperature programmed desorption technique. The TPD experimental results showed the formation of three ammonia isotopologue species. Assuming a deuteration process with direct H-D substitution reactions between adsorbed ammonia species and D atoms, a simple kinetic model is developed to estimate the rate constants of the gas-surface reactions involving isotopic ammonia species and D atoms.

Identical control experiments were performed with CH_3OH+D surface reactions system, where the deuteration process is ruled by H-D abstraction-addition mechanism [3]. The deuteration process of methanol is ten orders of magnitude faster than that of ammonia.

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Radiation transport in expanding Universe: the effect of non-thermal photons on the chemistry of primordial Universe.

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Every radiative transition from an upper atomic level i to a lower level j is associated with the emission of a photon; in the early Universe, eventually this is a possible cause for spectral distortion $I_{ij}(\nu)$ to the CMB. Assuming a very narrow emission-profile, the observing frequency ν at some redshift $z < z_{em}$, is related to the rest frame frequency, ν_{ij} , of the transition $i \rightarrow j$ by $\nu = \nu_{ij}(1 + z)/(1 + z_{em})$ where the redshift at which the transition happens is labeled z_{em}. In principle these photons could have some effects on the chemistry of the primordial Universe. In the present contribution, the H_2 chemistry is investigated; to this extent the main formation channels for molecular hydrogen, namely the H_2^+ and H^- pathways, are considered separately. In particular, the photodestruction processes studied are H_2^+ photodissociation and H^- photodetachment. The cross-sections calculated by Mihajlov et al. 1997 and by Tegmark 1997 have been used, respectively.

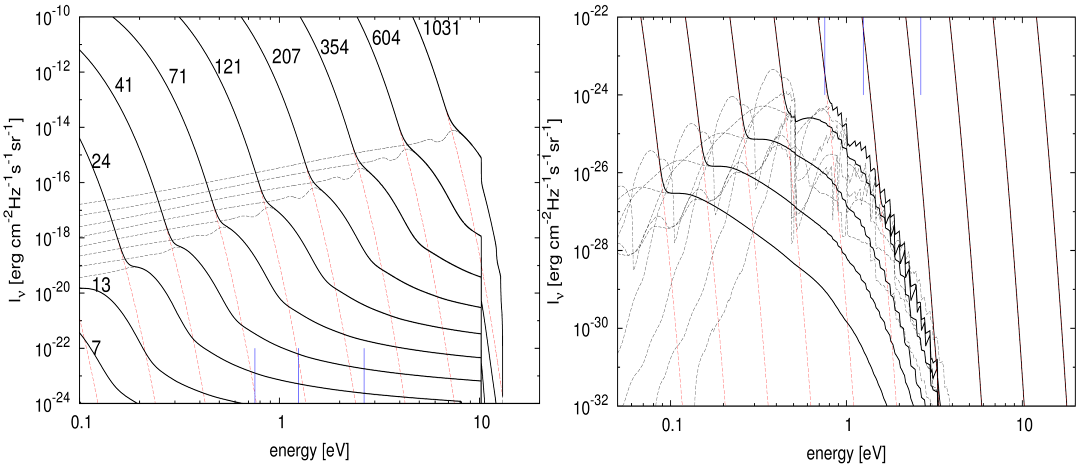

Fig. 1:
Distortion spectra used to evaluate the effect of non-thermal photons to-reaction rates. Left panel: recombination photons (from primordial H and He recombination); right panel: non-thermal derived from the radiative cascade of H_2

Using the spectra shown in Figure 1, the fractional abundances of the most relevant atomic and molecular species have been calculated implementing a time-dependent chemical model. In Figure 2 the comparison between the case of including non-thermal photons (labelled “with ntp”) and without (labelled “without ntp”) is provided. Important effects can be derived for low redshifts because of the less efficient H- channel in the presence of non-thermal photons.

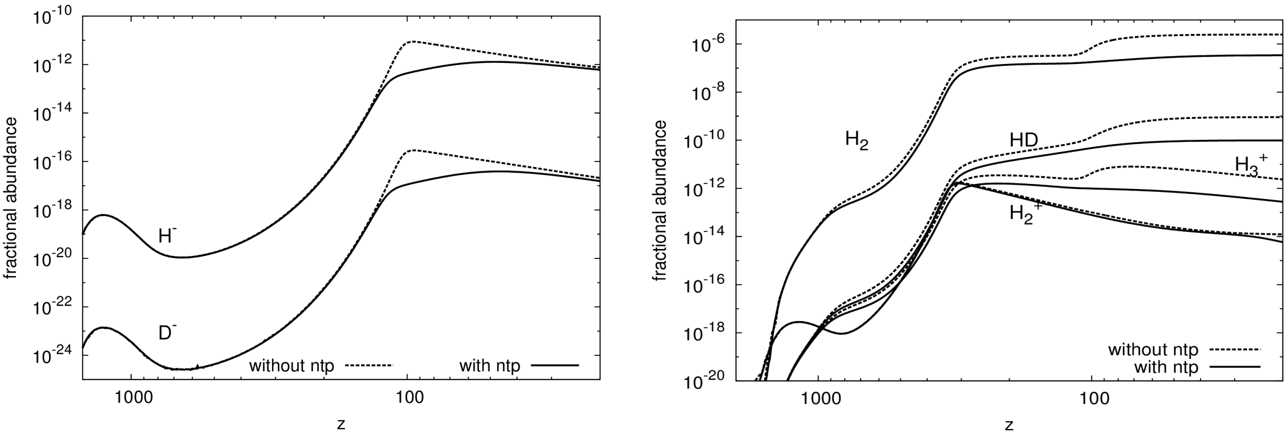

Fig. 2 : Fractional abundances of chemical species as a function of the the redshift z. The dashed curves correspond to the kinetic model in which the effect of non thermal photons has not been included; the solid curves represent the fractional abundances obtained in the presence of non-thermal photons in the chemistry.

Excitation and chemistry of interstellar hydrides

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Hydrides play a central role in astrochemistry as significant reservoirs of heavy elements. Excitation studies of interstellar hydrides deserve a particular attention because the reactive processes with the most abundant colliders (electrons, H and H_2) can compete with or even dominate the energy transfer processes. The objective of the cross-disciplinary project HYDRIDES is to address this challenging problem both theoretically and experimentally [1]. In addition to the production of fundamental molecular data, the analysis of available astronomical spectra, especially from the Herschel space telescope, is our second objective. Such studies have been so far hampered by the lack of accurate collisional cross sections and rate coefficients for the relevant species. We will present the most recent results of the project, with a special emphasis on comparisons between theoretical and experimental state-specific cross sections.

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[1] See http://ipag.osug.fr/Hydrides

The spatial distribution of methanol in the prestellar core L1689B

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Complex organic molecules (hereafter COMs) have represented a challenged to modern astrophysics since their very first detections. Nevertheless the formation of COMs has not been completely understood yet. Each new detection supposes the apparition of new scenarios and formation routes, and a new enigma for the astrochemical community. Although the first COMs were detected towards high-mass star forming regions (e.g. Cummins et al. 1986), their low-mass counterparts have shown a similar composition (Cazaux et al. 2003, for example).

Until recently, the theory for COMs formation suggests that they are synthesised on the surface of dust grains (Garrod & Herbst 2006). Simple molecules and atoms accrete onto the grains were they can be hydrogenated. Under this scenario, radicals (like HCO, CH_3 and CH_3O among others) would play a crucial role. In particular, they can diffuse on the grain surface during the protostellar warm-up (at temperatures of $\sim$ 30-40 K) and form new molecules. Finally, the content of the dust ices is released to the gas phase at temperatures higher than about 100 K. However, the detection of COMs in prestellar cores (Bacmann et al. 2012, Cernicharo et al. 2012) poses a challenge to this scenario: the mobility of radicals under the very cold temperatures typical of these objects ($\sim$ 10 K) is almost negligible. In consequence, new models and theories have arose recently (Cernicharo et al. 2012, Vasyunin & Herbst 2013, Balucani et al. 2015, Ruaud et al. 2015).

The spatial distribution of the simplest COMs, the methanol molecule (CH_3OH) is crucial for the understanding of the formation processes of COMs together with the chemical evolution of the cloud. In some of the astrochemical models published recently (e.g. Vasyunin & Herbst 2013, Balucani et al. 2015), methanol plays a crucial role in the formation of more complex constituents.

In this work we present methanol emission in the prestellar core L1689B located in the Ophiuchus molecular cloud. We have studied the spatial distribution of ten different transitions of CH_3OH. The molecular lines mapped were modelled using the radiative transfer code RATRAN (Hogerheijde & van der Tak 2000). From out best model, achieved by a χ^2 minimisation, we have derived a density and a CH_3OH abundance profiles. We discuss the implications of the derived profiles in the present work.

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Modeling carbon monoxide hydrogenation physisorbed on amorphous solid water

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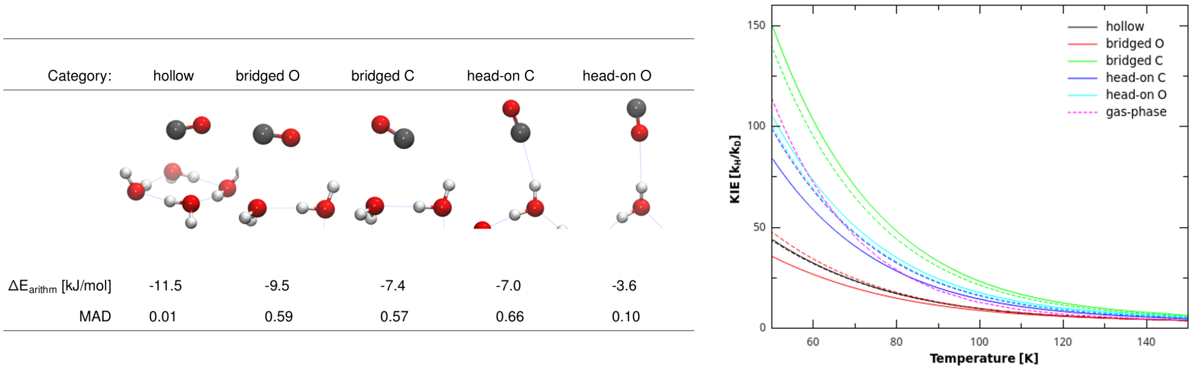
The consideration of gas-grain reactions is indispensable to understand molecular abundances in the interstellar medium (ISM).

We employed density functional theory (M08-SO/def2-TZVP) to investigate several aspects of carbon monoxide weakly bound to water clusters composed of up to eight water molecules (on a set of overall 250 structures). Categorizations have been made upon several criteria (structural analysis, adsorption energies, IBBA [1] derived partial charges). Ultimately the effect of different binding motifs on the kinetics of the first hydrogenation on a cluster with four water molecules has been calculated using transition state theory with tunneling corrections. Our results corroborate the findings of T.P.M. Goumans on a system with two water molecules [2].



Category:	hollow	bridged O	bridged C	head-on C	head-on O
ΔE_{arithm} [kJ/mol]	-11.5	-9.5	-7.4	-7.0	-3.6
MAD	0.01	0.59	0.57	0.66	0.10

Fig 1: Left: Binding modes and corresponding binding energies of CO to a cluster with four water molecules, right: temperature dependence of the KIE for the bimolecular reaction $H_g + CO_{ads} \rightarrow HCO_{ads}$ on two representative geometries of each category. “Gas phase” is a comparative analysis at UCCSD(T)-F12/cc-pVQZ-F12-level.

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NON-ENERGETIC SURFACE FORMATION OF COMPLEX ORGANIC MOLECULES

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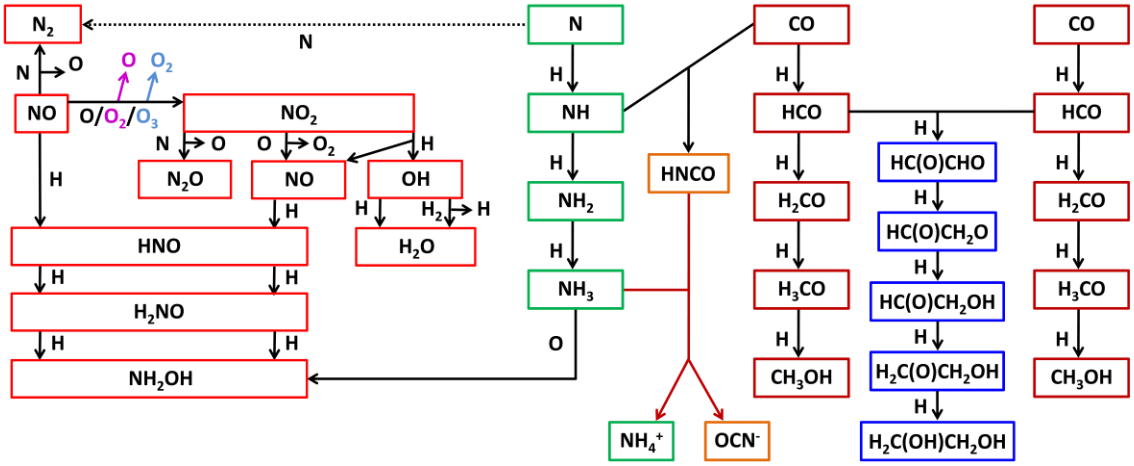
It is accepted that surface reaction mechanisms on cold interstellar dust grains initiate molecular chemistry through the formation of H_2, and likely dominate the formation of complex organic molecules (COMs; e.g., sugars and amino acids) in space [1]. For decades, surface complex molecule formation has been thought to be triggered largely by energetic processing. Here, I present the first laboratory evidence that the building blocks of sugars, fats, and proteins can be formed through non-energetic induced surface reactions under dark molecular cloud conditions. The focus is on the formation of hydroxylamine (NH_2OH), glycolaldehyde ($HC(O)CH_2OH$), and ethylene glycol ($H_2C(OH)CH_2OH$) by non-energetic surface hydrogenation of NO and CO containing ices, respectively [3-8]. These experiments aim at simulating the CO freeze-out stage in interstellar dark cloud regions, well before thermal and energetic processing become dominant. My talk reviews the most recent work performed at the Sackler Laboratory for Astrophysics in Leiden (NL) [8]. The experimentally established new reaction network is further implemented into astrochemical models to study their impact on the interstellar ice evolution under much longer timescales (10^5 yr) than possible in laboratories.



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Ab initio modeling of H_2 formation via an Eley-Rideal mechanism

COST Action 'Our Astrochemical History' CM1401
Working group 2 'surface chemistry'

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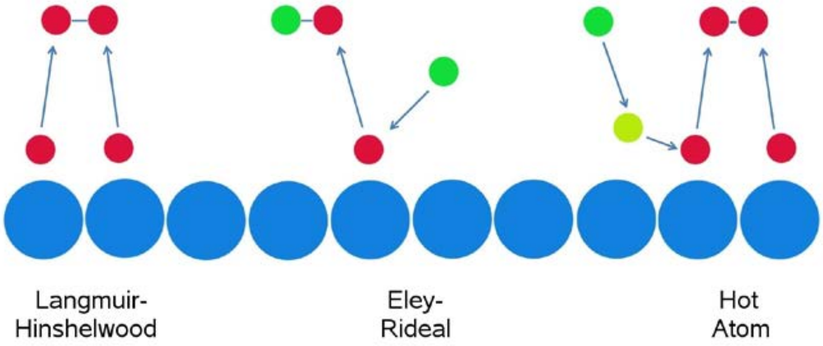
Molecular hydrogen, H_2, is one of the fundamental constituents of the universe, acting as the molecular feedstock for much of the chemistry occurring within the interstellar medium (ISM). Although gas phase models of the chemistry of interstellar clouds have been successful in explaining the abundances of some gas phase molecules, it has long been established that they cannot account for the large abundance of H_2. The general consensus of the astrochemical community is that (partly) carbonaceous interstellar dust grains assume a catalytic role in the formation of H_2 within the ISM. A variety of mechanistic models (Eley-Rideal, Langmuir-Hinshelwood, Hot Atom) exist, with the aim of elucidating the adsorption and recombination pathways of atomic hydrogen, as well as the subsequent desorption of the nascent H_2 molecule. First principles calculations have been performed in order to scrutinize the hydrogen-dust grain interaction, with a particular focus on modulating the well documented ~0.2 eV barrier associated with the chemisorption of an H atom atop a graphitic surface. As this barrier is effectively insurmountable under typical interstellar conditions ($T \leq 100$ K; $P \sim 10^{-13}$ Torr), we have investigated the potential role(s) of grain defects and surface relaxation in the H_2 formation process.



A New Experimental Approach to Determine Low-Temperature Product Branching in Multichannel Reactions: Chirped-Pulse in Uniform Flow

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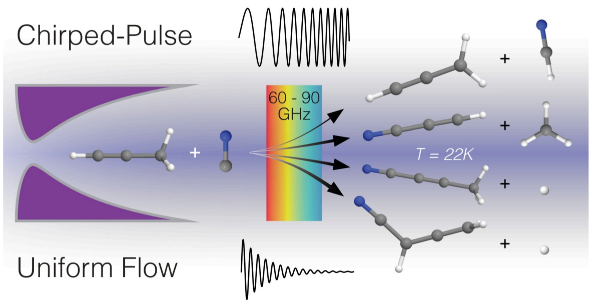
The interplay between fundamental laboratory investigations, theoretical advances, and chemical modeling has led to tremendous progress in advancing the understanding of the complex gas-phase chemistry in the outer space. Measured or calculated reaction rates are incorporated into models to identify the key pathways that control reaction outcomes. However, experimental studies often report the rate of reactant disappearance, with product identity and branching largely unknown. This limitation arises from considerable experimental challenges inherent to the quantitative detection of the full range of products of a given reaction, in particular for large polyatomic systems. To address these issues, we have developed a new approach incorporating chirped-pulse microwave spectroscopy in low-temperature uniform supersonic flows (Chirped-Pulse in Uniform Flow, C-PUF). This technique provides clear quantifiable spectroscopic signatures for polyatomic products in bimolecular or unimolecular reactions for virtually any species with a modest dipole moment. I will first illustrate the performance of the system with a few examples of photodissociation and reaction dynamics, and discuss a number of challenges unique to the application of chirped-pulse microwave spectroscopy in the collisional environment of the flow. A detailed study of the CN + C_3H_4 reaction using the C-PUF technique at 22 K will be presented eventually, for which line intensities from pure rotational spectra in the [60-90] GHz domain have been used to determine quantitatively the product branching from all the accessible reaction pathways. This work is a demonstration of C-PUF as a powerful technique for the astrochemical community.



C-PUF is used to probe quantatively all the products in the multichannel reaction CN + C_3H_4 at 22K.

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Perturbative triples correction for explicitly correlated Mukherjee's state-specific coupled cluster method

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This paper reports incorporation of the perturbative triples correction within the explicitly correlated Mukherjee's multireference coupled cluster method using the SP ansatz. In accord with the standard approximation, these corrections are not directly entered by the correlation factor amplitudes, but the explicitly correlated part of the effective Hamiltonian is included in full. The performance of the new method is tested on singlet methylene, potential curve of fluorine molecule and automerisation barrier of cyclobutadiene. It has been found that the convergence pattern of the MkCCSD(T)-F12 results with increasing basis set is improved by approximately one cardinal number, as compared to conventional MkCCSD(T). This improvement appears at the level of single and double excitations, whereas no significant impact of the explicit treatment of the electron correlation on the (T) correction has been observed, in analogy to a single-reference approach.

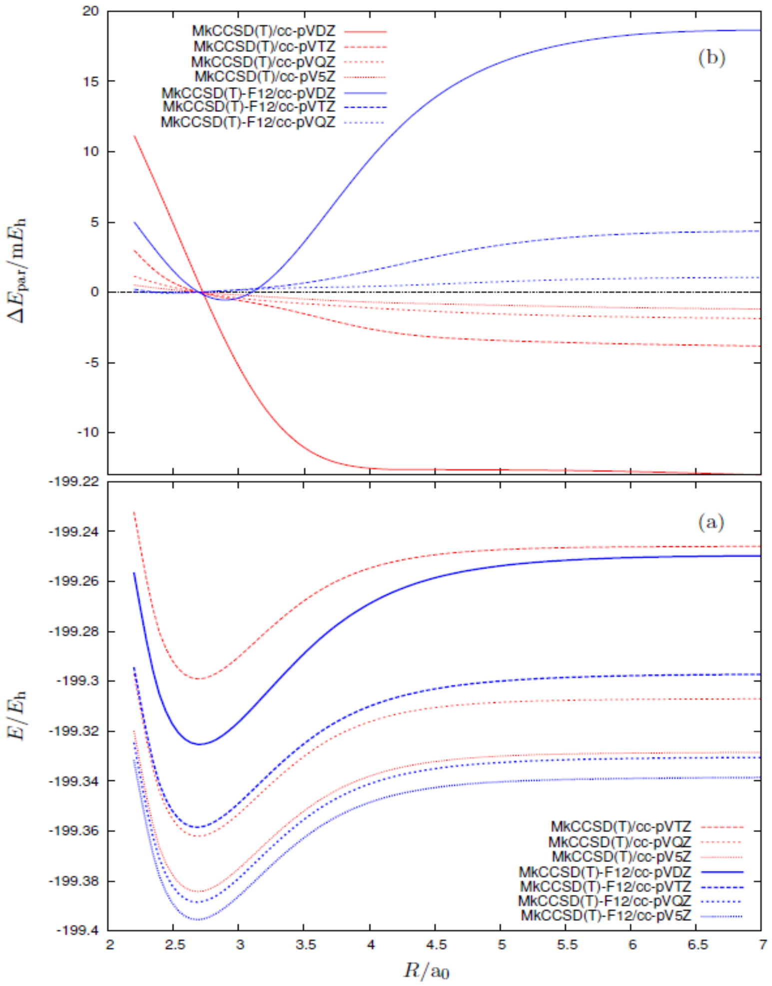

Figure 1: Potential energy curves (a) of the fluorine molecule calculated at MkCCSD(T) and MkCCSD(T)-F12 levels with cc-pVXZ basis sets using CAS orbitals. Deviations from the parallelity with respect to MkCCSD(T)-F12/cc-pV5Z curve are given in (b). $\Delta E_{par}=\Delta E_x-\Delta E_{ref}$; $\Delta E_x=E_x(R)-E_{method}(R_e)$, where "x" stands for any methods and "ref" for the reference curve.

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Improving Gas-Grain Models of Oxygen and Sulfur

Jacob C. Laas and Paola Caselli

Abstract:

Gas-grain astrochemical models have become a powerful tool for extending our understanding of various chemically-rich interstellar environments. Despite the success these models can achieve for predicting the abundances of relatively complex organic molecules, it remains a challenge to match the observed gas-phase depletions of elemental sulfur and oxygen. Furthermore, a number of recent observational studies have provided new constraints and also even hints of condensed-phase chemistry. We have begun to reconcile these shortcomings of gas-grain models using a model based on the OSU gas-grain astrochemical network. We report here on the progress that has been made and possible implications on related ice/refractory chemistry.

Ab initio study of H + CO rotation-vibration inelastic collision for astrochemical applications

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As the second most abundant molecule in the universe, carbon monoxide (CO) is rapidly becoming one of the best tracers of the astrophysical conditions. It is often not appropriate to assume local thermal equilibrium (LTE) in the dilute gas of astronomical sources. Accurate non-LTE modeling requires reliable collision rate coefficients of CO with its dominant collision partners H, H_2 and He.[1] Progress in ro-vibrational rate coefficients calculations has been slow. The difficulty of reliable H-CO ro-vibrational rate coefficients is related to the fact that HCO is a chemically bound species, in contrast with He-CO and H_2-CO that are bound only by weak Van der Waals forces. Lack of accurate three dimensional H-CO potential also blocks the availability of the accurate ro-vibrational rate coefficients.[2]

In this work, we present our new three dimensional H-CO potential[3], as shown in Figure1, which can produce multiple experimental data precisely. Based on the new potential, ro-vibrational rate coefficients for transitions of v=1-5, j=0-30 to v'<v, j' have accurately been calculated and extrapolated at the temperature range T=10-3000K. Our new rates are very different from what have recently been used in astrophysical modeling[1], as shown in Figure 2. The tests reveal that our work provides more comprehensive and accurate ro-vibrational de-excitation rate coefficient of H-CO system than any previously available data for astrophysical modeling.

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Figure 1 Two dimensional cut of three dimensional H+CO potential with CO bond fixed at r=2.1322 bohr.

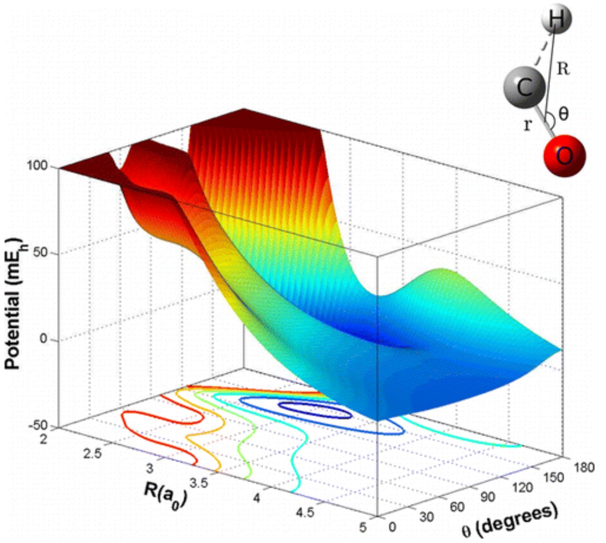
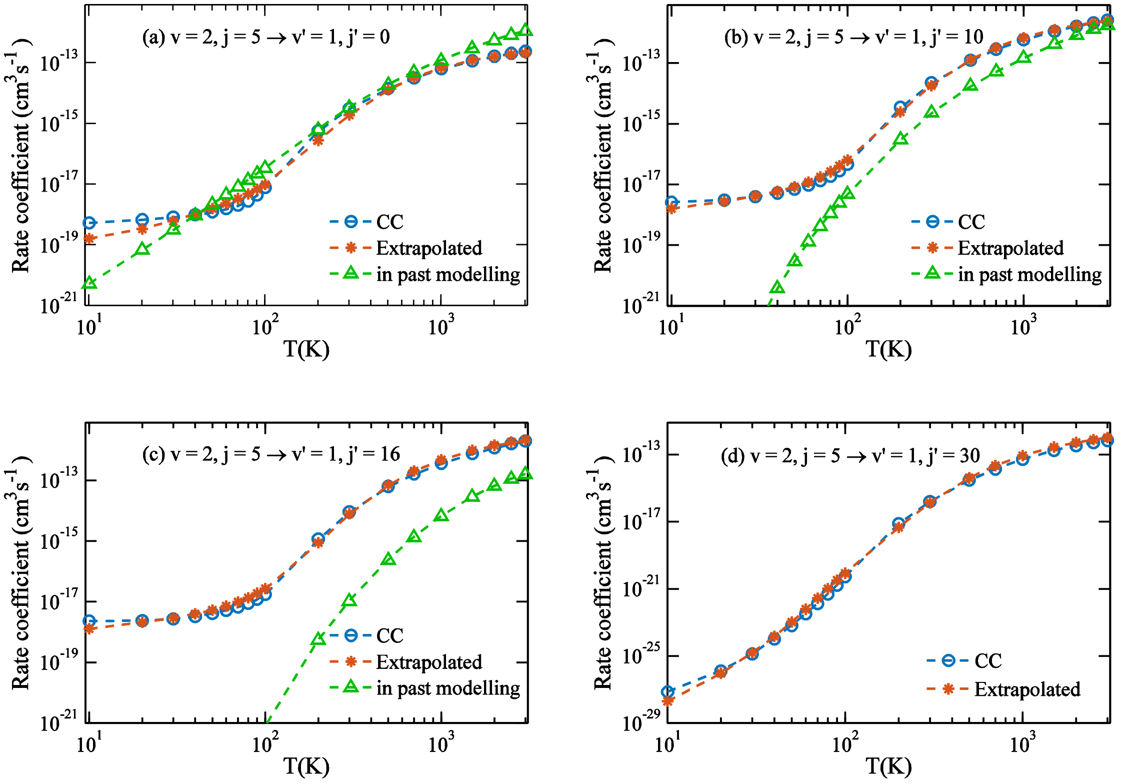


Figure 2 Examples of comparison of quantum mechanical, extrapolated rates and rates used in Thi et al. (2013)'s modeling for ro-vibrational transitions. Extrapolated rates are based on our new extrapolation method.



Review on hydroxylamine, a precursor to amino-acids

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Does life on earth come from interstellar space (IS)?

It has been recently demonstrated that part of the terrestrial water is of IS origin [1]. This raises the question whether materials like amino-acids or their pre-biotic molecular precursors could have been formed and brought to earth in the same way than water. Another question is whether these molecules were formed in the gas phase or through reactions on the surface/volume of ice-covered grains. This may then have occurred in the vicinity of proto-stellar cores or deep into a pristine dense molecular clouds at very low temperatures.

As far as bio-related molecules are concerned, chemistry with nitrogen-bearing molecules (like NH_3 and NO) is involved. I review recent experimental work showing that hydroxylamine (NH_2OH) could be formed either by surface or by volume reactions in conditions close to those prevailing in dense media. They use either electron-UV irradiation of water-ammonia ices [2] or successive hydrogenation of solid nitric oxide [3] or the simple oxidation of ammonia [4] or the reaction of ammonia with hydroxyl radicals in a rare gas matrix [5]. A step further, the synthesis of the simplest amino-acids, glycine (NH_2CH_2COOH) and L- or D-alanine ($NH_2CH_3CHCOOH$) has already been obtained via reactions in the gas phase involving NH_2OH^+ [6].

In addition to several earlier models demonstrating that the formation of all these molecules is possible in the gas phase, a new recent three-phase gas-grain chemical kinetics model of hot cores [7] shows that the results of ammonia oxidation we obtain are plausible by surface/volume reactions. Although none of the aforementioned molecules (except glycine in a sample of cometary origin) has been yet detected in the IS, they all are considered by many observers and modelers as likely targets of detection with ALMA.

A review of the present observational status will be presented and suggestions of conditions for future observations will be provided derived from the experimental constraints.

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Line emission for meteor matter: laboratory experiments and models.

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Meteors are able to contribute several components to planetary atmospheres. Metals like Cu and Fe and also lighter elements like S and Mg are evolved during the entry process at very high altitude which could not be reached by these components by other means (1). Using high power pulsed lasers it is possible to emulate the plasma emission using real meteorite samples to reproduce the meteor surface (2-4). Lines from metal elements are compared to results of meteor spectroscopy. In order to rationalize results, simple models are formulated based on flight dynamics, thermodynamics and kinetic theory. As an example, a sample of iron meteor is simulated, allowing to estimate the surface temperature, the ablation rate and the ratio of intensity of FeI lines during the entry trajectory (5,6)

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Electron-impact excitation and recombination of molecular cations

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Rate coefficients for electron-impact ro-vibrational excitation and dissociative recombination of molecular cations involved in the chemistry-modelling of the early Universe, interstellar media and planetary atmospheres are badly needed [1-3].

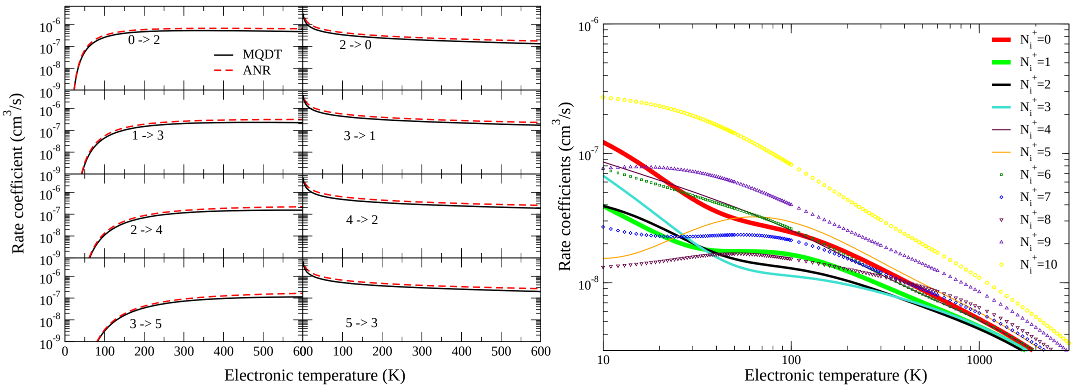

Figure 1. Rate coefficients for rotational excitation (left) and dissociative recombination (right) of vibrationally relaxed HD^+ on its lowest rotational levels N_i^+ [4].

Using the Multichannel Quantum Defect Theory (MQDT) and the R-matrix method within the Adiabatic-Nuclei Rotation (ANR) approximation, numerous data have been obtained for these reactions induced on H_2^+, HD^+ [4] – Figure 1, H_3^+, CH^+, CO^+, SH^+ and N_2^+[5]. Comparison with measurements in magnetic storage-rings (CRYRING, TSR) resulted in good agreement, and refined approaches are ongoing in view of the advent of the new generation of electrostatic devices (CSR, DESIREE).

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Neutral Na in cometary tails: a tracer of their chemical history

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Observations of comet C/1995O1 Hale-Bopp during the spring of 1997 led to the discovery of a neutral sodium tail whose origin is still not understood. Several possibilities were considered, as radiation pressure due to resonance fluorescence of sodium atoms, photosputtering and/or ion sputtering of nonvolatile dust grains and collisional interactions between micron-sized particles, though observations suggest a thermal desorption mechanism.

We propose to discussion a completely different scenario built upon chemical grounds for interpreting the origin of this sodium tail.

Based on the Gibbs energy minimization method, chemical equilibrium calculations show that sodium is trapped chemically as Na^+ during the condensation of refractory material in the protosolar nebula. In a second step, the comets parent bodies, originally composed of a conglomerate of rocks and ices, underwent a thermal heating due to radiogenic decay of short period elements at early epochs after their formation. This enabled the formation of liquid water in the nuclei, washing the Na^+ ions out of the refractory material. Once transferred to liquid water, the ionized sodium atoms acquired electrons from the forming ice, finally desorbing as neutral species with the ice sublimation.

Finally we propose that two Na reservoirs should coexist in a comet: one coming from the refractory dust, the other one from the icy matrix. Their relative importance would depend on the extent of the zone where liquid water formed within the nucleus and the time during which water remained liquid, thus favoring the Na^+ exchange between rocks and ice. These two key parameters would in turn strongly depend on the thermal history of the comet (amounts of radiogenic nuclides, orbital history, etc.). If our model is correct, the detection of Na originating from water ice would be a testimonial of the past aqueous alteration of the comet or its parent body.

Ionization Dynamics of Ammonia Dimer Studied by Methods of Quantum Chemistry

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The small ammonia clusters are believed to be present and stable in cold regions of our solar system (e.g. in atmospheres of gas giants or on the surface of comets and meteorites).[1,2] Atmospheres of planets as well as surfaces of meteorites and comets are constantly bombarded with hard ionizing radiation. We have focused on ionization of ammonia dimer as a model system for larger clusters and as a relevant system for biomolecules which contain amino group.

We have studied the structure of ionized ammonia dimer and the ultrafast processes triggered by the ionization occurring on a timescale of the tens to hundreds of femtoseconds. We employed the methods of quantum chemistry and also nonadiabatic molecular dynamics allowing for realistic description. The main conclusion is that the ionized ammonia dimer is highly unstable and decays. The intensity of decay is primarily driven by a position of the electron hole after electron removal. In the case of ground state ionization, the decay is usually preceded by intermolecular proton transfer leading to $\mathrm{NH_4^+}$ and $\mathrm{NH_2^{\cdot}}$ as a main product channel. The ionization resulting in electronically excited ions leads mainly to a formation of the $\mathrm{NH_3^+}$ and $\mathrm{NH_3^{\cdot}}$ fragments.

Acknowledgement: The support by the Grant Agency of the Czech Republic (Grants Number 13-34168 and 14-08937S) are gratefully acknowledged.

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Novel X-ray initiated processes in hydrogen bonded systems

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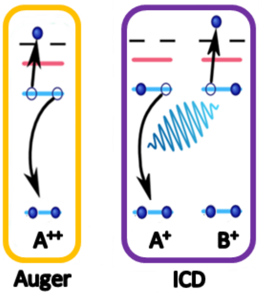
High energy radiation is routinely used in various areas of science and technology yet the ultrafast processes following the core ionization of atoms or molecules remain poorly understood. In addition to well-known Auger decay and X-ray fluorescence, new non-local relaxation processes, such as Intermolecular Coulombic Decay (ICD), were discovered only recently. In ICD, the second electron is ejected from a neighboring molecule.



In a collaboration with liquid beam photoemission experiments, a new relaxation pathway in liquid water was recently identified in our laboratory (so called PTM-CS process).[1] Here, core ionization triggers an ultrafast proton transfer. The subsequent Auger or ICD process then takes place for intermediary Zündel-like structure $[\mathrm{HO}^{*}\cdots\mathrm{H}^{+}\cdots\mathrm{H_2O}]$. We have shown that the same process takes place also in liquid hydrogen peroxide solution.[2] The PTM-CS process seems to be sensitively controlled by the hydrogen bond strength which we demonstrated both experimentally and theoretically in the case of solvated ammonia and glycine.[3] Since different relaxation pathways result in different transient reactive species, our findings may lead to a better understanding of biomolecular radiation damage.

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Tunneling in Astrochemically Relevant Systems: the Reaction $H_2 + OH \rightarrow H_2O + H$

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We studied the prototype reaction $H_2 + OH \rightarrow H_2O + H$. Although especially the surface reaction might be of huge importance in H_2O formation in dark interstellar clouds, the gas phase reaction is of interest because of its strong tunneling effect: even with a reaction barrier of 24.0 kJ mol^{-1} the reaction proceeds with a reaction rate of $8.35\ 10^{-19}$ cm^3 $molecule^{-1}$ s^{-1} at 15 K. Experimentally, a high kinetic isotope effect is observed.

We used instanton theory on an analytical potential surface [1]. In contrast to other methods, we can include multidimensional tunneling and, thus, calculate accurate reaction rates down to 15 K. Furthermore, we calculated the temperature dependence of all eight H/D-isotope combinations.

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Photodynamics of nitrophenols in atmosphere

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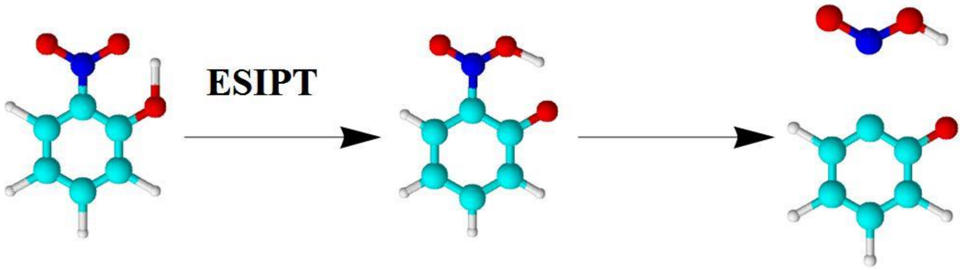
Recently, substituted nitroaromatic molecules have been identified as possible precursors for photolytic formation of nitrous acid (HONO) in lower atmosphere [1]. The mechanism of the HONO formation remains, however, unclear.

Here, we investigate ultrafast photodynamics of *ortho*-nitrophenol, using the methods of theoretical chemistry. We particularly focus on the initial step of the HONO formation which might be the Excited State Intramolecular Proton Transfer (ESIPT) between NO_2 and OH moieties.



We have characterized the potential energy surfaces (PES) of the canonical an aci-nitro forms of the *ortho*-nitrophenol both in the ground and excited states using multireference level of theory. Furthermore, we have performed non-adiabatic (surface hopping) molecular dynamics simulations of the dynamical processes triggered by the excitation into the ππ* excited state. It follows from our investigation that the excited state hydrogen transfer and aci-nitro isomer formation is energetically possible and indeed takes place within approximately 50 fs. The molecule then funnels its population back into the ground state, reconstructing the *ortho*-nitrophenol structure or staying in the one of the aci-nitro forms. From these structures, the formation of HONO is feasible.

Acknowledgement: The support by the Grant Agency of the Czech Republic via grants number 15-12386S and 14-08937S are gratefully acknowledged.

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Hydrogen Peroxide Synthesized From Porous Water Ice Irradiated By Swift Heavy Ions

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Water ice is found in several cold bodies of the Solar System, interstellar medium (ISM) and nearly young stellar objects, where it is frequently exposed to galactic cosmic ray and solar wind radiation [1]. In this work, chemical and physical changes induced by irradiation of heavy ion on pure porous amorphous solid water (ASW) at 15 K and 144 K are analyzed. H_2O pure ices were irradiated by 606 MeV $^{70}Zn^{26+}$ and 52 MeV $^{58}Zn^{13+}$ ion beams and monitored by mid-infrared spectroscopy (FTIR). The destruction cross section σ_d of water is calculated and it scale on the projectile electronic stopping power S_e, $\sigma_d \propto S_e$. The formation cross section of H_2O_2 (σ_f) is determined from the infrared absorbance increase rate as a function of the beam fluence. Furthermore, the relation $Y_0 \propto S_e^2$ is confirmed for porous water ice, where Y_0 is the sputtering yield of the ice film [2].

These findings are relevant to water-containing ices in the cold bodies of the Solar System (e.g., Europa and Enceladus) and in the ISM. As an astrophysical consequence, the effects of heavy cosmic ray irradiation need to be taken into account for a correct description of the physical-chemical evolution of cosmic water ice.

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Iron monocyanide (FeCN): an ab initio investigation of vibronic and spin-orbit effects in low-lying electronic states

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Experiments based on Fourier-transform microwave (FTMW) techniques [1] and millimeter-wave rotational spectroscopy [2], and on the other hand, *ab initio* quantum chemical methods, *e.g.* [3,4] did not predict the same ground electronic state of this molecule, which was found via radio telescope observation of the asymptotic giant branch star IRC +2016 [5]. The $^4\Delta$ state has been observed [5] and verified experimentally [1,2], and the $^6\Delta$ state was found to be the ground state theoretically. In 2014, DeYonker [6] reported that a $^4\Delta$ ground state is lower than $^6\Delta$ state by only 306 cm^{-1} at the *ab initio* composite method employing coupled cluster theory up to full CCSDTQ and large basis set CCSDT computation. It was reported that multireference methodologies failed to find the correct ground state.

We report the results of *ab initio* CASSCF, MRCI and RHF-RCCSD(T)-DK calculations of low-lying electronic states, namely, $^6\Delta$, $^4\Delta$, $^6\Pi$, $^4\Pi$ states arising primarily from configurations $\sigma\sigma\pi^2\delta^3$, $\sigma^2\pi^2\delta^3$, $\sigma\sigma\delta^2\pi^3$, $\sigma^2\delta^2\pi^3$, respectively, in the aug-cc-pwCVTZ(-DK) basis set. MOLPRO 2012.1 software package was used [7]. We have calculated bending potential curves for these states using both single-reference CCSD(T) and multi-reference CASSCF methodologies, and from these curves we analyzed the Renner-Teller effect using variational [8,9] and perturbational method [10]. As was expected, splitting of the curves for lowest-lying $^{4,6}\Delta$ states was found to be very small. Additionaly, spin-orbit splitting was calculated using Breit-Pauli operator in the framework of MRCI method with CASSCF wavefunctions. All results are compared with previous experimental and theoretical results.

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Quantum study of H_2, HD and D_2 Eley-Rideal formation on graphite at vanishing collision energies

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The isotope effect in the Eley-Rideal hydrogen recombination on graphite at vanishing collision energy has been investigated quantum dynamically. The considered energy range is relevant for the chemistry of the Interstellar Medium, where the H_2 molecule can form through Eley-Rideal recombination on the carbonaceous surface of interstellar dust grains.[1] The effect of the substitution of either one or both the H atoms with D atoms has been investigated, considering chemisorbed target atoms only. A time dependent wave packet method[2] has been used to perform quantum dynamics simulations, using a recently developed two-wavepacket approach to address the low collision energy regime, say down to $\sim 10^{-4}$ eV. Both Eley-Rideal (ER) and 'hot-atoms' (HA) formation cross-sections have been computed within the flat, rigid surface approximation,[3] using *ab initio* potential energy surfaces.[4] Results show that the isotope effect, which is strong in reduced-dimensionality collinear cases, disappears in full 3D calculations, *i.e.* when correctly taking into account non-collinear encounters (Fig.1(a)). This suggests that the dominant collision mechanism at low energy is less direct than commonly believed and involves some energy randomization prior to reaction. Product molecules are found vibrationally hot and rotationally cold (Fig.1(c,d)), with a narrow distribution of product vibrational states. On the other hand, trapping (HA) cross-sections depend, to a good approximation, on the projectile atom only, and is 4-5 times larger for D than for H on average (Fig.1(b)).

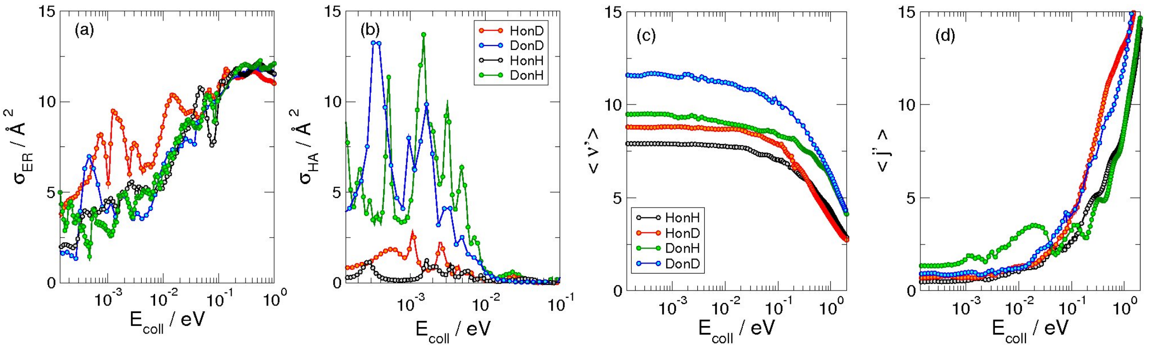

Figure 1: Eley-Rideal (a) and trapping (b) cross-sections and average vibrational (c) and rotational (d) quantum numbers for the four considered reactions as functions of the collision energy (logarithmic scale).

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Energetic criteria versus differential adsorption at interstellar grain surfaces:
The CHON isomers as a case study

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The CHON generic chemical formula covers four different isomers, isocyanic acid (HNCO), cyanic acid (HOCN), fulminic acid (HCNO) and isofulminic acid (HONC), the first three being identified in a large variety of interstellar environments. The knowledge of their relative abundance ratios with respect to the most stable one is a crucial data for constraining astrochemical models. For most of the species observed so far in the interstellar medium (ISM), the most abundant isomer of a given generic chemical formula is the most stable one (*minimum energy principle – MEP*). The few exceptions have been linked to different pathways of formation and destruction involving gas phase and/or surface processes that may be thought different according to the local temperature and the nature of the support (water ice, carbonaceous matter, silicate …).

In order to project some light on the interaction of the CHON isomers with interstellar grains as a function of the nature of the surfaces and to determine the influence of such interaction on their respective observed abundances, if any, the question was addressed by means of numerical simulations. Using first principle periodic density functional theory (DFT) to represent the interacting support as solid of infinite dimension, the adsorption energies were calculated on hexagonal ice, on graphene and on silica.

It was found that, whatever the nature of the surface, there were two different classes of isomers; one weakly bound (HNCO and HCNO) and one strongly bound (HOCN and HONC) with a ratio ~ ½ in adsorption energies. We have also shown that it is the hydrogen bonding which plays the discriminating role in the trapping of CHON species on grains surfaces.

The adsorption energies are in the order HOCN > HONC > HNCO > HCNO and are totally disconnected from the relative stabilities ordered as HNCO >HOCN >HCNO > HONC.

Whatever the environment, differential adsorption is an effective process and its contribution to the molecular abundances observed cannot be ignored, even if, in this case, it does not give a straightforward clue to the relative abundances observed for the CHON isomers. Nevertheless, the theoretical adsorption energies provided here could be profitably used for more realistic astrochemical modelings taking into account molecule-surface interactions.

Long time scale simulations of amorphous ice

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Amorphous ice, or amorphous solid water (ASW), is the most common form of ice in astrophysical environments and is believed to be the dominant component of comets, planetary rings and dust grains in interstellar molecular clouds. The surface of ASW catalyzes chemical reactions in interstellar space ranging from H_2 to complex organic molecules, and a deeper understanding of ASW is thus crucial for better models of chemical evolution in the universe. ASW is disordered and metastable with respect to crystalline hexagonal ice, and forms when water molecules are deposited on surfaces at temperatures below 140 K. However, the structure, morphology and formation mechanisms of ASW are poorly understood and have received much attention across many disciplines. Indeed, the structure and morphology of ASW depend sensitively on how it forms, where key parameters are temperature, deposition rate and deposition angle. While atomistic simulations of ASW are extremely challenging due to slow kinetics and the long timescales involved, state-of-the-art long timescale methods provide a possible means to study the atomistic mechanisms involved on relevant timescales. Here we will discuss atomistic simulations of the growth and long timescale evolution of ASW through the use of the adaptive kinetic Monte Carlo (AKMC) technique coupled to different interaction potentials for water molecules. The influence of temperature and deposition parameters is studied in detail and compared to available experimental results. Our results elucidate the structure and formation mechanisms of ASW under astrophysical environments and provide realistic structure models that can be used in further studies of chemical reactivity of ASW surfaces.

Isotopic fractionation of carbon in star forming clouds

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Abstract: In cold molecular gas in star forming regions, spectral line observations with millimeter telescopes readily detect isotopologues of species such as CO (^{13}CO, C^{18}O, C^{17}O) and HCO^{+} (DCO^{+}, H^{13}CO^{+}). Because of optical depth effects in dense star forming clouds, it is not straightforward to determine the relative abundances of the different isotopologues. However, by using radiative transfer codes, it is possible to self-consistently fit molecular emission line data and extract the isotopic fractionation information. Using data from ALMA, JCMT and Mopra telescopes, and the MOLLIE radiative transfer code with new isotopologues implemented, we show the variation of isotope ratios in examples of low mass and high mass star forming clouds. Species involving ^{13}C are found to be particularly enhanced compared to the expected galactic ^{13}C/^{12}C ratio. Reasons for this are discussed and comparisons made to other species with heavy isotope enrichment. The implications for the analysis of star formation processes such as disk and outflow generation are also briefly discussed.

Quantum Mechanical Tunneling of Atoms and its Influence on Deuteration of Interstellar Methanol

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Quantum tunneling of hydrogen atoms is generally accepted to play a crucial role in hydrogen transfer reactions. We use instanton theory, based on statistical Feynman path integrals, to find the most probable tunneling path and reaction rates. This is used to investigate the formation of H_2 on the surface of carbonaceous dust grains in space [1] as well as the deuteration of interstellar methanol [2]. In water, tunneling was found to cause a synchronization of the proton movement in Grotthuss chains [3].

These simulations were made possible only through algorithmic improvements in the instanton optimization. We developed a quadratically-converging optimizer as well as an adaptive partitioning of the instanton path.

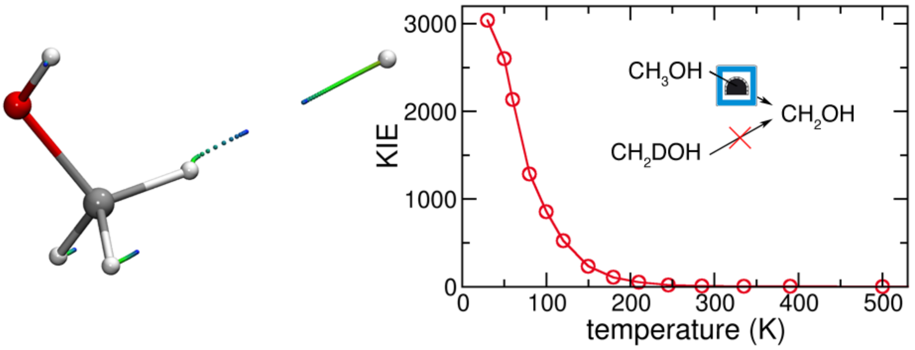

Fig 1: Left: tunneling path of H-abstraction from methanol by H, right: temperature dependence of the KIE.

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Small linear carbon chains: vibrational and electronic states

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The study of carbon chains type C_n and their ions has been attracted a significant effort due to their connection with the astrophysical observations, because pure carbon chains are abundant species in several sources such as the carbon rich circumstellar envelopes. In addition, they can play important roles in the reactivity of large systems containing carbon atoms. Carbon molecules have been considered responsible of the Diffuse Interstellar Bands (DIBs) [1]. Small chains are building blocks of larger species such as the fullerenes and the PAHs.

In spite of their astrophysical relevance, few bare chains have been observed in gas phase extraterrestrial sources. The shortest chain C_2, was the first detected, followed by C_3 and the linear-C_5 [2-3]. Detections were performed through the analysis of Infra-Red active vibrational excitations or through their electronic transitions because they present a zero dipole moment.

All the C_n chains present a large number of isomers, however, in this work we focus on the linear ones. The large stability of charged linear chains was used as argument to predict the presence of anions in the interstellar medium. We present computed molecular properties calculated using highly correlated ab initio methods (CCSD(T)-F12, MRCI/CASSCF). We determine structures, infrared frequencies and excitations energies to the lowest electronic states and electron affinities of the small chains type C_n (n=3,4,5,6,7). Special attention is given to the anions which relevance for reactivity is evident. Non-adiabatic effects and spin-orbit effects will be predicted.

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Shedding light on the formation of formamide (NH_2CHO), a crucial precursor of pre-biotic material

Ana López-Sepulcre

Understanding the origin of life on Earth represents one of the hot topics in modern science. One of the major questions is whether the original mechanism that led from simple molecules to life was connected to metabolism or to genetics, both intimately linked in living beings. Formamide (NH_2CHO) contains the four most important elements for biological systems, and it has recently been proposed as a pre-biotic precursor of both metabolic and genetic material, suggesting a common chemical origin for the two mechanisms (Saladino et al. 2012; Ferus et al. 2015).

Even though formamide was first detected in molecular clouds in 1971 (Rubin et al. 1971), dedicated observational studies have started only very recently, as its potential role as a key prebiotic molecule has become more evident. These studies report the presence of formamide in massive hot molecular cores (Adande et al. 2011; Bisschop et al. 2007), one low-mass protostar (Kahane et al. 2013), and the comet Hale-Bopp (Bockelée-Morvan et al. 2000). In the past months, the IRAM Large Program ASAI, dedicated to astrochemical studies of star-forming regions, has revealed new discoveries of NH_2CHO in several solar-type protostars (López-Sepulcre et al. 2015) and in outflow shock spots (Mendoza et al. 2014). The presence of formamide in such a variety of star-forming environments, as well as on a Solar System comet, opens the possibility of an exogenous delivery onto a very young Earth more than 4 billion years ago.

In this contribution, we will present our new ASAI results on formamide, and compare them to previous studies, to try to understand its formation mechanisms in the interstellar medium. We will discuss the different chemical pathways that have been proposed, which include gas-phase as well as gas-grain reactions. While our results suggest a strong chemical connexion with isocyanic acid (HNCO), perhaps pointing towards its hydrogenation on grain mantles as a likely formation route of formamide, there are recent experimental works that challenge this possibility. This, coupled with alternative gas-phase and grain formation routes that still need to be explored observationally and experimentally, reflects the importance of joining efforts with experts on both theoretical and experimental chemistry in order to make progress. Further dedicated observational studies, particularly with interferometers, are also crucial in order to place constraints on the various formation pathways so far proposed.

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The dynamics of bimolecular reactions involving a van der Waals complex and a submerged barrier

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There are a number of bimolecular reactions that can have negative activation energies. Such reactions can be extremely fast and some of them are interesting in astrochemistry. Their rates are modelled using statistical rate theories, and very little is known about their dynamics. Most of the reactions charactericzed by a negative activation energy proceed over a van der Waals complex with a submerged barrier. One of the most widely studied class of reactions of this kind involves alkyl radicals with hydrogen halides, $R + HX \rightarrow RH + X$, with X = Br, I and R = alkyl. $HBr + CH_3 \rightarrow Br + CH_4$ is the prototype of this class of reactions. Experimental data for this reaction are remarkably different. Recent experimental and theoretical kinetic studies revealed small negative activation energies at 298-550 K but they could not give definite conclusion about the observed features and the mechanism of the reaction.

In this work we report on quasiclassical trajectory calculations performed to explore the detailed mechanism of the reaction of $HBr + CH_3 \rightarrow Br + CH_4$ and to find the origin of negative activation energy and the nonlinear Arrhenius plot. In our calculations we used the new global ab initio potential energy surface developed by Czakó [1] and corrected it in the reactant region. The rate coefficients obtained with the QCT method match excellently those measured by Seetula [2], by Nicovich et al. [3] and Seakins et al. [4] (Fig. 1). The role of the $BrH\text{-}CH_3$ van der Waals complex and the effect of the rotationally and vibrationally excitation of reactants will be discussed in the presentation.

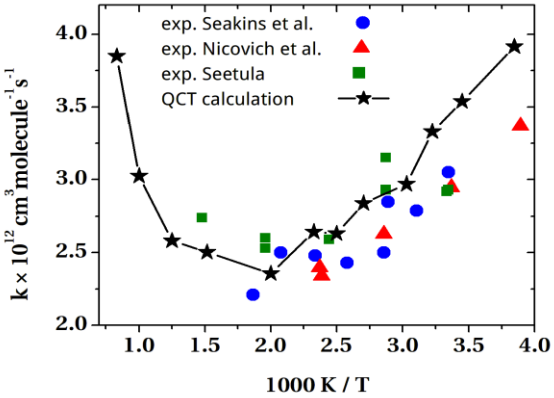

Fig 1. Thermal rate coefficients of the $HBr + CH_3 \rightarrow Br + CH_4$ reaction

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DIAGNOSTICS AND MODELING OF COLD LABORATORY PLASMAS WITH HIGH HYDROGEN CONTENT;
APPLICATIONS TO MOLECULAR ASTROPHYSICS.

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Cold plasmas of molecular precursors produced in low pressure glow discharges involve intricate mechanisms of great interest in many scientific and technological fields, such as thin film growth, surface conditioning and so on. In particular, hydrogen containing cold plasmas are currently used in microelectronic devices production, can simulate the border conditions of plasmas generated in fusion reactors, and are efficient sources of very reactive radicals and ions, whose study contributes to clarify the appearance of complex compounds in different regions of interstellar molecular clouds or in Jovian planet ionospheres.

In this work, low pressure glow discharges of mixtures of hydrogen with simple molecules and atoms and different isotopic compositions are experimentally diagnosed, and the main mechanisms controlling their behavior are elucidated by kinetic modeling. According to theoretical predictions supported by experimental data, the formation of new molecular species takes place mainly at the reactor surfaces and competes with the fast wall recycling of the precursors, which are previously dissociated by electron impact. On the other hand, the ion distributions result mainly from the balance between electron impact ionizations, which depend markedly on electron energies, and ion-molecule reactions in gas phase, for which the proton affinity of the different neutral species plays a key role.

The first detection of the deuterated ammonium ion (NH_3D^+) in the interstellar medium [1,2], and the refined infrared spectroscopic characterization of the isotopomers $^{36}ArH^+$ and $^{36}ArH^+$ [3], the first noble gas molecules found in space [4,5], exemplify the successful interaction between plasma spectroscopy and astronomical observations.

Acknowledgements

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Mass spectrometry diagnosis of hydrocarbon containing plasmas with relevance for molecular astrophysics of hot cores

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We present here results related to mass spectrometry diagnosis of atmospheric pressure plasma containing hydrocarbons. The plasma generated in dielectric barrier discharge configuration presents typical properties that match some thermodynamic parameters of hot cores regions of interstellar plasmas. The most important features are temperature, around 300 K in specific conditions and chemical dynamics, as well the ratio between volume and surface chemistry assisted by electrons. Thus, transient and stable molecular families are generated in plasma volume and on surfaces, some being relevant for the chemical processes ongoing in molecular hot cores. Depending on the gas feed and external parameters driving the plasma, specific neutral or ionized molecular populations can be generated.

Molecular beam mass spectrometry (HPR-60, Hiden Analytical, 0-2500 amu range) was selected as diagnosis method of chemical families generated in plasma volume, together with other techniques such as emission spectroscopy and laser induced fluorescence. Surface processes on graphite are evaluated based on final reaction products, studied by Raman spectroscopy.

The experimental set-up consists on a parallel plate system to host the plasma and a mass spectrometer coupled to the plasma volume (Fig. 1). High voltage sin wave (2.6 kV amplitude, 1 kHz frequency) is applied on power electrode and plasma pulses (up to 75 mA discharge current) are ignited in a ternary gas mixture: helium, 2.45 L/min flow rate, hydrogen, 1 mL/min flow rate, butane (C_4H_{10}), 4.25 mL/min flow rate.

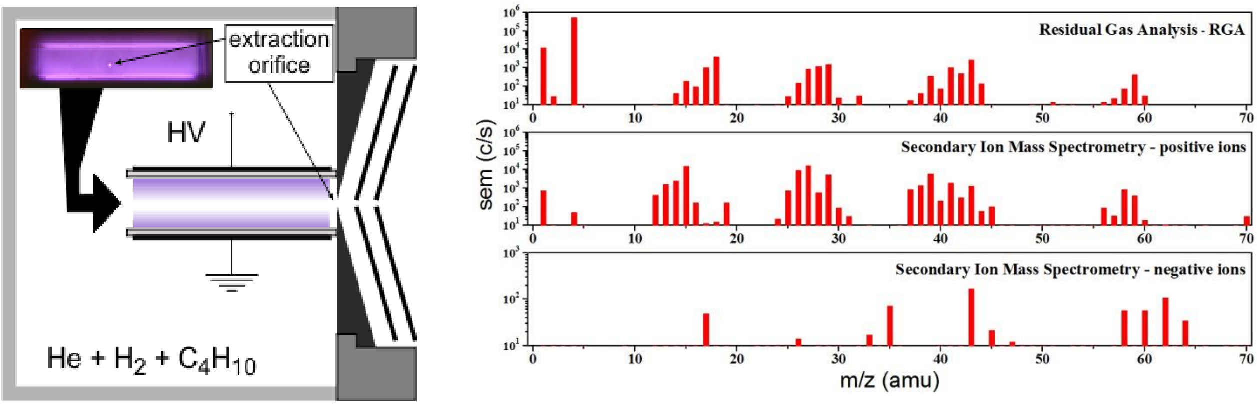

Fig. 1. Sketch of the non-equilibrium plasma at atmospheric pressure – mass spectrometer assembly (left side) and typical mass spectra of C_4H_{10} containing plasmas (right side).

Overall mass spectra of the all studied hydrocarbon containing plasmas at atmospheric pressure plasmas indicate the existence of efficient fragmentation and recombination processes, due to plasma active species. High mass molecules are dissociated and recombination / clustering phenomena lead to a rich mass distribution. Hydrocarbon radicals or complex hydrocarbons, present also in molecular hot cores, are the typical species identified in the spectra.

The mass spectrum of neutral gas inside the reactor shows signatures of C_nH_{2n-1}, C_nH_{2n}, C_nH_{2n+1} species, with n from 1 to 4. The same pattern is visible also for positive ions spectrum, with a small difference: the appearance of a higher mass ion at 70 amu, i.e. C_5H_{10}. The negative ions spectra show only few signals, nevertheless some with higher mass than the C_4H_{10}. Further analyses should be carried out in order to elucidate the precise nature of molecular fragments and clusters formed in these types of hydrocarbon plasmas and their relevance for the physical processes ongoing inside hot molecular cores.

Acknowledgements

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Modeling the reactivity of polycyclic carbonated molecules on icy grains

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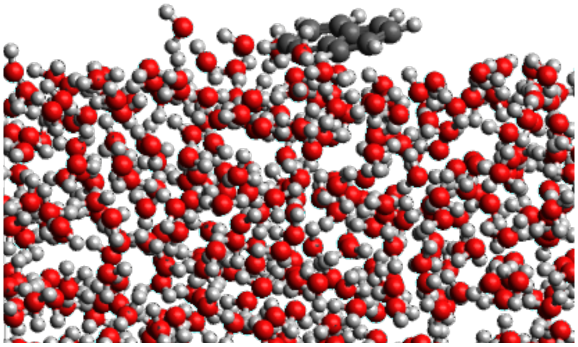
Polycyclic Aromatic Hydrocarbons **(PAHs)** have an astrophysical interest since the discovery, in 1984, of the Aromatic Interstellar Bands **(AIBs)** observed between 3 and 15 um. These bands are assigned to vibration modes of PAHs, which, after absorption of UV light of stars, emit in the infrared region. PAHs are also good candidates to explain the Diffuse Interstellar Bands **(DIBs)**, which are weak absorption bands measured between 0.38 and 1.3 um on the extinction curve of our galaxy. In molecular clouds of the ISM, gases are condensed on dust particles and form ice mantles essentially made of water. PAHs may also been condensed on/in these ices and contribute to the complex chemistry occurring on these grains [1]. This heterogeneous chemistry plays a fundamental role in presence of water, which catalyzes photochemical processes.

Although ice has been extensively investigated by IR spectroscopy [2], few studies of ices containing PAHs have been reported. To shed light on the unexpected role played by PAHs in cosmic ice chemistry, IR spectroscopy experiments on the cryogenic codepostion of PAH and water are achieved at the Institut des Sciences Moléculaires (ISM, Bordeaux) [3]. In connection with these experiments, we are modeling PAHs interacting with various icy environnements using a muti-scale multi-method approach. The aim is to discriminate the configuration that could best describe the experiments and give quantitative indications on the effect of the environment on the IR spectra.



Snapshot issued from a MD simulation of a Napthalene adsorbed on a HDA ice slab at 77K.

The adsorption of PAH molecules is modeled by means of classical molecular dynamics simulations on amorphous ice surfaces. A detailed analysis of the resulting configurations will be performed before using these geometries as initial structures for ab initio (DFTB) calculations of the emission spectra [4]. We know that the experiments do not reproduce exactly the astrophysical conditions, in terms of pressure and rate deposition, but the validation of our simulations with comparison to the experimental data will give credit to the extension of our model to astrophysical conditions.

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Strength of water-water interaction depends on local environment

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Interaction potential between two water molecules depends on their distance, orientation of each molecule and local environment as well [1,2]. When two water molecules find themselves at a favorable distance and orientation, two water molecules experience a particularly strong attractive interaction called hydrogen bonding. Although hydrogen bond is very important for its effects on the elements of life, industrial applications, and bulk water properties, there is no scientific consensus on its true nature and origin. In this study we use quantum mechanical methods to calculate the strength of the hydrogen bond in different local environments, such as, next to other water molecules, next to an ion, a nonpolar solute, non-polar plane and dipoles. The local environment effects are considerable even for the second coordination shell. These calculations provide novel insights into the nature of hydrogen bonding and its influence on the intermolecular potential in water.

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Anion Chemistry on Titan: systematic studies of the growth and stability of large negative ions

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Synopsis The reactions of $C_{2n+1}N^-$anions and their complexes with cyanoacetylene, HC_3N, and hydrogen cyanide, HCN, were studied experimentally using methods of tandem mass spectrometry. The reactions described in detail in this communication may represent a possible way of formation of large anions found in the ionosphere of Titan.

Cassini CAPS-ELS spectrometer revealed the presence of large negative ions in the ionosphere of Titan [1]. Recently, a mechanism has been proposed for the possible formation of these ions, in whith the cyanoacetylene, HC_3N, played a key role [2]. Chemical ionization technique (NCI and APCI-) were used successfully to prepare model complex $(HC_3N)_x.C_yN^-$ anions in the gas phase. The reaction itself and CID experiments was studied using a Waters Quattro Premier TM tandem quadruple mass spectrometer operating in negative ion mode and VG ZAB2-SEQ mass spectrometer. CID mass spectra of these anions, as well as their ion molecule reactions with HC_3N support the previously proposed reaction scheme [2,3]. Quantum chemistry calculations revealed details of the ion structures, energetics and reaction mechanisms. High-energy CID spectra of $(HC_3N)_x.C_yN^-$ anions showed a complexity of ionic and neutral products that can be expected to be formed by the high-energy ion precipitation observed at Titan [4].

Presented experiments show that in spite of its low abundance in Titan atmosphere [5], the cyanoacetylene is probably one of the most important species in the ionospheric chemistry of Titan.

Acknowledgement

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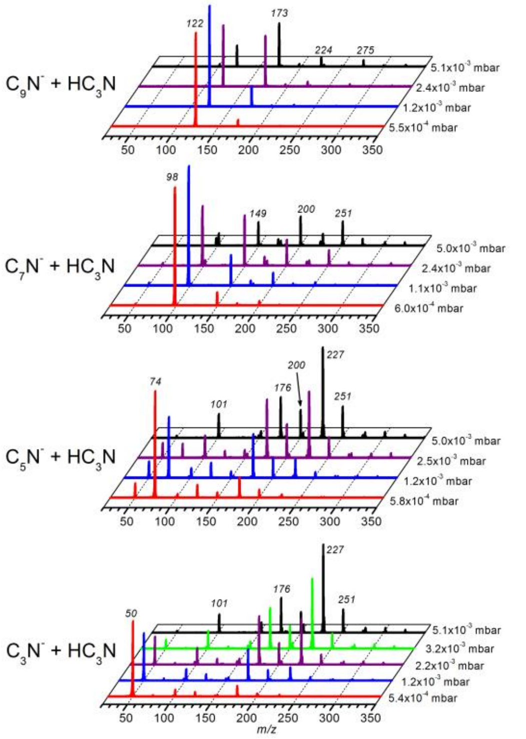

Figure 1. Pressure dependent mass spectra of reactions of C_xN^- anions (x =3,5,7,9) with HC_3N.

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Other

UV photodesorption of methanol and formaldehyde: CO mediated mechanisms and photochemistry

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In cold regions of the Interstellar Medium (ISM), like star-forming regions or protoplanetary disks, molecules form or accrete on the surface of dust grains. The resulting icy mantles represent the main reservoir of molecules beside H_2. In the very low temperature regions, thermal desorption can be neglected, but energetic processes, for instance induced by cosmic rays or photon impact on the ices, can promote their desorption and therefore enrich the gas phase. The photodesorption rates are usually considered in several regions of the ISM in order to explain abundances of molecules in the gas phase [1,2]. For instance, recent surveys in the horsehead nebula of small organics (formaldehyde H_2CO and methanol CH_3OH), partially or totally formed in the condensed phase, suggest that photodesorption is at the origin of their observation in the gas [3]. However, the photodesorption rates and mechanisms for these species, much probably embedded in CO-rich ices, are still largely unknown.

These last years, we have developed a new experimental approach for the study of the UV photodesorption from simple model ices, using the brilliance and the tunability of synchrotron radiation from the DESIRS beamline at the SOLEIL facility. These photon energy-resolved studies allows for the determination of absolute energy-dependent photodesorption rates that can be applied to any interstellar-relevant UV field. Moreover, the method gives valuable information on the underlying molecular mechanisms in the ice, highlighting the crucial role played by the composition of the ice on the overall photodesorption efficiency [4].

Using this approach, we have investigated the photodesorption of CH_3OH and H_2CO, from pure ices and in CO-rich icy mixtures. Wavelength-dependent photodesorption rates have been derived both for the intact species but also for the photofragments. We have indentified the role played by the CO-matrix, which can in some cases promote the desorption of the intact molecules by indirect energy transfer, but also play the opposite role when the photochemistry is at the origin of the desorption.

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Methanol photoproducts revisited by the VAHIIA system

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Studying organic volatile compounds (VOC) coming from the heating of interstellar/cometary ice analogs through laboratory simulations is of great interest in understanding the reactivity that leads to the formation of the organic refractory residues available in interplanetary objects. They will enlighten us on conditions prevailing on the primitive nebula and during the formation of the Solar system and will support understanding and interpreting observational data. Experimental simulations consist of irradiating and warming-up an ice analog under ultrahigh vacuum conditions reproducing astrophysical environments.

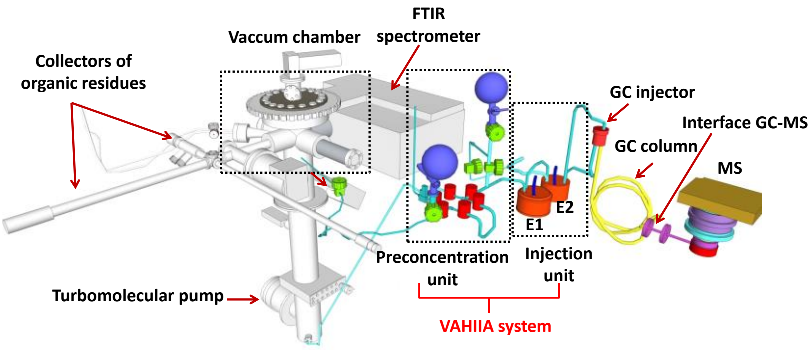

Figure 1: The VAHIIA experimental set-up

To analyze the VOC formed in these conditions by gas chromatography (GC) coupled to mass spectrometry (MS), different analytical challenges need to be addressed such as: the low pressure under which the VOC are formed in the vacuum chamber (10^{-8} mbar) since their analysis by GC-MS is conducted at atmospheric or close to atmospheric pressures; and the low sensitivities due to slow desorption kinetics in the vacuum chamber while a narrow injection is needed to ensure the best GC efficiency. To overcome these challenges, we developed an analytical interface called VAHIIA [1] that links directly the cryogenic chamber where the VOC sublime to the GC-MS where they are analyzed (Figure 1). By this means, an online transfer of the compounds to the analytical instrument is ensured, maintaining the representativeness of the sample and avoiding compound losses, a common problem in multi-procedural methodologies for VOC analysis.

We use this system to characterize products coming from the VUV irradiation of a pure methanol ice at 20 K and its subsequent warming [2]. While previous experiments have identified up to 10 photoproducts [3–6], our system allows the identification of about 30 different photoproducts. Furthermore, by using the GC-MS we were able to quantify the abundance of 21 photoproducts and determine for each their branching ratio and yield relatively to methanol [2]. These new results are available for astronomers for refining their chemical models.

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Interference between Overlapping Resonances: A Route to Coherent Control of Resonance Lifetimes and Photofragment Distributions in the Weak-Field Limit

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

It has been recently shown that the lifetime of an overlapping resonance is no longer an intrinsic property of the resonance state, but instead it strongly depends on the amplitudes of the other overlapping resonances populated in a superposition [1]. This is the basis of a control scheme which, in its simplest version, creates a superposition of two overlapping resonances in the complex Ne-Br_2(B,v'=27), using one pump laser pulse to excite each of the two resonances. By varying the delay time and the ratio of amplitudes between the two pump pulses, it is possible to control the amount of population that is simultaneouly excited to both resonances, and therefore to control the intensity of interference between them [2,3]. In this way, an enhancement by a factor of three of the lifetime of one of the resonances is achieved (see Fig. 1, left panel) [2].

In the second control scheme, a single fixed bandwidth pump pulse is used to excite the same superposition of two resonances in Ne-Br_2(B,v'=27). By applying different linear chirps to the pulse, interference between the resonances can be controlled. As a result, phase effects of increasing intensity are produced in the transient vibrational populations of the Br_2(B,v_f<v') fragment as the chirp rate β_0 increases (see Fig. 1, right panel) [4]. These pure pulse phase modulation effects occur for a long time window (about 200 ps) after the pulse is over.

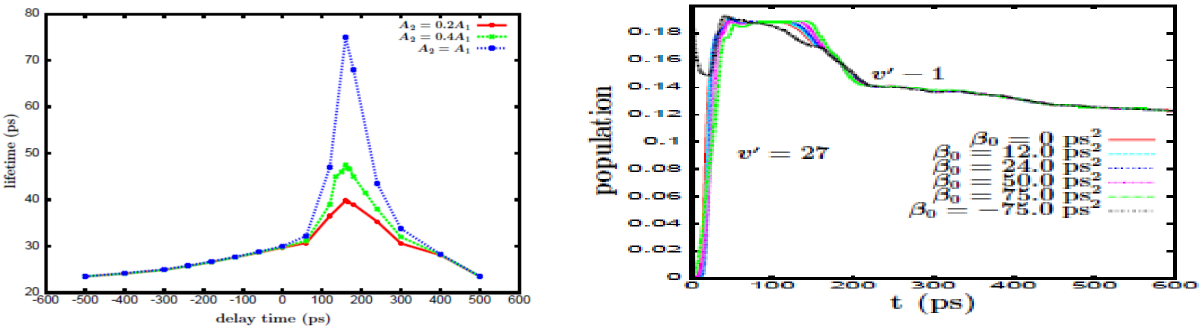

Figure 1: Resonance lifetimes vs delay time and three different ratios of amplitudes between pulses (left panel). Transient Br_2(B,v_f=v'-1) fragment vibrational populations using different pulse chirps (right panel).

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Diffusion-limited reactivity in interstellar ices

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Interstellar grains are thought to play an important role in the formation of complex molecules in the interstellar medium. However, the low temperature and scarcity of reactants present in their ice mantle strongly limit the formation of complex molecules in their bulk. Whether or not long time scale can counterbalance this diffusion-limited solid-state reactivity at low-temperature strongly depends on both the reaction rate constant and the diffusion coefficients of the reactants.

As a model system we chose two reactants, CO_2 and NH_3, which are abundant in interstellar ices and which have been shown in the laboratory to react thermally in ices [1] to give NH_2COOH and $NH_4^+NH_2COO^-$. Using classical molecular dynamic simulations we calculated the diffusion coefficients of CO_2 and NH_3 in a low density amorphous (LDA) ice mimicking the interstellar ices [2]. We studied the $NH_3 + CO_2$ reaction in a cluster of water molecules using a Density Functional Theory based method [3] and studied the same reaction in a periodic LDA ice model using an *ab-initio* molecular dynamic approach [4]. We measured the diffusion of CO_2 in the bulk of vapor-deposited compact ices using isothermal kinetic experiments [2]. We studied the kinetics of the NH_3 and CO_2 solid-state reaction in ice from a set of isothermal experiments monitored by FTIR spectroscopy [3]. Theortical and experimental results are compared and astrophysical implications are discussed.

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Dissociation of acids on the quasi-liquid layer of ice and on wet quartz

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Ionization of acids at interfaces is a topic of interest to atmospheric and astrochemical science. We have employed ab initio molecular dynamics to study the ionization of some strong inorganic acids on ice and on quartz.[1-4]

The ice quasi-liquid layer (QLL) forms on ice surfaces below the bulk ice melting temperature. It is abundant in the atmosphere and its importance for atmospheric chemistry is widely recognized. It can also be significant in planetary atmospheres and interstellar medium. In the present work, we have studied the microscopic mechanisms of acid ionization on the QLL. The model system QLL is established by nanosecond timescale simulations with empirical force fields, while the reactivity of the QLL is studied using ab initio molecular dynamics. We find that the QLL is highly reactive, exhibiting stable crystalline point defects, which contribute to efficient acid solvation, ionization, and proton transfer. We study in detail deuterated hydrogen iodide (DI) and nitric acid (DNO_3).[2] Ionization in both cases benefits from the abundance of weakly bonded hydrogen-bond single-acceptor double-donor water molecular species available on the QLL in high concentrations. Picosecond timescale ionization is demonstrated for both molecular species.

We also present a study of HCl ionization on wet hydroxylated (0001) α-quartz.[3] Such a surface is present in the environment as a component of dust or of an 'urban surface' and can also play a role in interstellar medium. HCl is found to ionize within a few picoseconds. The ionization process is exoergic, with most of the temperature increase due to formation of hydrogen bonds prior to the ionization. In agreement with existing studies of HCl in water clusters, in liquid water, and at the air-water interface, the main determinant of ionization is the degree of acid solvation by neighbouring water molecules. Predicted spectroscopic signatures showing the presence of solvated hydronium ion are presented.

Our results suggest high reactivity of acid ionization and proton transfer at temperature ranges appropriate for the troposphere and lower stratosphere, and can also be important in planetary atmospheres and interstellar medium.

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Decomposition of acetic acid by electron transfer collisional experiments

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Molecular species within the interstellar medium are subject to radiation and particle induced reactions (e.g. charge transfer, radiative association, proton and cation transfers), with relevance to particular pathways yielding cation and anion formation. Regarding the former, such chemistry may be driven by cosmic radiation, UV and X-rays, high-energy particles emerging from stars or other structures (e.g. supernova), all contributing for such diversity of species [1]. Notwithstanding, anionic species formation are relevant in particular to their role in the synthesis of interstellar molecules, where dissociative and radiative attachment, radiative association of anions and ion-pair formation have been recognized to be the main pathways. Ion-pair formation has also been identified long ago as a relevant process in molecular synthesis [2], where electron induced chemistry is also prevalent in the formation of organic molecules within ice mantles on dusty grains in the interstellar medium (ISM) [3]. Acetic acid has been found in the ISM and we have performed extensive ion-pair formation studies in collisions of neutral potassium atoms with these neutral molecular species. The negative anions formed in the interaction region, as a function of the collision energy (typically between a few eV up to 300 eV in the lab frame) were time-of-flight (TOF) mass analysed. Collision induced dissociation yielding OH^- formation has been comprehensively studied in CH_3CCOH, CD_3COOH and CH_3COOD species [4]. Relevant intramolecular electron transfer with considerable geometry change of the temporary negative ion has been identified to be the main mechanisms in such anionic formation.

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Ro-vibrational excitation of H_2 by H: Towards a revision of the ortho-para-H_2 conversion and of the cooling mechanism in astrophysical media

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In the Universe, the most abundant element is hydrogen and collisions involving H_2 molecules and H atoms are crucial to the thermal balance and chemistry of astrophysical media. Indeed, the cooling by infrared emission of H_2 following its collisional excitation is the most important cooling mechanism in the early universe [1]. Moreover, in photon-dominated regions (PDRs) of the interstellar medium, which are exposed to sources of ultraviolet radiation, there exists a region of overlap of atomic and molecular hydrogen and the kinetic temperature in this region is also controlled by inelastic H_2-H collisions [2].

At last, in astrophysical media, the distribution of molecular hydrogen between its ortho (nuclear spin I=1) (hereafter o-H_2) and para (nuclear spin I = 0) (hereafter p-H_2) forms is a key parameter for the physical chemistry of interstellar molecular clouds and early universe. Radiative transitions as well as inelastic collisions are inefficient to convert o-H_2 into p-H_2 or reverse. Conversion between ortho- and para-H_2 only occurs through reactive collisions leading to hydrogen or proton exchange [3].

Accurate study of collisions between H_2 and H are then crucial in order to qualitatively and quantitatively model many astrophysical media. In this talk, We report fully-quantum time-independent calculations of cross sections and rate coefficients for the collisional (de-)excitation of H_2 by H from low to high temperatures [4,5]. Our calculations are based on the H_3 global potential energy surface of Mielke et al. [6]. The reactive hydrogen exchange channels are taken into account. New collisional data are obtained for the ro-vibrational relaxation of highly excited H_2 for temperatures ranging from 100 to 5000 K. We also provide a comparison with the available experimental rate coefficients at room temperature. We show that the ortho-para conversion of H_2 are significant processes at temperatures above ~300 K. The new results significantly differ from previous data presently used in astrophysical models, especially at low temperatures, the difference being essentially due to the inclusion of the reactive channels. The impact of these new data in astrophysics is discussed. In particular, the cooling mechanism will have to be reviewed in several astrophysical media. The importance of the ortho-para-H_2 conversion by hydrogen exchange in astrophysics is also discussed.

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Computer Modelling of State-to-State Energy Transfer in Large Gas Ensembles of Atmospheric and Astrophysical Interest.

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The author and co-workers [1] have developed a computational model of state-to-state energy transfer in large gas ensembles. This is based on the fast, accurate Angular Momentum (AM) theory [2] of collision-induced state change in atom-diatom and diatom-diatom collisions. The latter was developed following a series of experiments in the author's laboratory designed to identify the motive force for collision-induced change and has been widely tested on state-to-state energy transfer, molecular dissociation and elementary atom-molecule reactions.

This theory forms the basis of a computational model capable of following state-to-state energy flow in gas ensembles throughout many cycles of collisions. The model comprises up to 10,000 atoms/molecules of up to three different species that form the initial ensemble. Each is initially in a specific rovibrational state at specified collision energy. The evolution of the quantum state populations of each species and translational energies are followed in series of collision cycles through to equilibration. Rotation, and vibration state populations are available after each collision cycle in the form of state populations and/or modal temperatures of vibration (T_v) rotation (T_r) and translation (T_t)

The figure below is an example of one mode of data presentation. Two examples will be discussed in detail. (1) Disposal of exothermicity from the $H + O_3 \rightarrow OH^*$ reaction in Earth's mesosphere. (2) Translational cooling of hydrogenic species in post recombination early Universe by translation-to-internal energy conversion.

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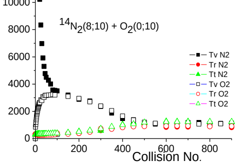

Modelling spin-state chemistry of deuterated ammonia

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We report on a new gas-grain chemistry model (Sipilä et al. 2015b) that contains multiply deuterated species and separates out the different nuclear spin isomers of molecules with several H and/or D nuclei. The nuclear spin branching ratios are calculated using symmetry rules under the assumption of complete scrambling. The method has been previously used for systems consisting of five H and/or D nuclei by Hugo et al. (2009). The present model is an evolved version of our previous spin-state chemical model (Sipilä et al. 2015a) which included the spin chemistry of hydrogenated species calculated with the formalism of Oka (2004), based on angular momentum algebra applied to nuclear spin statistics.

We apply the model to studying the particular case of (deuterated) ammonia, for which the model predicts that the relative abundances of NH_3, NH_2D, NHD_2, and ND_3, as well as their nuclear spin ratios, depend strongly on the kinetic temperature and the gas density. This is illustrated by Figure 1, where we plot the spin-state ratios of the deuterated forms of ammonia as functions of time at different densities (upper panels) or temperatures (lower panels). According to the present model, the deuteration of ammonia occurs primarily in reactions between NH_3 and the deuterated forms of H_3^+, i.e., H_2D^+, D_2H^+, and D_3^+.

In cold, dense interstellar cores, the deuterated isotopologs of ammonia concentrate on the nuclei of these objects. The spectral lines of the mentioned species are therefore likely to be extremely useful probes of the deep interiors of prestellar cores. The ground-state rotational lines of NH_2D, NHD_2, and ND_3 are observable from the ground (e.g., Roueff et al. 2005).

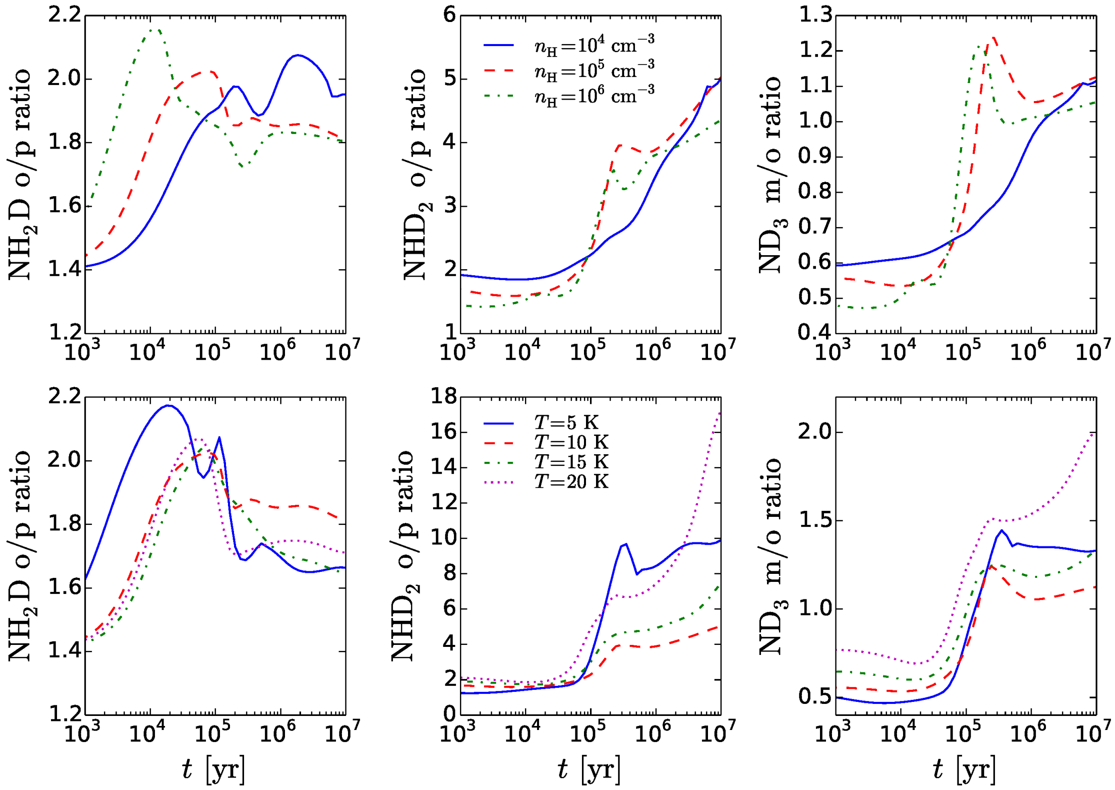

Figure 1. Spin-state ratios of deuterated ammonia as functions of density at different densities (upper panels) or temperatures (lower panels).

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