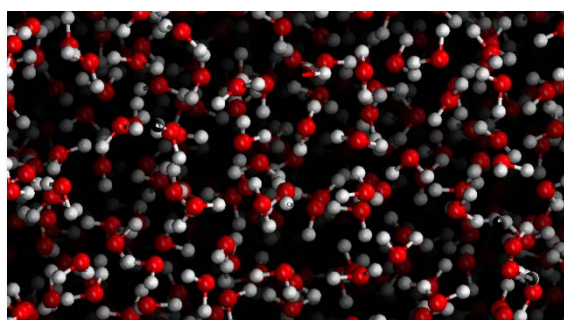


Les glaces astrophysiques: observations, modèles, expériences de laboratoires

Atelier conjoint du Groupement de Recherche 3533 Edifices Moléculaires Isolés
et Environnés (EMIE) et du programme national Physique et Chimie du Milieu
Interstellaire (PCMI)

03-04 OCTOBRE 2019 au CNES à PARIS



GDR 3533
Edifices Moléculaires
Isolés et Environnés
(EMIE)



Programme

jeudi 3 octobre 2019

HEURES	ÉVÉNEMENT
13:50 - 14:10	Introduction - par Geraldine Feraud, Florent Calvo pour GDR EMIE et Jean Hugues Fillion pour PCMI
14:10 - 15:00	Observations of interstellar ices and their physico-chemical evolution - Emmanuel Dartois
15:00 - 15:25	Linking ice observations to laboratory studies of ice structure - Jennifer Noble
15:25 - 15:50	Laboratory astrophysics studies of Thermal and Photon-Induced Desorption from molecular ices - Mathieu Bertin
15:50 - 16:05	Deposition and annealing of interstellar ices: a mixed neutron scattering and molecular dynamics study. - Pierre Ghesquiere
16:05 - 16:30	Pause café
16:30 - 16:55	Des ions et des glaces - Philippe Boduch
16:55 - 17:20	Modèles et données de l'astrochimie de surface - Valentine Wakelam
17:20 - 17:55	Etude expérimentale de la formation du manteau moléculaire à la surface des poussières froides - François Dulieu
17:55 - 18:15	Présentations flash poster
18:15 - 19:00	Table ronde - 3 thèmes
19:00 - 20:00	Session posters avec apéritif

vendredi 4 octobre 2019

HEURES	ÉVÉNEMENT
09:00 - 09:25	Theoretical description of interstellar ices from a multimethod approach - Céline Toubin
09:25 - 09:50	Adapting heterogenous catalysis calculations to the astrochemistry world - Françoise Pauzat
09:50 - 10:15	GRAINOBLE - Un modèle astrochimique gaz-grain multicouche - Vianney Taquet
10:15 - 10:45	Pause café
10:45 - 11:00	Energetic processing of hydrocarbons molecular species by ionizing radiation towards the formation of cyclic species - Suvastika Indrajith
11:00 - 11:15	Les glaces astrophysiques comme sources de diversité moléculaire au sein des phases gazeuse et solide - Grégoire Danger
11:15 - 11:30	Ammonium salts detected on the surface of comet 67P/Churyumov-Gerasimenko, relics of interstellar ice chemistry? - Olivier Poch
11:30 - 11:45	Thermal desorption of molecules from graphite and amorphous water ice surfaces - Henda Chaabouni
11:45 - 12:00	Stepwise microhydration of biomolecular building blocks: size-induced segregation and proton-induced charge transfer - Florent Calvo
12:00 - 13:30	Plateaux repas & session posters 2
13:30 - 13:55	Formation du premier sucre (glycéraldéhyde) par des processus radicalaires dans les glaces interstellaires/cométaires - Fabrice Duvernay
13:55 - 14:20	Contribution of the DFTB scheme to the modeling of water clusters - Aude Simon
14:20 - 14:45	Stability of PAH clusters - Sébastien Zamith
14:45 - 16:00	Table ronde - Conclusions

Orateurs invités :

M. Bertin (LERMA, Paris)
P. Boduch (CIMAP, Caen)
E. Dartois (ISMO, Orsay)
F. Dulieu (LERMA, Cergy-Pontoise)
F. Duvernay (PIIM, Marseille)
J. Noble (PIIM, Marseille)
F. Pauzat (LCT, Paris)
A. Simon (LCPO, Toulouse)
V. Taquet (Arcetri Astrophysical Observatory, Florence)
C. Toubin (PhLAM, Lille)
V. Wakelam (LAB, Bordeaux)
S. Zamith (LCAR Toulouse)

Orateurs sélectionnés :

F. Calvo (LiPhy, Grenoble)
H. Chaabouni (LERMA, Cergy-Pontoise)
G. Danger (PIIM, Marseille)
P. Ghesquière (The Open University, GB)
S. Indrajith (CIMAP, Caen)
O. Poch (IPAG, Grenoble)

Posters :

R. Dupuy (LERMA, Paris)
I. Fourré (LCT, Paris)
P. Ghesquière (The Open University, GB)
A. Lafosse (ISMO, Orsay)
J. Mascetti (ISM, Bordeaux)
H. Rothard (CIMAP, Caen)

Le présent recueil de résumés présente les résumés des contributions orales (invitées ou sélectionnées) triées par ordre alphabétique, puis les résumés des posters.

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Les organisateurs remercient Salem TACINE (laboratoire LCT) pour la gestion, ainsi que Michel Viso et le CNES pour leur assistance logistique.

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Laboratory astrophysics studies of Thermal and Photon-Induced Desorption from molecular ices

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The ever increasing resolving power and sensibility of the new generation of space and ground-based telescopes (ALMA, NOEMA, future JWST...) bring more and more evidence of the important chemical richness in the interstellar medium. In its colder regions (star and planet formation regions), the majority of species either form directly, or accrete, onto the surface of dust grains, resulting in the formation of molecular icy mantles which are believed to be the main reservoir of molecules besides H₂. These ices are expected to be the siege of an important chemistry, which in return enrich the gas phase by desorption processes. To better understand to what extent the interstellar ices will play a major role in the chemical complexity of the interstellar medium requires however to constrain and quantify these desorption phenomenon, that can be either thermal or non-thermal (i.e. induced by the impact of energetic particles or by exothermic recombinative chemistry).

In this presentation, I will show our research which deals with the experimental study of the desorption phenomenon from molecular ices. Thermal desorption is studied by the Temperature Programmed Desorption method (TPD) in order to obtain intrinsic parameters (adsorption energies, pre-exponential prefactors) that can be used to model the thermal desorption fluxes from the icy grains. The non-thermal desorption induced by photons – usually referred to as photodesorption – is quantitatively studied using the high brilliance and monochromaticity of the synchrotron radiation. The output of the synchrotron beamlines DESIRS and SEXTANTS of the SOLEIL synchrotron center are used to study the photodesorption from simple and composite molecular ices in the VUV (7 – 16 eV) and soft X-rays (400 – 1000 eV) ranges respectively. The method we employ results in the determination of absolute photodesorption yields of given neutral or ionic species as a function the incident photon energy. This allows both for estimating average photodesorption yields in regions with different VUV and X-ray fields, and for getting precious information on the initial microscopic steps responsible for the photodesorption process, thus opening the way to the determination of the implied molecular mechanism.

In the presentation, I will go through the different method which we employ and present some representative example which illustrate some striking properties of the photodesorption phenomenon in the VUV and the soft X-ray energy range.

Des ions et des glaces

Philippe Boduch¹

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Au cours de cet exposé, je vais présenter la pertinence de l'utilisation des faisceaux du GANIL (Grand accélérateur National d'Ions Lourds, Caen, France) pour simuler le rôle des rayons cosmiques ou des vents stellaires sur l'irradiation des glaces d'intérêt astrophysique. Les installations de notre accélérateur étant ouvertes à la communauté scientifique, les dispositifs expérimentaux utilisés pour des telles expériences seront aussi décrits. Je finirai par la présentation de quelques exemples allant de l'implantation d'ions soufre à basse énergie dans une glace de H₂O dans le cadre d'une application aux lunes joviennes à l'irradiation par des ions de très hautes énergies de glaces composées de molécules simples ou complexes.

Philippe Boduch, CIMAP/GANIL. boduch@ganil.fr 0231454876.

Stepwise microhydration of biomolecular building blocks: size-induced segregation and proton-induced charge transfer

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In this contribution we have computationally explored the structures of several molecules of prebiotic interest (uracil [1], 2-aminooxazole [2] and hydantoin [3]) in contact with a controlled number of water molecules and their response to a collision with an impinging proton. The methodology combines a standard exploration using force fields, followed by refinement using approaches with an explicit description of electronic structure, typically (but not exclusively) DFT. We have also considered the adsorption of these molecules on model ice surfaces, whose influence on the charge transfer cross sections upon proton impact is discussed.

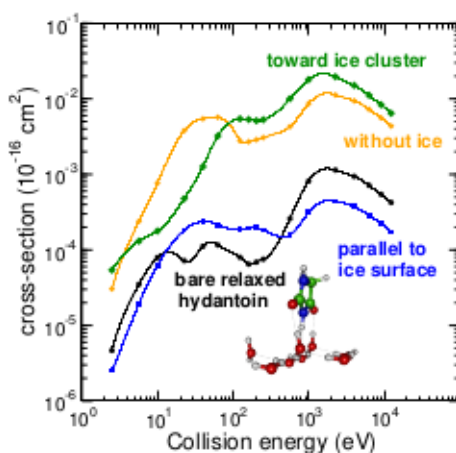


Figure 1 Charge transfer cross section between a colliding proton and hydantoin adsorbed on a crystalline ice surface, as a function the proton energy

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Thermal desorption and reactivity of complex molecules from graphite and amorphous water ice surfaces

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Complex organic molecules with more than 6 atoms (C,N, H, O) are species of great relevance in pre-biotic chemistry and precursors for the formation of amino acids during the course of chemical evolution leading to the origin of life in earth. These molecules are predicted to be formed in the gas phase and even by grain surface reactions. Formamide (NH_2CHO) and methylamine (CH_3NH_2) are the most abundantly amine-containing molecules observed in many astrophysical environments (prestellar and protostellar objects, hot corinos, massive hot cores and even in comets) [1-3]. The presence of these molecules in the gas phase may result from thermal desorption of interstellar ices at brightness temperatures between 100 and 200 K, where icy mantle undergo sublimation or destruction. We present laboratory experimental results for the temperature programmed desorption of formamide and methylamine from analogues of interstellar dust grain surfaces (graphite HOPG and ASW ice). The aim of this work is to understand the interaction of these amino molecules with the water ice and compare their desorption energies [4]. Thermal desorption experiments of formamide and methylamine ices were performed with a cryogenic ultrahigh vacuum setup at surface temperatures 40-240~K, and in the sub-monolayer and monolayer regimes. Using temperature programmed desorption data, we provided the desorption energy distributions of these molecules from water ice surface and even from graphite substrate. We compare the desorption behaviors of these two molecules from water ice surfaces. Implication of the high binding energies (5050-8420~K) of these molecules with respect to that of the water ice (4930~K) is discussed. We also give some experimental results about the reactivity of some complex organic molecules, studied in laboratory LERMA-Cergy with H (and D) atoms on graphite and amorphous water ice surfaces using RAIRS and TPD-QMS spectroscopy's surface analysis methods. We propose mechanisms for the abstraction-addition reactions.

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- [2] Lopez-Sepulcre. A, et al., MNRAS, 449, 2438 (2015);
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Les glaces astrophysiques comme sources de diversité moléculaire au sein des phases gazeuse et solide

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Des molécules organiques complexes sont détectées dans les phases gazeuse et solide d'objets astrophysiques. L'origine de ces molécules fait encore l'objet de débats, mais une grande partie est supposée se former à la surface de grains glacés. Ces glaces observables dans des nuages moléculaires denses vont être altérées par des processus hautement énergétiques (photons VUV, ions, électrons) au cours de la formation d'étoiles. Ces altérations permettent l'activation des molécules initialement présentes dans ces glaces, aboutissant au développement d'une réactivité chimique importante. Dans certains environnements tels que la nébuleuse solaire, ces grains peuvent être réchauffés, libérant en phase gazeuse une grande partie des molécules organiques complexes initialement formées à la surface ou au sein de ces glaces. Les molécules non volatiles restent sur les grains conduisant à la formation de résidus organiques réfractaires. Une partie des grains transformés peut alors s'accumuler, ce qui entraîne la formation d'objets interplanétaires tels que les comètes ou les astéroïdes. Par conséquent, une partie de la matière organique présente dans les objets du système solaire pourrait provenir de glaces observées dans le milieu interstellaire.

Sur la base d'expériences en laboratoire, nous développons une stratégie pour étudier les correspondances potentielles entre les glaces d'objets astrophysiques et les molécules organiques observées dans le gaz et les résidus organiques réfractaires de ces objets. Nous démontrons l'impact de la composition initiale de la glace sur l'abondance des molécules observées en phase gazeuse [1] ainsi que sur la composition moléculaire des résidus restants [2] après la désorption des composés les plus volatils.

[1] N. Abou Mrad, F. Duvernay, R. Isnard, T. Chiavassa and G. Danger. The Astrophysical Journal, 2017, 846, 124

[2] A. Fresneau, N. Abou Mrad, L. LS d'Hendecourt, F. Duvernay, L. Flandinet, F-R Orthous-Daunay, V. Vuitton, R. Thissen, T. Chiavassa, G. Danger. The Astrophysical Journal, 2017, 837, 168

Observations of interstellar ices and their physico-chemical evolution

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In the relatively shielded environments provided by interstellar dense clouds in our Galaxy, infrared astronomical observations have early revealed the presence of low temperature (10-100 K) ice mantles covering tiny grain “cores” composed of more refractory material. These ices are of specific interest because they constitute an interface between a solid phase under complex evolution triggered by energetic processes and surface reactions, with the rich chemistry taking place in the gas phase. The interstellar ice mantles present in these environments are immersed in a flux of ultraviolet photons and cosmic ray particles that produce new species via photolysis/radiolysis processes, affect their structure which may change, and induces desorption of molecules and radicals from these grains. These energetic events can be simulated in the laboratory for a better understanding of astrophysical processes. This talk will be dedicated to describe astronomical observations of ices. Then it will focus on some aspects of the possible evolution, in an astrophysical context and based on laboratory experiments, of the interstellar ices physico-chemical evolution resulting from the interactions with swift ions and photons, including recent experiments on main ice species to complex organic molecules sputtering,

Etude expérimentale de la formation du manteau moléculaire à la surface des poussières froides

François Dulieu
LERMA

Le gaz et la poussière sont deux composantes essentielles du milieu interstellaire, et de la formation des étoiles et des planètes. Leur interaction est complexe et les atomes et molécules peuvent se condenser à la surface des grains modifiant dans le même temps la composition du gaz et l'évolution chimique qui s'y déroule.

Les possibilités de diffusion et de réaction à la surface des grains transforment également le gaz qui s'accrète, et donne naissance aux manteaux de glace, dont l'eau et le CO₂ sont les éléments observés les plus abondants.

Depuis une dizaine d'année, notre équipe étudie le collage, la diffusion, la réactivité et la désorption des atomes et molécules sur des surfaces d'intérêt astrophysique. Durant mon exposé j'illustrerai ces étapes essentielles, et les mécanismes clés que nous avons mis à jour. Enfin, le rôle particulier de l'eau dans la construction du manteau de glace sera discuté, notamment ses propriétés de dissipation d'énergie et de catalyse.



Formation du premier sucre (glycéraldéhyde) par des processus radicalaires dans les glaces interstellaires/cométaires

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Les observations du milieu interstellaire ont conduit à l'identification de plus de 200 molécules. Parmi celles-ci, une cinquantaine appelées molécules organiques complexes (MOC), possèdent au moins six atomes (H, C, N ou O). Dans les régions de formation d'étoiles, ces MOC sont susceptibles d'être incorporées dans le matériau de formation de petits corps, tels que les comètes, les astéroïdes ou les planétésimaux. Parmi l'ensemble des MOC détectées à ce jour, le glycolaldéhyde $\text{HOCH}_2\text{OHCHO}$ (GA) et l'éthylène glycol $\text{HOCH}_2\text{CH}_2\text{OH}$ (EG) sont les plus complexes [1]. Récemment, ces deux molécules ont pu être identifiées dans l'environnement de la comète Tchouri par l'instrument COSAC de la sonde Rosetta.

Des résultats de laboratoires récents démontrent que ces deux molécules peuvent être efficacement formées par des mécanismes radicalaires initiés par des processus non énergétique (hydrogénation) ou énergétiques (UV, électrons, etc) [2].

Dans cette étude expérimentale et théorique, nous nous sommes intéressés aux mécanismes de formation des homologues supérieurs du GA et EG le glycéraldéhyde $\text{HOCH}_2\text{CH}(\text{OH})\text{CHO}$ (GCA) et le glycérol $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ (GCO) à partir de l'irradiation d'analogues de glaces interstellaires contenant du formaldéhyde. Les radicaux ne sont cependant pas faciles à étudier en raison de leur très grande réactivité, même à basse température [3]. Dans le but de plus facilement contrôler les processus de réaction, nous avons utilisé pour cette étude, la technique d'isolation en matrice cryogénique de gaz rares. Dans ces conditions nous sommes capables de piéger les radicaux et de les isoler les uns des autres à très basse température (10 K). Les radicaux formés peuvent être alors aisément caractérisés par spectroscopie infrarouge ou RPE. Par chauffage rapide de l'échantillon à 35 K, le gaz rare (argon) sublime et les radicaux ainsi libérés de leurs cages matricielles réagissent pour former les MOC GA, EG, GCA et GCO par des processus radicalaires comme cela se produit sur les grains interstellaires [4]. Ces études expérimentales sont complétées par des calculs quantiques permettant une meilleure description des mécanismes de formation des MOC détectées dans nos expériences.

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Deposition and annealing of interstellar ices: a neutron scattering and molecular dynamics study

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Water is one of the most abundant molecules in space and is seen in the form of molecular mantles covering interstellar dust grains. These so called "dirty-ices", are formed in cold and dense regions of the interstellar medium by adsorption of the surrounding gas molecules onto silicate dust particles. During their deposition, these ices form in a highly-porous and amorphous state called Amorphous Solid Water, but during the evolution of the interstellar clouds towards star formation, temperature and pressure increase what can induce several physical and chemical processes within the ice layer. This can strongly impact the physical conditions of the interstellar medium like its extinction but also the chemical abundances in both the solid and gas phase. Studying the structural properties of these ices and especially their porosity is therefore crucial to constrain the physical and chemical evolution of the ISM.

In order to treat these questions, we developed a mixed theoretical and experimental approach using state-of-the-art techniques to constrain the ice microstructure during both its deposition and heating upon desorption. Neutron scattering experiments[1] and molecular dynamics[3] results will be presented and draw a reasonable scenario schematized in Figure 1 about ice microstructural evolution in the interstellar medium and to give better constraints to astrochemical models.

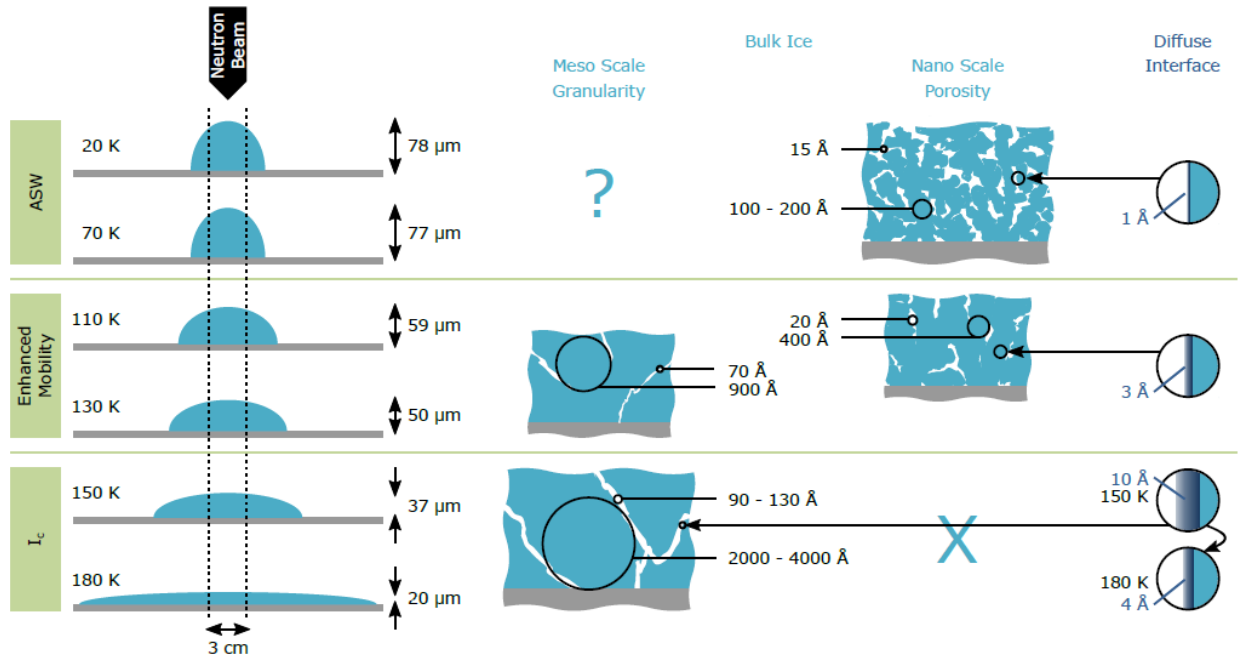


Figure 1 Cartoon summarizing the temperature induced structural changes in ASW. [2]

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Energetic processing of hydrocarbons molecular species by ionizing radiation: towards the formation of cyclic species

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Recently, Cassini-Huygens mission brought interesting results concerning one of Saturn's biggest satellites, Titan. In fact, it has been shown that this moon's typical orange-brownish haze layers could be due to the presence of aerosols. These aerosols are essential for Titan's climate, radiation balance and atmosphere chemistry. The formation of such aerosols is a complex process ranging from the molecular scale to large particle scale. Polycyclic Aromatic Hydrocarbons (PAHs) have been identified by Cassini's spectrometers. PAH and their clusters are important components in terrestrial soot formation and their presence in Titan's atmosphere can be considered as a nucleation agent, which triggers aerosol formation in the low temperature atmosphere. However, since it is mainly composed of nitrogen, methane and a small amount of more complex hydrocarbons, understanding the way such PAHs are formed is mandatory [1].

In order to understand the formation process of larger particles, we have studied collisions of low energy ions with loosely bound clusters of molecules. We aim to analyze either the fragmentation processes - which occur due to the transfer of energy and charge - and on the other hand, the complementary processes which lead to molecular growth and the formation of new, larger, covalently bound molecules. These processes are based on the energy transfer into the heavy particle system (nuclei). In the case of ion collisions, this can take place either by electronic excitation or by the direct knockout of an atom from the molecule. In the first case, the process ends up in longer time scale via coupling into vibrational motion degrees of freedom, while in the latter we obtain a prompt (fs) removal of atoms during the ion-molecule collision. By the knockout of an atom, highly reactive radicals and molecular species are formed which on very short time scales ($\leq$ ps) react with their neighbor molecules in the cluster. When several atoms are kicked out along the ion trajectory in the cluster, large covalently bound systems can be formed.

We present results on cluster systems containing linear chain molecules like butane and butadiene. We will discuss the formation of ring structures and the path to aromatic molecules. The irradiation of hydrocarbons clusters using different radiation sources (electrons, ions and UV photons) allows to determine the balance between ionization induced reactivity and collision induced one. The latter is the typical collision occurring in Titan's atmosphere involving slow and heavy ions (few keV O cations). It has been shown that this triggers reactivity, as observed in C₆₀ clusters [2] or PAH ones [3].

References

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Linking ice observations to laboratory studies of ice structure

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Ice in the interstellar medium exists in a range of compositions and structures depending on its local environment and physicochemical history. From its formation in molecular clouds to its incorporation into protoplanetary disks and eventually into planetary systems, ice is subject to energetic processing which will modify its structure, composition, and state.

Interstellar ices are observed principally via their IR absorption bands along lines of sight towards continuum point sources. Information about the observed ices, including the determination of their molecular-level structure and composition, can be inferred by comparison to laboratory experimental and theoretical studies, most directly via IR spectroscopic studies. In this talk I will present some recent laboratory studies of ices, using examples of ice mixtures and selective irradiations to show how, despite its broad absorption features, we can extract precise information about an ice's structure using only IR spectroscopy. Studies of this type will be critical in interpreting data from future observations, including those from JWST, whose higher sensitivity and spectral resolution will allow us an unprecedented insight into the nature of interstellar ices.

Adapting heterogenous catalysis calculations to the astrochemistry world

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The role assigned to icy grains in the interstellar chemistry evolution has been significantly enlarged in the last decade. Since the methods available to get some insight into this new facet of astrochemistry were issued from other domains, they had to be adapted to the constraints of a very specific environment. To represent water ices and evaluate the interactions, reactive or non-reactive, with atoms and molecules, two types of simulations could be used: the cluster approach or the solid state approach. Here we focalize onto the second one. All the simulations presented have been carried out with the Vienna ab initio simulation package (VASP) (Kresse & Hafner 1993; 1994).

A/ Methodological aspects

- 1) Solid state computational methods for *molecular* crystals: a few necessary adaptations
 - a) The basis of this treatment relies on the generalized gradient approximation (GGA) in the form of the Perdew and coworkers (1996) exchange-correlation functional (PBE). The effect of introducing part of HF exchange has to be considered.
 - b) To get a better description of the weak electronic effects implied in most of the reactions (long-range van der Waals interactions in addition to hydrogen bonding), we have to use the corrective scheme initially developed by Grimme and coworkers (2010).
 - c) The core electrons are kept frozen and replaced by pseudopotentials generated by the plane augmented wave method (PAW), and plane wave basis sets are used.
- 2) Ices modeling: a decisive but controversial step for the reliability of the results
 - a) Modeling solid water has attracted increasing attention in the past fifteen years. Levering on the conclusions of these works, we used a periodic representation of solid water in the form of hexagonal ice *Ih* composed of bi-layers of water molecules. The ice surface was described by the (0001) Miller indices. This choice of an apolar ice satisfying the Bernal-Fowler arrangement is computationally relevant.
 - b) However, the choice of using pure crystalline ices might be considered questionable; a representation of amorphous ices or at least irregular surfaces has to be possible. This problem will be debated.

B/ Applications to space chemistry

- 3) A key parameter: The adsorption energy of molecules *on interstellar surfaces*
 - a) The link between produced and observed interstellar abundances (ices trapping versus MEP)
 - b) Surfaces modeling versus TPD experiments (defects influence)
- 4) Reactivity of interstellar molecules *on water ice surfaces*
 - a) Mediation of water ices in the reaction: the case of HCN/HNC formation
 - b) Reactivity with OH issued from ice radiation breaking
- 5) Storage and formation *into the bulk* of water ices
 - a) Confinement of O₂ and S₂ in the ices of comet 67P
 - b) Endogenous origin for Na, K, Ca in Europa atmosphere

Ammonium salts detected on the surface of comet 67P/Churyumov-Gerasimenko, relics of interstellar ice chemistry?

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The nucleus of comet 67P/Churyumov-Gerasimenko exhibits a broad spectral reflectance feature around 3.2 μm , ubiquitous throughout the surface, whose attribution has remained elusive since its discovery [1,2]. Based on laboratory experiments, we have shown that this absorption band is mainly due to ammonium (NH_4^+) salts mixed with the dark desiccated surface material of the cometary nucleus. The depth of the band is compatible with semi-volatile ammonium salts being a major reservoir of nitrogen in the comet, which could dominate over the refractory organic matter and volatile species. Consequently, the abundance of nitrogen in this comet may be closer to the solar elemental composition than previously thought [3].

How, when and where these ammonium salts formed before being incorporated in the cometary dust? Ammonium salts have been tentatively detected in the environment of proto-stars [4] and numerous laboratory experiments have shown that they can be produced via acid-base reactions of NH_3 in ices as cold as 10 K [5]. Therefore, their detection on comet 67P suggests a possible compositional link between comets and the proto-solar nebula. Were these salts mostly formed in the interstellar ices? or in the proto-planetary disk? or in the comet, during the thermal processing of the ices? Tackling this issue of the origin(s) of these ammonium salts requires the combination of further experimental and theoretical studies (mechanisms, kinetics) to improve numerical models of the evolution of icy grains throughout these stellar phases, and future observations to search for their spectral signatures in these environments.

If they form early on, these ammonium salts might influence several properties of astrophysical ices, their chemical evolution (new chemical pathways, evolution during irradiation?), exchanges with the gaseous phase, as well as the coagulation efficiency of icy-salty grains to form planetesimals.

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Contribution of the DFTB scheme to the modeling of water clusters

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The Density Functional based Tight Binding (DFTB) scheme is an approximate DFT method which allows to describe large systems or run long on-the-fly molecular dynamics simulations. In this respect, it allows the determination of properties requiring extensive simulations such as finite-temperature spectra or thermodynamic properties. In this talk, we will focus on the description of water clusters within the DFTB scheme in its Self Consistent Charge formulation [1]. Describing intermolecular interactions within such clusters is a challenge and we had to modify the initial SCC-DFTB potential in order to insure their proper description [2]. Details about the potential will be given. Insights into the developed methodologies used to determine their structures and retrieve macroscopic properties will also be provided. Finally, applications of astrophysical interest will be detailed, focusing on water clusters/ice interacting with polycyclic aromatic hydrocarbons (PAHs) [3,4,5]. We will discuss to which extent the obtained computational data can be compared to experiments/observations.

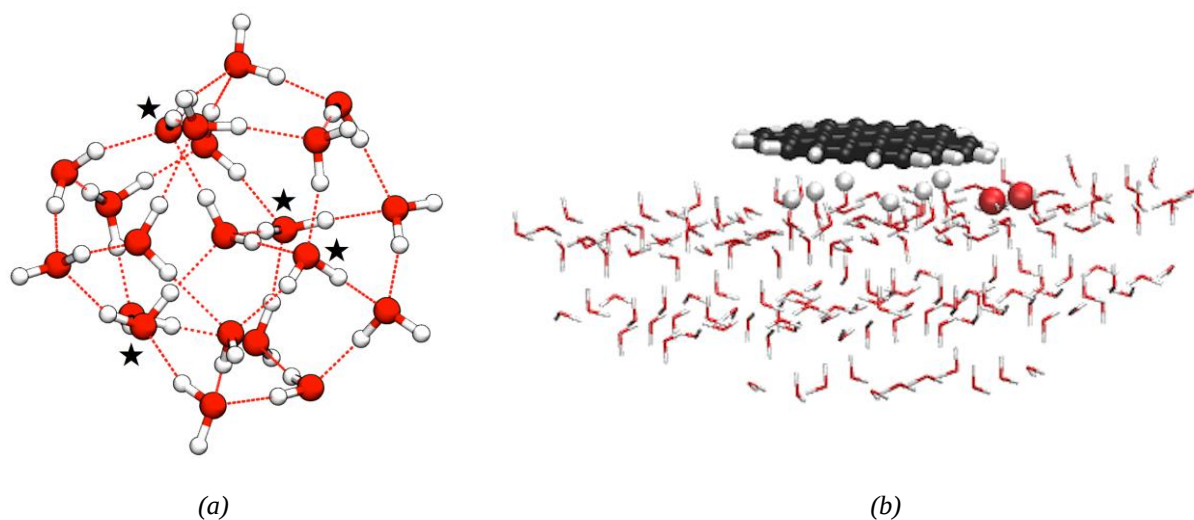


Figure 1 Examples of SCC-DFTB optimized structures of (a) $(\text{H}_2\text{O})_{21}\text{H}^+$ [2] and (b) ovalene adsorbed on hexagonal ice [4] (H and O atoms of the ice surface interacting with the PAH are highlighted)

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GRAINOBLE - Un modèle astrochimique gaz-grain multicouche

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De nombreux modèles astrochimiques liant la chimie en phase gazeuse à la chimie de surface ont été développés depuis plus de 30 ans afin d'expliquer la composition chimique des glaces interstellaires et la présence de molécules organiques complexes saturées observées dans les nuages moléculaires froids et les zones de formation stellaire. Le développement de ces modèles s'effectue maintenant en étroite collaboration avec des chimistes théoriciens et expérimentateurs afin d'obtenir des contraintes précises sur les processus physiques et chimiques survenant au sein des glaces hétérogènes. J'effectuerai dans cette présentation une revue historique des modèles astrochimiques ainsi que des différentes méthodes associées afin de traiter les processus physico-chimiques survenant à la surface des grains interstellaires. Je prendrai ensuite l'exemple du modèle astrochimique GRAINOBLE développé depuis dix ans, offrant un compromis entre complexité chimique et suivi réaliste des processus au sein des glaces. Je décrirai ses principales caractéristiques et je discuterai les principaux résultats obtenus avec ce modèle.

Theoretical description of interstellar ices from a multimethod approach

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Even if the ISM remains a cold environment with only few energy available, dynamics effects cannot be neglected since the surface state may be significantly altered due to thermal energy dissipation. It is possible to carry electronic structure calculations on reduced and distorted structures that may reproduce somehow a thermally relaxed surface. Classical molecular dynamics based on a semi-empirical potential remains a method of choice to account for explicit dynamical effects and for large scale surfaces. Within the classical description of the intermolecular forces, only physisorption is accessible. This limitation can be overcome through the combination of dynamics/force field simulations and Self-consistent charge density functional tight binding (SCC-DFTB) calculations. This will be illustrated in the case of the adsorption of PAHs on crystalline and amorphous ices. We will present a complete description of PAH-ice interaction in the ground electronic state at low temperature, providing the binding energies and barrier heights necessary to the on-going improvement of astrochemical models.

ACKNOWLEDGMENTS

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Modèles et données de l'astrochimie de surface

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La chimie de surface interstellaire est probablement le champ de recherche en astro chimie qui présente le plus de degré de progression possible. D'une part, les contraintes observationnelles sont peu nombreuses (par rapport aux observations dans le gaz) et difficiles à interpréter. D'autre part, les expériences de laboratoire indiquent un comportement des espèces dépendant très fortement de l'environnement et donc des conditions expérimentales à explorer très vastes. Pour ces raisons, les modèles astrochimiques doivent simplifier les processus de surfaces à un degré dont le réalisme n'est pas bien mesuré. Dans cet exposé, je présenterais les formalismes actuellement utilisés dans ces modèles, leurs limitations et la marche de progression possible.

Stability of PAH clusters

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We have studied the thermal evaporation of positively charged pyrene clusters $(Py)_n$ for sizes between $n=2$ and $n=40$. Charged pyrene clusters are produced in a gas aggregation source [1] and are thermalized right after their production. Their temperature can be varied from 25 to 300 K. We use TOF mass spectrometry techniques to mass select the thermalized clusters and characterise their evaporation as a function of their initial temperature. Evaporation manifests itself in the TOF mass spectra as peaks appearing at smaller sizes.

Phase Space Theory (PST) is used to calculate microcanonical evaporation rates, which are in turn used to simulate the temperature dependant evaporation probability.

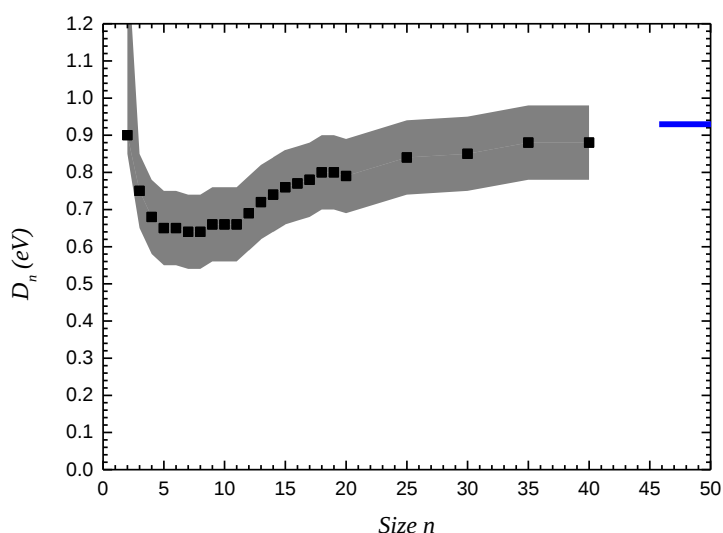


Figure 1 Dissociation energies of Pyrene clusters obtained by best fit of the experimental data using PST. The grey shaded area represent the uncertainty in the determination of the dissociation energies. The horizontal blue line is the vaporization enthalpy of bulk Pyrene at 298 K [3].

The parameters entering the PST, such as harmonic frequencies, are obtained from DFTB calculations [2]. The only free parameter is the dissociation energy D_n , which is therefore deduced by best fit of the experimental data.

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UV and X-ray induced desorption from water ice

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Non-thermal desorption processes play a key role in the exchanges between the gas phase and the icy solid phase of cold regions of the interstellar medium, where a lot of molecules are expected to freeze out on dust grains with the temperature forbidding their thermal escape. These processes have been used to explain otherwise puzzling gas phase observations of simple molecules like CO in dense cores or cold H₂O in outer parts of protoplanetary disks. They are also invoked as ways to get complex organic molecules (COMs) presumably formed on grains into the gas phase. Considerable experimental efforts have therefore been devoted to the understanding and quantification of these processes, in particular specific ones such as UV photodesorption and chemical desorption.

Here we will present experimental results on photodesorption by UV and X-ray photons applied to the case of water ice, the main component of ice mantles. In each case the different desorbing species are quantified, with derivation of astrophysically relevant quantities, and the mechanisms discussed. In the UV range the important role of chemistry in desorption is highlighted through temperature and isotope effects. In the X-ray range the Auger electron scattering dominates neutral desorption but not ion desorption.

Gas phase versus ice formation of amines: Experiments, theory and tentative search in the interstellar medium

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Beyond NH₃, only one primary alkylamine, CH₃NH₂, has been identified in the ISM and the reason why is still not understood: it could occur in gas phase or at the surface of interstellar grains, which are often covered by ices. Considering that the most efficient chemical transformation of the molecular mantle during its formation on grains is hydrogenation, the formation of amine by reduction of nitriles/isonitriles seems intuitive. In molecular clouds at ~10 - 20 K, H atoms are abundant and highly mobile on the surfaces. Full hydrogenation of HCN/HNC, which has been studied both in the gas phase[1] and on HCN ice[2] leads to the same end product, methylamine.

In order to take into account any possible difference between the formation of primary and secondary amines, we investigated, at both the experimental and theoretical levels, the hydrogenation processes of CH₃CN and CH₃NC, which would lead to the simple primary CH₃CH₂NH₂ and secondary CH₃NHCH₃ amines, (i.e. ethylamine and dimethylamine respectively).

The energetics of the hydrogenations paths, each composed of four successive elementary steps, were obtained using density functional theory, after benchmarking against high level post Hartree-Fock procedures. On the way to CH₃CH₂NH₂ we found that, the first addition, though exothermic by 20 kcal.mol⁻¹, is opposed by an activation barrier of ~8 kcal.mol⁻¹: this should be considered as a real obstacle to the reaction. By contrast, on the way to CH₃NHCH₃, reaching the first transition state requires less than 3 kcal.mol⁻¹, whereas the barrier to the third hydrogenation is only 4.5 kcal.mol⁻¹. Therefore hydrogenation of CH₃NC is probable, at least by tunneling effect. These findings are in agreement with experimental results, carried out under ultra-high vacuum, in which CH₃CN (or CH₃NC) and H atoms are co-deposited onto gold surfaces: CH₃CN does not react with H atoms, whereas the hydrogenation of the isonitrile works all the way through dimethylamine. In presence of H₂O, the formation of dimethylamine is clearly enhanced, but our calculations based on a continuum modelling failed to reproduce this trend: the reasons why will be discussed, and some clues to tackle this problem will be presented.

Observational results for molecules relevant to this study are also reported.[3]

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Amorphous Solid Water particle production for collision experiments

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Planet formation processes are experimentally investigated by low velocity collisions between protoplanetary analogues produced in the laboratory. Previous collision studies have employed both silicates [1] and crystalline ice particles [2]. The latter yields sticking probabilities that are too low to account for the observed rates of planet formation leading to the so called “bouncing barrier” [3]. Nevertheless, proto-planetary disk particles may comprise both amorphous and crystalline ice material. Therefore, the study of amorphous ice particle collisions is vital to our understanding and has never been achieved because of the difficulty to produce, store and use such samples. Our work aims to design and use an experiment to produce μm HGW particles (Hyper-quenched Glassy Water), one of the three low density forms of amorphous water. We will do so by spraying water droplets in a cryoliquid which is liquid ethane. This technique has been developed by Cryobiologist to freeze samples in their living (*ie* not crystalline) state, but never with astronomical purposes. Those particles will be used as protoplanetary analogues in microgravity for collision experiment.

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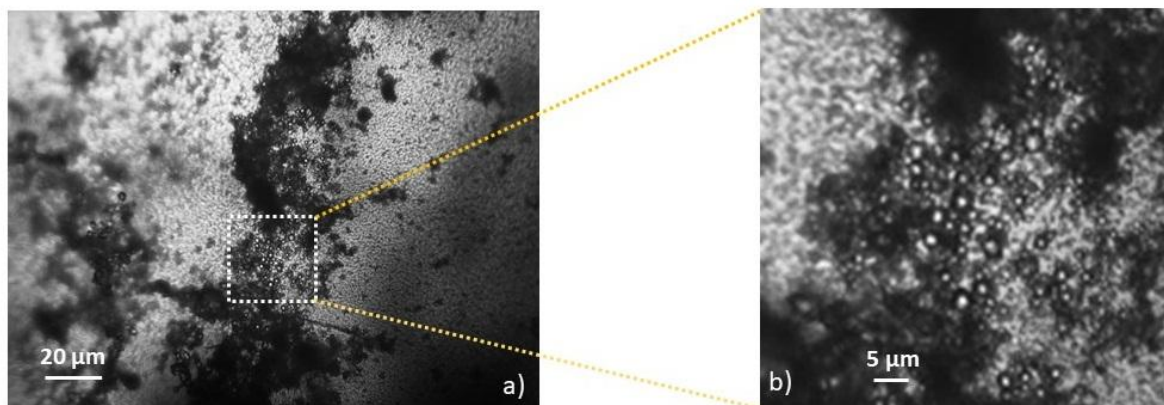


Figure 1: Optical microscopy image of ice particles produced in liquid Nitrogen

Ammonia ices under low-energy electron irradiation - Towards quantitative desorption rates and effective cross sections

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NH₃ is known to be a major component in ice mantles in molecular clouds with up to ~15 % of H₂O in certain regions of the interstellar medium [1]. Model predictions cannot account for the abundance of NH₃ [2], suggesting that desorption or conversion to other compounds should be considered. Among the various thermal and non-thermal mechanisms responsible [3], this study is dedicated to processes induced by low energy electrons (LEE, energy < 20 eV) [4]. LEE interactions with matter are considered to be the primary driving force in many radiation-induced desorption and chemical reactions in ices [5].

As schematized in figure 1, multilayers of NH₃ isotopologues (¹⁴NH₃, ¹⁵NH₃, and ¹⁴ND₃) (~10 ML) were deposited on copper at 28 K and crystallized under annealing at 60 K. High-Resolution Electron Energy Loss Spectroscopy (HREELS) and Temperature Programmed Desorption (TPD) were used to control the film morphology and estimate film thickness, respectively. LEE irradiation (1-20 eV) was performed at 28 and 60 K. Electron Stimulated Desorption (ESD) was used to detect neutral fragments/molecules desorbing during irradiation while HREELS and TPD were used to characterize processed residues.

The desorption of intact NH₃ was observed which resulted in the direct erosion of the film proceeding through a mechanism consistent with desorption processes induced by electronic transition (DIET). Different fragmentation and recombination processes were also observed as evidenced by the detection of neutral radicals NH_x (x = 1,2), and stable molecules N₂ and H₂. Aside from desorption, a wealth of chemical processes was also observed at 13 eV. Temporal ESD at this energy allowed for the estimation of the effective cross section of NH₃ desorption and observing the delayed desorption of N₂ and H₂. TPD analysis of the residues also provided evidence of diazene N₂H₂ and hydrazine N₂H₄ synthesis in the film.

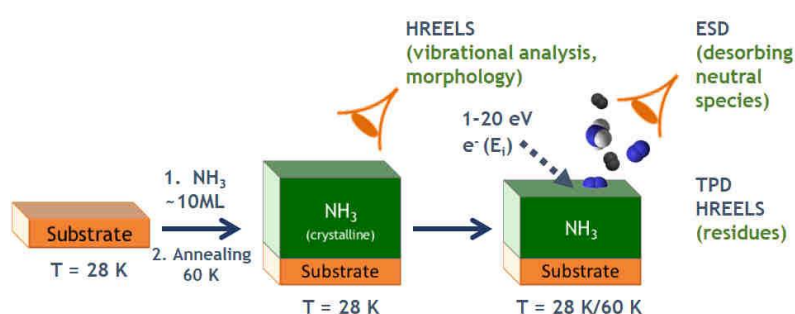


Figure 1 Scheme of the procedure used to study electron-induced processes in molecular layers of ammonia and its isotopologues

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PAHs on/in water ice: structures, energetics and spectra from FTIR experiments and a multi-method theoretical study

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Polycyclic Aromatic Hydrocarbons (PAHs) have been proposed to be the carriers of the Aromatic Interstellar Bands (AIBs), a set of infrared (IR) emission bands observed in the [3 - 15 μ m] range in many regions of the interstellar medium (ISM). In dense environments, PAHs are likely to condense onto or integrate into water ice mantles covering dust grains and to contribute to the complex grain chemistry [1]. Understanding the role of ice in the processes involving adsorbed PAHs is therefore a key issue in astrochemistry. Our joint theoretical (classical molecular dynamics/force field simulations and SCC-DFTB calculations) and experimental (matrix isolation/solid phase FTIR spectroscopy) study has given rise to several conclusions, namely: the role of water clusters [2] and of the ice structure [3] on the photo-reactions of PAHs with water ice. We will present evidence of how the surface of amorphous solid water (ASW) is perturbed by the adsorption of PAHs [4] and a complete description of PAH-ice interaction in the ground electronic state at low temperature, providing the binding energies and barrier heights necessary to the on-going improvement of astrochemical models [5a]. The influence of ice on the ionization potential (VIP) of PAHs [5b] will be discussed, together with its astrophysical implications.

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Radiolysis of COMs in condensed phase

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Ices are omnipresent in cold regions in space (comets, dust grains, transneptunian objects, surfaces of planets and their satellites). Such ices are mainly formed from small molecules (water, nitrogen, carbon oxides, methane etc.); also larger, complex organic molecules (COMs) may be present. Temperatures of objects containing COMs cover a wide range, from 10 K in dense molecular clouds, through 25 K to 150 K in the outer Solar system, up to >300 K in the inner Solar system. Ionizing radiation (UV photons, electrons, ions from solar wind and cosmic rays) induces physicochemical processes such as radiolysis and subsequent formation of new molecules. At CIMAP (Caen, France), using different beam lines (ARIBE, IRRSUD, SME) of the GANIL facility, and at UNILAC of GSI (Darmstadt, Germany), the interaction of swift highly charged heavy ions with astrophysical ices was studied in a wide projectile energy range from keV to GeV [1,2]. We present results on the radiolysis and radiosensitivity of nucleobases (adenine, cytosine) at different temperatures (15-300 K). We also discuss the (still open) question if the presence of water (omnipresent in space environments), has a protective effect or, on the contrary, enhances radiosensitivity [2]. To this aim, icy mixtures of water and pyridine at different concentrations were irradiated.

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**Ion radiation in icy space environments:
Synthesis and Radioresistance of Complex Organic Molecules**
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