The Astrochemical Week
COST Action CM1401
Faro / Olhão

Portugal

16-20 January 2017

`https://astrochem2017.sciencesconf.org/`

Contents

The region of Olhão

Olhão is a major port and actually the largest fishing port in the Algarve. It is full of character with Moorish-style houses, an influence from the commercial links with Africa. Although Olhão only really became a town of note in the 19th century, it was first mentioned in 1378. At this time it would have been a very small fishing settlement of a handful of people, living in huts made of wood, reeds and straw on the beach. By 1679 it was important enough to need the building of the fortress of São Lorenço to defend it from pirates. Olhão is a town of many 'faces' - if you approach from the fishing port side it looks, and is, very industrial and, unless you are particularly interested in fishing boats and warehousing it doesn't look very attractive.

However, around the corner from the dock the road runs along the water front and there is a long, very pleasant, paved promenade with cool gardens (Jardim Pescador do Olhanense) to escape the heat of the sun. If you are driving to Olhão there is plenty of parking along this water front road (Avenida 5 de Outubro) but do remember to get your pay and display ticket from one of the machines.

There are two market buildings side by side along the water front, which are a 'must visit' for the huge variety of extremely fresh fish and sea food straight from the port and the vast array of locally grown fresh fruit and vegetables. Olhão is well known for it's fish market, in particular and if you haven't got anywhere to cook some yourself, then try one of the numerous local cafes along the roadside nearby - you won't be disappointed!

The market halls are surrounded by pavement cafes and it's a great place to sit and enjoy the view of the boats moored along the water front in Olhão Marina and the sand spit beach ilhas of Armona and Culatra just a short distance off shore behind them. We have enjoyed lovely afternoons in Olhão, where we walked along the water front and through the gardens, sat outside a jazz cafe watching the boats, people cycling around and local people going about their day.

Next it's time to venture into the historic heart of Olhão and the easiest road to follow is directly across from the gap between the market halls. Here, many of the buildings are the elegant merchant's homes with wrought iron balconies, carved stonework and tile decorations and are such a contrast to the busy port area of Olhão. At the centre of the town at the end of Avenida da República, in the Praça da Restauração, is the church of Nossa Senhora do Rosário, built in 1698 with contributions from the fishermen when it was the first stone building in Olhão. It's a very graceful building with a baroque facade and somehow quite a surprise!

The building behind the church, on the other side of the square, is the Compromisso Marítimo -the fishermen's mutual society, which was founded in the 18th century - it is also home to the Olhão city museum. In a niche above the doorway is a statue of Nossa Senhora do Rosário (Our Lady of the Rosary).

While you are in this area there is another church at the back of the Compromisso Marítimo - the chapel of Nossa Senhora da Soledade which is 17th century and the original church of the then fishing village. In the surrounding narrow, cobbled streets are a wide variety of inviting shops and pavement cafes that tempt you to linger! Well, after the sightseeing you need a break! This historic area of the town is really rather picturesque and gives a totally different view of Olhão from the port and the fishermen's quarter.
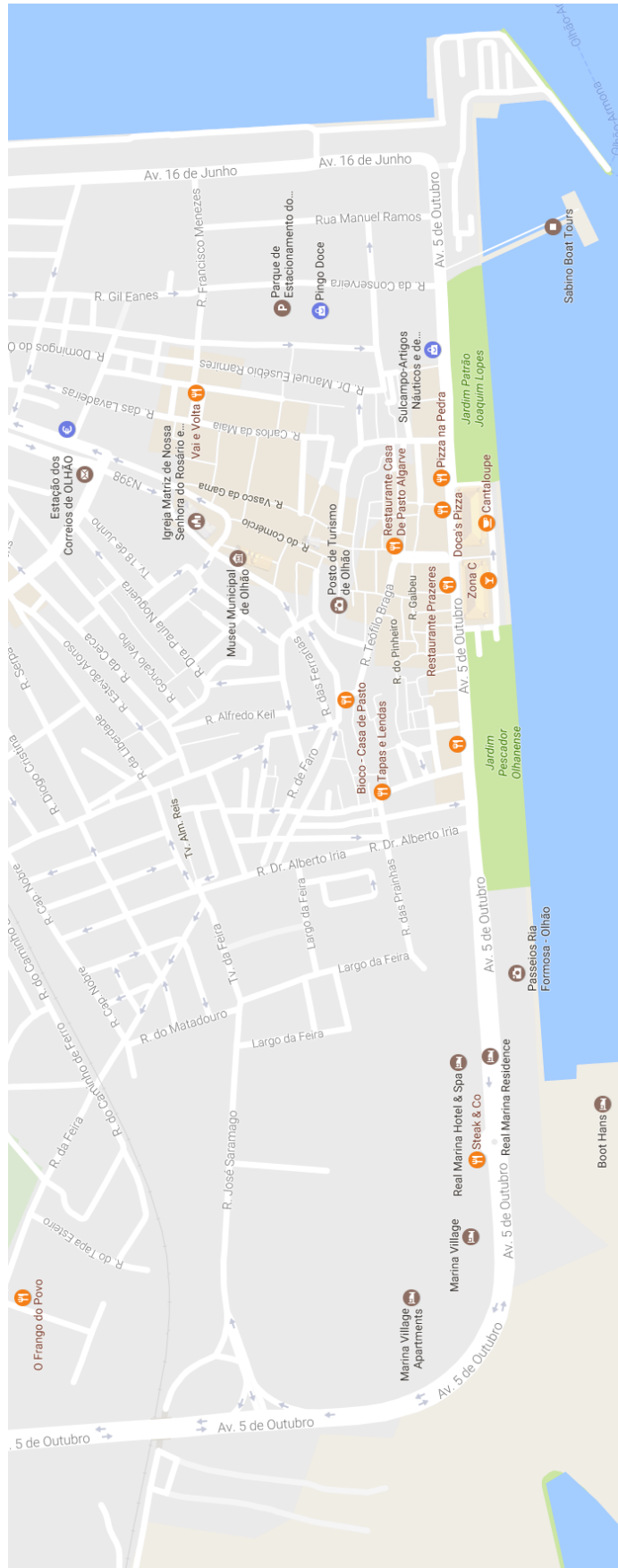
Olhão itself doesn't have a beach as it is on the Ria Formosa lagoon system but the ferries for the ilhas run from the quayside near the gardens at the eastern end of the market halls. There are regular services throughout the year, although fewer in number during the winter.

Ilha da Culatra is surrounded by beautifully clear water, with many species of fish, so it is perfect for diving and snorkelling. Ilha do Farol is not a separate ilha, but the area at the western end of Culatra where the lighthouse is ('Farol' meaning 'lighthouse' in Portuguese) and again offers visitors a large expanse of sand and warm water. Ilha da Armona, the closest ilha to Olhão, has a few restaurants and holiday chalets and large expanses of golden sand for a very relaxing day at the beach!

Olhão is definitely a city on the up as far as tourism is concerned, with new apartments and the 5* Real Marina Hotel & Spa at the western end of the water front and the Ria Shopping centre with it's 3 floors of shops and restaurants and cinema on the EN125 towards the town centre. There are also several companies offering a variety of boat trips to the ilhas, fishing trips and general coastal cruises as well as the regular ferries. Being close to Faro means short transfer times so you are on holiday before you know it! [1]

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[1]Taken from the site http://www.olhaouncovered.com/

Map of Olhão taken from https://maps.google.com/

WG2 - Chemistry inside ices

Program

09:00	Dmitry Semenov/Herma Cuppen	Introduction
09:25	Patrice Theulé	Chemistry in the ice mante
10:10	James Stubbing	Adsorption and Thermal Processing of Benzene and Toluene Ices
10:30		**Coffee break**
11:00	Stephane Coussan	Restructuring of ice by means of IR irradiation
10:50	Joëlle Mascetti	Photochemistry of PAH in water ice and of PAH: water complexes
12:10	Vincente Timon	Theoretical models for interstellar carbonaceous dust and icy mixtures
12:30		**Lunch**
14:00	Vianney Taquet	Modelling of physical and chemical processes in the bulk of interstellar ices
14:50	Tushar Suhasaria	CO2 ices in quiescent dark molecular clouds
15:10	Albert Rimola	From surface phenomena to inside bulks. Insights from a computational chemistry point of view
16:00		**Coffee break**
16:30	Gavilan	The XUV complex refractive indices of nitrogen-rich organics
17:00	Stephanie Milam	Ice observations with JWST
17:50		**Conclusion of the Workshop**

THE XUV COMPLEX REFRACTIVE INDICES OF NITROGEN-RICH ORGANICS

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The complex refractive indices of tholins, solids analogs to organic aerosols in the atmosphere of Titan, have been measured over a wide spectral range, including the soft X-ray, vacuum-ultraviolet (VUV), and the UV-Visible. The soft X-ray and VUV spectral ranges are in particular relevant to radiative transfer models of solar irradiation of primitive atmospheres and may elucidate the (anti-)greenhouse potential of photochemical aerosols. Thin films were grown using the PAMPRE capacitively coupled plasma setup [1]. Gas mixtures consisting of CH_4/N_2 -5:95 were used to simulate Titan's average atmospheric composition. To simulate photochemical aerosols in the primitive Earth, we used gas mixtures of $N_2/CO_2/H_2$ and $N_2/CO_2/CH_4$.

State-of-the-art laboratory techniques were employed to determine tholin refractive indices. These techniques include VUV ellipsometry (performed in collaboration with the Metrology Light Source in Berlin) and synchrotron X-ray spectroscopy (XAS, performed at the SEXTANTS beamline of the SOLEIL synchrotron). While VUV spectroscopy reveals new electronic transitions due to plasmon resonances in tholins, X-ray spectra reveal the C and O absorption K-edges of these solids. The refractive indices are compared to previous experimental data [2]. We will discuss the implications on the optical properties of tholins on the radiative modeling of astrophysical environments where nitrogen rich organics are abundant.

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[2] Khare, B.N., Sagan, C., Arakawa, E.T., Suits, F., Callcott, T.A., Williams, M.W., 1984a. Icarus 60, 127–137.

General Meeting

Program

Tuesday - 17 Jan 2017

08h30		**Registration**
09h15	João Brandão	Welcome address
09h25	Wiesenfeld	Report on 2 years of 'Our Astrochemical History'
09h50	Parker	Imaging O2 Astrochemistry
10h30		**Coffee break**
11h00	Jørgensen	
11h40	Vastel	WG1 and WG4 report
12h10	LW or Wing-Fai THI	Garching Theory meeting report
12h40	Coppola	State-to-state study of the $D+H_2$ (v=0,j) collisions and their astrophysical implications
13h00		**Lunch**
14h30	Richardson	Reaction rates & tunneling (provisional title)
15h10	Sahnoun	Explicitly correlated multi dimensional potential energy of $HNCO-H_2$ interacting system
15h30	Lopes	Gas-phase ion-molecule chemistry: controlled reactions of CH_3^+ and C_3N^-
15h50	Gronowski	Quantum chemical insight into the gas-phase reactivity of simple sulfur-bearing triatomic molecules
16h10		**Coffee break**
16h30	Brünken	Spectroscopy in cryogenic ion traps on molecular tracers for astrophysics
17h10	Bizzocchi	Doubly ^{15}N-substituted diazenylium: THz laboratory spectrum and fractionation models
17h30	Canosa	Reactivity of formaldehyde toward oh radicals at ISM temperatures
16h10		**Party / Poster Session**

Wednesday - 18 Jan 2017

09h00	Meisner	Reaction Rates and Kinetic Isotope Effects of the Reaction H_2 + OH $\rightarrow$ H_2O + H: Impact of Atom Tunneling and an Ice Surface
09h20	Juvela	Nuclear spin effects in the deuteration of ammonia
09h40	Mazankova	FTIR diagnostics of Nitrogen-methane atmospheric glow discharge used for a mimic of prebiotic atmosphere
10h00	Senent	Weak intramolecular interaction effects on the structure and torsional spectra of ethylene glycol, an astrophysical species
10h20		**Coffee break**
10h50	Marinakis	Rotational excitation of interstellar radicals (OH, CH, and PO) with He
12h00		**Boat from the hotel**
13h00		**Lunch at Farol (Lighthouse) Island**
15h30		**Boat back to the hotel**
17h00	Posters	
	Management Committee meeting	

Thursday - 19 Jan 2017
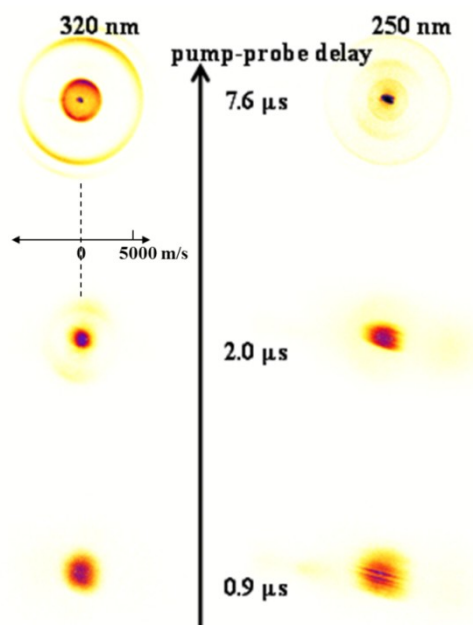
09h00	To be announced	
09h40	Cernuto	Destruction processes of complex organic molecules in the interstellar Medium (ISM)
10h00	To be announced	
10h20	García-Vela	Ab initio study of the photodissociation of radical molecules of astrochemical interest
10h40		**Coffee break**
11h10	Cuppen	WG2 Report
11h35	Fillion	WG3 Perspectives
12h00	To be announced	
12h20	Muchova	Theoretical modelling of photoemission in condensed phase
12h40	Fredon	Simulations of energy dissipation and non-thermal desorption
13h00		**Lunch**
14h30	Milam	Next generation airborne and space telescopes: JWST, SOFIA, and beyond
15h10	Michoulier	Adsorption of PAHs on interstellar ice viewed from molecular dynamics
15h30	Bromley	Reactivity of hydrogen on nanosilicate grains: the role of silicate stoichiometry and chemisorbed water
15h50	Andersson	Mechanisms of SiO oxidation: implications for dust formation
16h10		**Coffee break**
16h45	Core group	Report from MC meeting, Finances Prospects for 2017/2018
17h20	Brandão	Farewell and invitation to WG3
	Wiesenfeld & Jerosimovič	Invitation to next meeting and school

IMAGING O$_2$ ASTROCHEMISTRY

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Molecular oxygen, O$_2$, is a fascinating molecule involved in many processes occurring on Earth and the interstellar medium (ISM). Cold gases, which are observed in regions of the ISM where thermal desorption is negligible, may arise from photo-desorption from icy grains, especially in regions with high UV flux. In this study we carry out velocity map imaging (VMI) experiments[1] on ultraviolet photo-desorption of O$_2$ molecules and O atoms from an O$_2$-ice surface at 20K. The information we obtain should give more insight into similar processes taking place at icy interstellar grains. We have recently completed our "ice-machine" apparatus which combines the Velocity Map Imaging technique with an ultra-high vacuum ice surface setup with controlled doping and surface analysis by thermal programmed desorption. Using state selective ionization of desorbed molecules by REMPI and full 3-D velocity information from the imaging technique it is possible to gain more detailed insight into the processes occurring on ice surfaces. A set of VMI images of nascent O(^{3}P$_2$) atoms produced by laser desorption at 320 nm and 250 nm is shown in Fig 1. At early time delays between desorption and probe, a plume of O atoms (first O(^{3}P), slightly later O(^{1}D)) is observed as it passes the detection laser pathway. With a slightly longer time delay (2 µs), the O atom image begins to reveal a higher velocity component which we believe is the signature of electronically excited O$_2$ (a$^1\Delta_g$) molecules[2]. At the longer time delay (7.6 µs) the O atom plume has passed and a clear signature of relatively cold O$_2$ X($^3\Sigma_g$-) molecules leaving the surface remains. At the shorter desorption wavelength of 250 nm the O$_2$ (a$^1\Delta_g$) signal is stronger than at 320 nm. These observations and their underlying processes will be described in more detail in this talk. We acknowledge support by the NWO-CW TOP project 715.013.002 and collaboration with H. Linnartz (Leiden) and H. Cuppen (RU).

Fig. 1 Raw VMI images of O(^{3}P$_2$) atoms ejected from a 20K O$_2$-ice surface following laser desorption at 320 nm and 250 nm with the indicated time delay between desorption and detection 1.5 mm above the surface. The various rings in the images are signatures of hot O(^{3}P) atoms and O$_2$ X($^3\Sigma_g$-) and (a$^1\Delta_g$) molecules.

References

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[2] Z Farooq, DA Chestakov, B Yan, GC Groenenboom, WJ van der Zande, and DH Parker, *Photodissociation of singlet oxygen in the UV region* Physical Chemistry Chemical Physics **16**, 3305-3316 (2014).

EXPLICITY CORRELATED MULTI DIMENSIONAL POTENTIAL ENERGY OF HNCO-H2 INTERACTING SYSTEME

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2 Institut de Planétologie et d'Astrophysique de Grenoble (IPAG)
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In the goal of studing of HNCO by H_2 and calculating the rate coefficients,The collision potential energy surface (5D-PES) of the HNCO-H_2 interacting system is calculated at the explicitly correlated coupled cluster method with single, double and perturbative triple excitations (CCSD(T)-F12) in conjunction with the augmented correlation-consistent aug-cc-pVDZ basis set. This PES is incorporated into quantum dynamical calculations to give cross-sections for rotational transitions among the 22 first levels of HNCO. The exact quantum close-coupling (CC) method is used for total energies up 200 cm^{-1} . These rate coefficients are of great importance for the detection of HNCO in interstellar medium.

These cross sections are averaging by using the Boltzman velacity distributions to calculation rate coefficients at temperatures <50K.
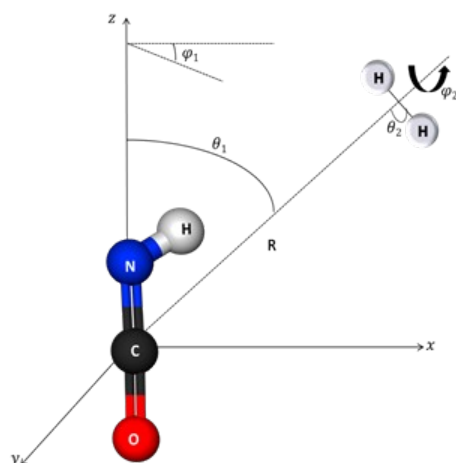

Figure 1: Jacobi coordinates of the HNCO-H2 system with respect to the HNCO center of mass, G, and principal axis (Gx, Gy, Gz).

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[3]On the accuracy of explicitly correlated methods to generate potential energy surfaces for scattering calculations and clustering: application to the HCl–He complex,Yosra Ajili, Kamel Hammami, Nejm Eddine Jaidane, Mathieu Lanza, Yulia N. Kalugina, François Lique and Majdi Hochlaf

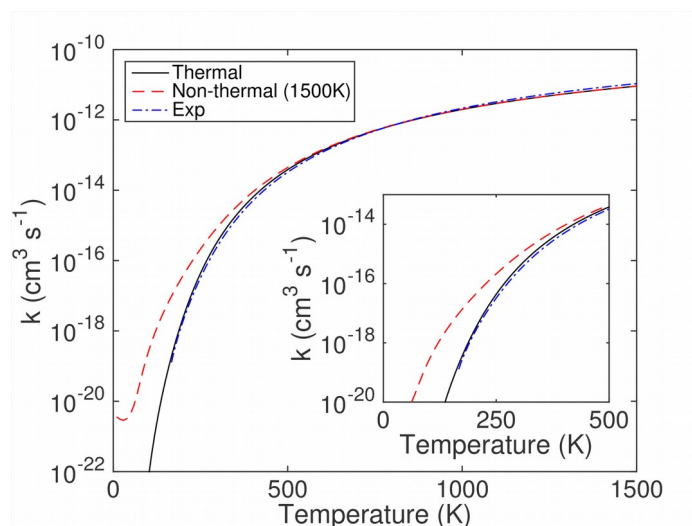# STATE-TO-STATE STUDY OF THE D+H_2 (V=0,J) COLLISIONS AND THEIR ASTROPHYSICAL IMPLICATIONS

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We report fully-quantum time-independent calculations for the collisional excitation and dissociation of H_2 by D, two astrophysically relevant processes. Our calculations are based on the recent H_3 global potential energy surface (PES) by Mielke *et al*. We do observe an increase of the reactive rate coefficients with increasing rotational state of the reactant at low temperature. At higher temperature, D+H_2(v = 0, j=0-5) → HD+H rate coefficients tend to be similar whereas for j > 5, the reactivity increase significantly. At low temperatures, the reactive process is negligible compared to the inelastic ones. The availability of rotationally resolved collisional data for chemical processes involving HD is fundamental for a reliable modeling of internal molecular states's kinetics; as a consequence, a proper and more realistic description of the HD formation and cooling mechanisms due to this molecular species is expected by the use of these new reaction rate coefficients, especially at low temperatures. In this direction, work is in progress on evaluating new collisional data for HD-H inelastic collisions.

Temperature dependence of the rate coefficients for the reaction D + H_2 → HD + H. Comparison between theory and experiments. The dashed line correspond to the thermal average assuming a non-equilibrium rotational distribution with characteristic temperature T_{rot} = 1500 K.

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GAS-PHASE ION-MOLECULE CHEMISTRY: CONTROLLED REACTIONS OF CH$_3^+$ AND C$_3$N$^-$

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In this contribution, we will present recent results concerning ion-molecule reactions of both cations and anions obtained with the CERISES set-up: a guided ion-beam experiment.

First, we will report on reactions of the CH$_3^+$ ion with several small hydrocarbon molecules (CH$_4$, C$_2$H$_2$, C$_2$H$_4$…). The originality of these experiments is to monitor the effect of internal degrees of freedom (vibrational, electronic) on reactivity. Control of the degree of internal excitation in the parent-ion is achieved by producing the CH$_3^+$ ions *via* direct photoionization of a molecular beam of CH$_3$· radicals and by tuning the energy of the VUV photon (DESIRS beamline, synchrotron SOLEIL). Branching ratios and absolute reaction cross-sections have been obtained for different reactive systems, and their dependence on vibrational and electronic excitation of the parent ion will be discussed [1]. This will guide us to identify the systems for which further state-to-state reactivity experiments are relevant. The CERISES experiment indeed also allows for pure state selection of the parent ion thanks to photoelectron-photoion coincidence techniques [2].

In addition to cations, it is now possible to study the reactivity of anions on CERISES. The first results obtained concern the reaction of the C$_3$N$^-$ ion with the acetylene molecule. In this latter experiment, we focus on the control of collision energy of the parent-ion with the reactant molecule. Three reactive channels leading respectively to C$_2$H$^-$, CN$^-$ and C$_5$N$^-$ have been observed. Although, formation of the last two products is exoergic, all reaction pathways exhibit large barriers as confirmed by the observation of energetic reaction thresholds for all of them [3]. The contribution of this reaction to the growth of larger anions is thus unlikely.

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[3] Lindén et al., J. Phys. Chem. A, (2016) **120**, 5337-5347

QUANTUM CHEMICAL INSIGHT INTO THE GAS-PHASE REACTIVITY OF SIMPLE SULFUR-BEARING TRIATOMIC MOLECULES.

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We present an analysis of potential energy surfaces representing stoichiometry of $CH_2N_2S^+$ and CH_2NOS^+, which describe hydrogenation of HCN and HNC by HNS^+ and HSO^+. In the course of these reactions, intermediate species of a particular stoichiometry can be formed for which a number of different isomers might exist. In our studies, we use high-level *ab initio* quantum chemical methods to explore the potential energy surfaces of selected sulfur-bearing cations potentially formed (as a short-lived intermediated species) over the course of astrochemically relevant ion-molecule reactions. Four stable isomers of CH_2NOS^+ stoichiometry were identified: $HS-NH-CO^+$, H_2SNCO^+, $HSNCOH^+$, $HNCSOH^+$. A similar number of stable isomers were identified for the $CH_2N_2S^+$ stoichiometry: H_2NCNS^+, H_2NSCN, H_2NNCS^+, and two conformers of $HSNCNH^+$. These cations appear to be crucial for identification of other reactions channels which may lead to creation of simple sulfur- and oxygen-bearing molecules, like H_2CS^+, $HSCO^+$, H_2NCO^+, HNCO. Reaction enthalpies, transition states between selected stable isomers, and all their dissociation channels were examined.

SPECTROSCOPY IN CRYOGENIC ION TRAPS ON MOLECULAR TRACERS FOR ASTROPHYSICS

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Molecular ions are important constituents of the interstellar medium. They are major drivers of the chemistry particularly in cold and dense molecular clouds, which are sites of star formation, and are valuable molecular tracers of the physical and chemical conditions in a variety of astronomical environments. Their identification in space relies on accurately known transition frequencies provided by laboratory spectroscopy. Conventional absorption spectroscopy has in the past successfully been applied for spectroscopic studies of molecular ions, but is often hampered by low number densities and spectral congestion due to the multitude of species produced at high excitation energies in the discharge cells used for their formation.

These limitations can be overcome by performing experiments on mass-selected ions in cryogenic ion trap instruments. In the Cologne laboratory astrophysics group we have in the past years developed sensitive action spectroscopic methods based on Laser Induced Reactions (LIR) [1]. For LIR measurements only a few thousand mass-selected ions are stored and cooled in a 22-pole ion trap, and their light-induced excitation is probed by the outcome of an endothermic ion-molecule reaction. Highly accurate ro-vibrational transition frequencies are obtained by using a narrow-bandwidth optical parametric oscillator (OPO) calibrated with a frequency comb in combination with the cold temperature of the ions [2]. In certain cases even purely rotational transitions can be measured with high-resolution either directly [3] or via a two-photon double-resonance scheme [4,5]. Very recently, our group used an even more general action spectroscopic scheme based on LIR, which utilizes a change of the rate of ternary He-attachment to the stored, cold ions depending on their internal ro-vibrational or rotational excitation [6].

In this talk we will give details on the experimental and methods development for vibrational and rotational ion spectroscopy in cryogenic traps, including recent results on, e.g., the spectroscopy of deuterated variants of CH_3^+ [5], and of reactive hydrocarbon radical ions of the form $C_nH_m^+$. We will also demonstrate the strong interplay of our laboratory work and astrophysical observations with selected examples, e.g. the confirmation of l-C_3H^+ in photon-dominated regions [7], of NH_3D^+ in a star-forming region [8], and the first detection of para-H_2D^+ and ortho-D_2H^+ in the cold molecular envelope around a young protostellar core [9].

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Doubly ^{15}N-substituted diazenylium:
THz laboratory spectrum and fractionation models

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Isotopic fractionation in dense molecular cores has been suggested as a possible origin of large ^{14}N/^{15}N ratio variations observed in the Solar System, depending on the object, the source of the material, and the molecular carrier. While chemical models can explain some observed variations with different fractionation patterns for molecules with –NH or –CN functional groups, they completely fail to reproduce the observed ratios in diazenylium (N_2H^+). The observations of doubly ^{15}N-substituted species could provide decisive hints for improving the chemical models of isotopic fractionation. The only N-containing molecule which can exhibit appreciable abundance of its doubly subtitued ^{15}N-form is N_2H^+, but the spectroscopic data for this isotopic variant are very scarce.

We investigated the rotational spectra of $^{15}N_2H^+$ and $^{15}N_2D^+$ in the laboratory well into the THz region by using a source-modulation microwave spectrometer equipped with a negative glow discharge cell. For each isotopologue of the H- and D-containing pair, nine rotational transitions were accurately measured in the frequency region 88 GHz – 1.2 THz. The analysis of the spectrum provided very precise rest frequencies at millimetre and submillimetre wavelengths, useful for the radioastronomical identification of the rotational lines of of $^{15}N_2H^+$ and $^{15}N_2D^+$ in the ISM. Furthermore, an extended chemical reaction network have been used to estimate what ranges of ^{15}N fractionation in doubly ^{15}N-substituted species could be expected in the interstellar medium.
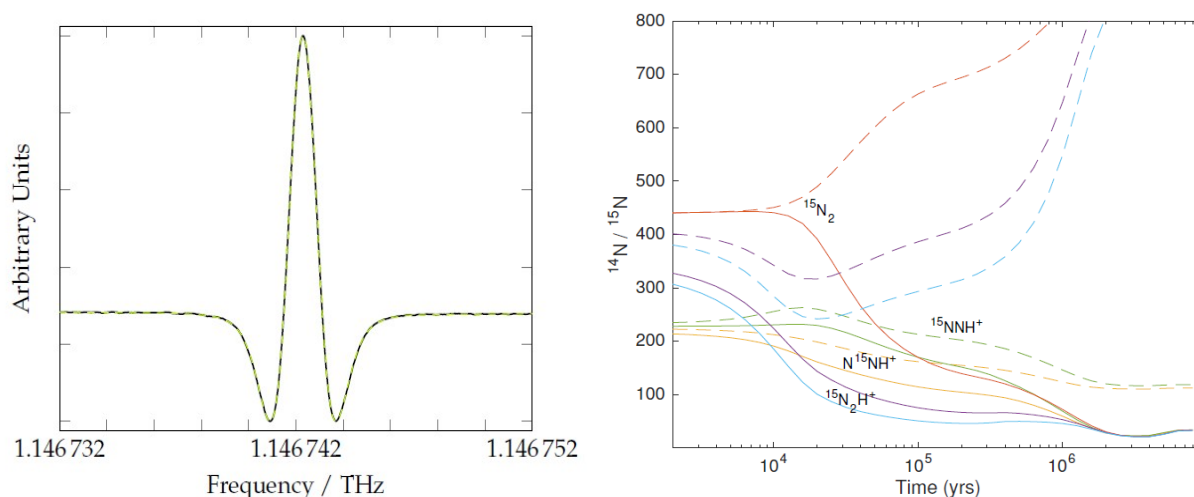
Figure 1: (*left*) Spectrum of the $J = 13 - 12$ transition of $^{15}N_2H^+$ (solid black line) and fitted profile (dashed line); total integration time: 300 s. (*right*) The ^{14}N/^{15}N ratio in the doubly substituted species and the singly substituted diazenylium, using different fractionation networks.

REACTIVITY OF FORMALDEHYDE TOWARD OH RADICALS AT ISM TEMPERATURES

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Complex Organic Molecules (COMs) have been identified in many interstellar environments. For quite a long time, COMs have been observed in "lukewarm" objects such as hot cores and hot corinos. Grain surface chemistry was claimed to be the source for the synthesis of such species during the warm-up of grains at temperatures > 30 K and subsequent desorption. In contrast, only a few observations were available in the cold gas environments until recently. Investigations of the dense core B1-b and prestellar cores shed a new light on the mechanisms responsible for the presence of COMs in such objects (T ~10 K) for which the previous mentioned formation process on grains does not hold. Gas-phase reactions (left apart at first sight) were reconsidered as a possible route to the formation of COMs in cold environments.

In this context we have focused our interest in the reaction of OH + H_2CO (formaldehyde) which we studied experimentally using the recently developed pulsed CRESU (French acronym meaning Reaction Kinetics in a Uniform Supersonic Expansion) apparatus of the University of Castilla-La Mancha (UCLM). The CRESU environment allows one to generate a wall-free ultra-cold supersonic gas flow by isentropic expansion through a Laval nozzle which ensures uniformity of the flow in terms of temperature and density for several tens of centimetres [1,2]. This chemical reactor is coupled to laser techniques for the production of OH by pulsed photolysis (PLP) and for its detection by laser induced fluorescence (LIF) [3].

We measured the total rate coefficient $k(T)$ for the disappearance of the OH radical in the presence of H_2CO in the temperature range 22 – 107 K and found that $k(T)$ increased by a factor of 6 when the temperature was decreased within this range. Combining our results with older investigations at temperatures higher than 200 K, a U-shape curve for $k(T)$ was obtained. This result will be discussed in the astrochemical context because it partly resolves the discrepancy between the observed HCO/H_2CO abundance ratio and the calculated one.

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DISSOCIATIVE CHARGE TRANSFER OF INTERSTELLAR DIMETHYL ETHER AND METHYL FORMATE IN COLLISIONS WITH He+

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Collisions with He+ are an important pathway for the decomposition of complex organic molecules in the interstellar medium (ISM). We have carried out dissociative charge transfer reactions of He+ with two O-containing organic molecules, ubiquitous in ISM: dimethyl ether CH_3OCH_3 (DME) and methyl formate $HCOOCH_3$ (MF). Since they have a prebiotic relevance, several models were developed to explain how these molecules are formed and destroyed in the ISM [1].

The reactions have been investigated by using the home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) apparatus. Absolute cross sections and product branching ratios have been measured as a function of the collision energy in the hyperthermal energy range (i.e. from about 0.1 to 7 eV). The presence of the molecular ion was not observed among the products for these reactions, which means that the nascent DME and MF radical cations are formed in a dissociative state. Insights on the charge transfer process for the system DME–He+ have been obtained by investigating the nature of the nonadiabatic transitions between the reactant and product potential energy surfaces. The PES has been represented by using a semi-empirical method in order to model the inter-molecular interactions [2]. The observed crossings confirm the experimental conclusion: He+ captures an electron from an inner valence orbital of the organic molecule, having binding energies about 12 eV higher than the HOMO. An improved Landau-Zener model has been developed in order to obtain the total integral cross section to be compared with the experimental results. Intermolecular interaction and electron densities of the orbitals involved in the reaction turned out to be key points to describe the dynamics of the dissociative charge transfer. A remarkable agreement is obtained between the experimental and calculated total cross sections at low collision energy, which is the most relevant range for the interstellar environment. These results represent a significant starting point to estimate rate constants for destruction of DME by collisions with He+ ions in the ISM at low temperatures.
Implementation of the same model on the experimental results for MF is in progress.

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REACTION RATES AND KINETIC ISOTOPE EFFECTS OF THE REACTION
H$_2$ + OH → H$_2$O + H:
IMPACT OF ATOM TUNNELING AND AN ICE SURFACE

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Atom tunneling plays a crucial role in reactions in cryogenic environments like in the interstellar medium. The reaction of H$_2$ with the hydroxy radical is one of the most important routes of water formation in astrochemistry although it possesses an activation energy of 24 kJ mol^{-1}. We present reaction rate constants of both the gas-phase reaction as well as the reaction on a water ice surface calculated with semiclassical instanton theory. The results are compared to harmonic transition state theory (HTST) to quantify the impact of atom tunneling [1]. For the gas-phase reaction we used a fitted potential energy surface [2]. For the reaction on the ice surface we used density functional theory coupled to TIP3P water using a QM/MM framework. We depict the importance of atom tunneling and ice surfaces for this reaction at the conditions in the interstellar medium.

Figure 1: Left: Arrhenius plot of the reaction of H$_2$ + OH → H$_2$O + H in the gas phase compared to the reaction on the surface. Right: Transition state structure of the reaction on a water ice surface.

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HCN hyperfine anomalies and the HCN/HC15N ratio

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Nitrogen is one of the most abundant and reactive metals in the ISM. Nitrogen bearing species are among the best tracers of the dense ISM. The $^{14}N/^{15}N$ ratio displays large variations in the primitive solar system which could be a sensitive probe of the conditions in the protosolar nebula. Therefore Identifying and characterising isotopic reservoirs in earlier stages, like prestellar cores, is fundamental. This requires reliable tracers of the isotopic ratio of the Nitrogen reservoirs.

HCN is arguably a highly desirable target: abundant, easy to detect, and a direct tracer of atomic Nitrogen [1]. The current work focuses on measuring $HCN/HC^{15}N$ directly, i.e. not depending on unreliable double isotopic measurements[2] (ex. $HCN/HC^{15}N$ = $H^{13}CN/HC15N \times 12C/13C$). The main difficulty lies in the high opacity of the main isotopologue. In particular, its rotational transitions present anomalies on their hyperfine ratios. These hyperfine anomalies are our key to measure the column density of HCN [3,4].

To solve this anomalies we have used an state of the art 1-D radiative transfer code that takes into account the overlap of hyperfine components[5] using the most update *ab initio* hyperfine collisional coefficients for HCN[6]. The results of this analysis suggest that the 14N/15N ratio in HCN is small (~130) which is much smaller than the ratio measured in other carriers like ammonia[5], suggesting that two reservoirs of Nitrogen are present at the prestellar phase.

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FTIR DIAGNOSTICS OF NITROGEN-METHANE ATMOSPHERIC GLOW DISCHARGE USED FOR A MIMIC OF PREBIOTIC ATMOSPHERE

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This work extends our previous investigation of nitrogen-methane (N_2-CH_4) atmospheric glow discharge for simulation chemical processes in prebiotic atmospheres. We present results obtained by Fourier Transform Infra Red spectroscopy (FTIR). The theory of the evolution of life was given by Oparin and it is based on the possibility of the synthesis of organic compounds by abiotic processes from inorganic species. Possible energy sources for these processes include UV radiation, electric discharges, shock waves, radioactivity, cosmic rays, solar wind, volcanoes or hydrothermal vents [1]. Sixty years ago, the Miller Urey experiment showed that many biologically important organic compounds, including sugars and amino acids, could be formed by methane, hydrogen, ammonia and water to spark discharge. They detected products like HCN, aldehydes, ketones and the ammonia in liquid water [2].

This work is focused on experiments with water (H_2O) addition to the atmospheric glow discharge fed by N_2-CH_4 mixture and diagnostic of this discharge by FTIR. The discharge was created between two stainless steel electrodes separated by a 2 mm gap. The electrode system used the standard configuration of the gliding arc discharge but due to the low applied power as well as low gas velocity the discharge is not moving along the electrodes. The discharge was operated with an applied voltage of 400 V and current in range 15 mA to 40 mA in pure nitrogen enriched by 1−5 % of CH_4 at the total flow rate of 100 sccm and H_2O vapour admixture (2%). Flow rates of all gases through the reactor were regulated using mass flow controllers (Bronkhorst). There was connected bottle gas washing with the high purity water just before the entrance to the reactor.

All recorded spectra were be processed, hydrogen cyanide (HCN) was found to be the most abundant product at wavenumbers of 720 cm^{-1}. Ammonia (NH_3) was identified at 966 cm^{-1}. The other major products were acetylene (C_2H_2) as well as carbon monoxide (CO) and water (H_2O). These products were recognized in all gas mixtures. The products concentrations are strongly dependent on the gas mixtures composition.

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WEAK INTRAMOLECULAR INTERACTION EFFECTS ON THE STRUCTURE AND TORSIONAL SPECTRA OF ETHYLENE GLYCOL, AN ASTROPHYSICAL SPECIES

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A variational procedure of reduced dimensionality based on CCSD(T)-F12 calculations is applied to understand the far infrared spectrum of Ethylene-Glycol [1] a detected molecule in gas phase [2]. This molecule can be classified in the double molecular symmetry group G_8 and displays nine stable conformers, *gauche* and *trans*. In the gauche region, the effect of the potential energy surface anisotropy due to the formation of intramolecular hydrogen bonds is relevant. For the primary conformer, the ground vibrational state rotational constants are computed at 6.3 MHz, 7.2 MHz and 3.5 MHz from the experimental parameters [3].
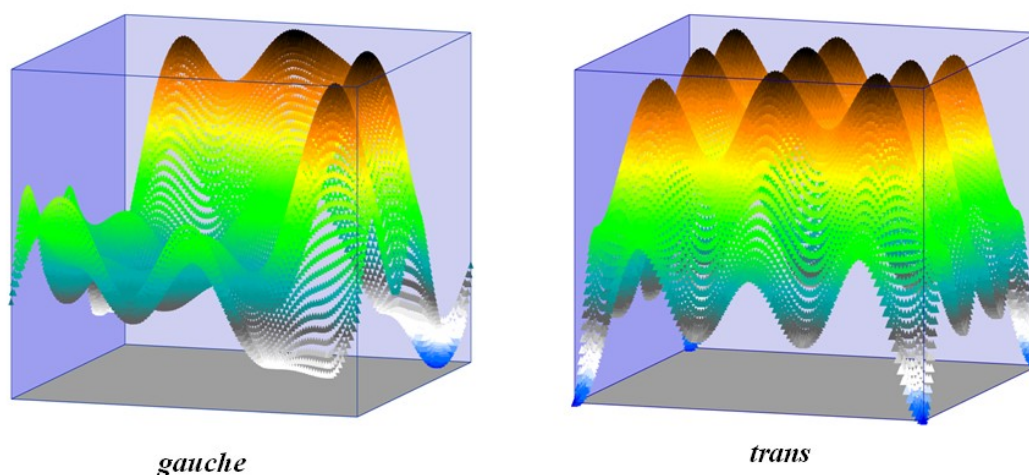

gauche　　　　*trans*

Figure 1: Potential energy surface of ethylene glycol in the gauch and trans regions

Ethylene glycol displays very low torsional energy levels whose classification is not straightforward. Given the anisotropy, tunneling splittings are significant and unpredictable. The ground vibrational state splits into 16 sublevels separated ~142 cm^{-1}. Transitions corresponding to the three internal rotation modes allow assign previous observed Q branches. Band patterns, calculated between 362.3 cm^{-1} and 375.2 cm^{-1}, between 504 cm^{-1} and 517 cm^{-1} and between 223.3 cm^{-1} and 224.1 cm^{-1}, that correspond to the tunnelling components of the v_{21} fundamental (v_{21} = OH-torsional mode), are assigned to the prominent experimental Q branches [1].

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ROTATIONAL EXCITATION OF INTERSTELLAR RADICALS (OH, CH, AND PO) WITH He

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He + OH collisions play an important role in astrophysical chemistry, in particular in the modelling of OH masers. The most recent *ab initio* PES was presented by Kalugina *et al.* [1], and hyperfine cross sections were presented by Marinakis *et al.* [2]. Here, we will extend our work to the calculation of rate coefficients and a comparison with observations.

The methylidene (CH) radical plays a significant role in the interstellar medium, in the sun and stellar atmospheres, and in comets. It is one of the most abundant diatomic radicals in molecular clouds and has become a common probe of the diffuse interstellar medium. We extend our previous work on He + CH [3], and we present the first quantum mechanical calculations of rate coefficients and comparison with experimental data.

There is an increased interest in the key probiotic molecule PO as the P-O bond is key for the formation of DNA. The collisions of PO have not been studied so far. We will present the first *ab initio* He-PO PES and quantum mechanical calculations of the rotational and hyperfine excitation. Our results will be compared with new experimental data.

Figure 1: Relative state-to-state He + OH (F_1, 1.5f) inelastic cross sections [1]. Squares – experimental values, solid line – present calculations with an averages PES for $v = 0$; dashed line – present calculations with 2D potential for $r = r_0$; dotted line – previous calculations.

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AB INITIO STUDY OF THE PHOTODISSOCIATION OF RADICAL MOLECULES OF ASTROCHEMICAL INTEREST

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Several radical molecules of astrochemical interest have been studied theoretically in order to characterize the electronic states (and the couplings beteeen them) involved in the different photodissociation pathways leading to fragmentation of the radical. Specifically, the radicals studied are CH_3, CH_3CH_2, and the methoxy family CH_3X (X = O, S). Highly correlated ab initio techniques have been used in the studies. In the cases of CH_3 [1]-[3] and CH_3X (X = O, S) [4], the potential-energy surfaces and couplings for the corresponding ground and excited electronic states were characterized using a two-dimensional representation that includes the CH_2-H and CH_3-X dissociative coordinate and the CH_2 and CH_3 umbrella angle, respectively. For the CH_3CH_2 radical, there are three possible dissociative coordinates (namely CH_3-CH_2, CH_3CH-H, and H-CH_2CH_2), and the different electronic states involved in those dissociation pathways have been characterized along with their corresponding couplings by using a one-dimensional representation in the above three dissociative coordinates [5]. The possible photodissociation mechanisms of the radical molecues studied are discussed in the light of the ab initio data obtained. Recent experimental results on the photodissociation of CH_3 [1], [2] have been successfully interpreted with the aid of the present theoretical results.

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THEORETICAL MODELLING OF PHOTOEMISSION IN CONDENSED PHASE

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Photoemission spectroscopy is a valuable tool for revealing electronic structure of molecules in both the gas and condensed phase. The molecular level insight is typically obtained by *ab initio* modelling which can interpret the experimental findings. However, theoretical modelling of photoemission is a complex and difficult case.

We present a suitable computational approach for modeling photoemission spectra in the condensed phase. We combine *ab initio* based path-integral molecular dynamics simulations greatly accelerated with the so called colored noise thermostat (PI+GLE)[1] method with effective estimate of ionization energies *via* the optimally tuned range-separated hybrid functionals (OT-RSH)[2]. We can also account for nuclear quantum effects; e.g. the method can capture the isotope effect. We will also briefly discuss the results for hydrogen peroxide. The present approach seems to be a promising route to modelling photoemission spectra in the condensed phase and on interfaces.

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SIMULATIONS OF ENERGY DISSIPATION AND NON-THERMAL DESORPTION

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Dust particles covered by icy mantles play a crucial role in the formation of molecules in the Interstellar Medium (ISM). These icy mantles are mainly composed of water but many other chemical species are also contained in these ices. These compounds can diffuse and meet each other to react. It is through these surface reactions that new saturated species are formed. Photodissociation reactions are also thought to play a crucial role in the formation of radical species [1]. Complex organic molecules are formed through an intricate network of photodissociation and surface reactions.

Both type of reactions release energy. Surface reactions are typically exothermic by a few eV, whereas photodissociation reactions are triggered by the absorption of a UV photon, resulting in the formation of highly excited products. The excited reaction products can apply this energy for desorption or diffusion, making products more mobile than predicted when considering only thermal hopping. The energy could further lead to annealing or deformation of the ice structure.

Here we would like to quantify the relative importance of these different energy dissipation routes. For this we performed thousands of Molecular Dynamics simulations for three different species (CO_2, H_2O and CH_4) on top of a water ice surface. As a first start, only excitation into kinetic energy is considered and the applied substrate is a proton disordered crystalline ice I_h surface.
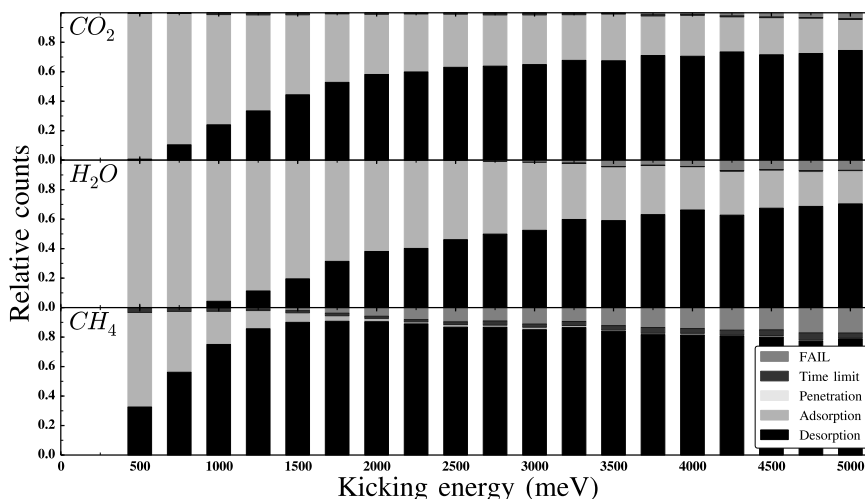

Figure 1: Relative fractions of the outcomes of the simulations as a function of the initial translational kinetic energy. Simulations performed in the *NVE* ensemble.

The simulations show that a large fraction of the molecules can desorb depending on the binding energy of the species and the excitation energy, as depicted in Figure 1. The species that remain adsorbed typically travel 100 Å (see Figure 2) for H_2O but it could be as far as 1100 Å. This may have severe consequences for surface chemistry since it provides an additional opportunity for species to diffuse and to find reaction partners. The surface structure of the water ice plays a crucial role in this.

Figure 2: Unwrapped coordinates of the H_2O at the end of the *NVE* simulations. The colormap represents the initial translational kinetic energies given to the H_2O admolecule. The grid squares represent the replications of the box due to periodic boundary conditions.

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NEXT GENERATION AIRBORNE AND SPACE TELESCOPES: JWST, SOFIA, AND BEYOND

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Next generation airborne and space-based telescopes and instrumentation will offer unprecedented sensitivity and spatial resolution at wavelengths that are inaccessible from the ground due to the Earth's atmosphere. These spectral regions host a number of astrochemically significant molecular lines including: CO_2, H_2, NH_3, etc. The Herschel Space Observatory, Hubble Space Telescope, Spitzer Space Telescope, and Kuiper Airborne Observatory have advanced research on virtually every topic in space science, notably Astrochemistry. These facilities work in concert with large ground-based facilities to address key questions of chemical complexity, origin of life or biomolecules, and molecular inheritance throughout star and planet formation, among others. It is not well understood how complex species are formed on the surfaces of grains or in the gas-phase in the interstellar medium. Laboratory and astrochemical models show that complex organic molecules, COMs, are formed in radical diffusion reactions in interstellar/cometary ices, though gas-phase mechanisms have also been considered for certain species. Clearly, disentangling the various molecular formation (and destruction) mechanisms, and therewith the origin of the chemical complexity observed in the interstellar medium and our Solar System, requires a multiwavelength approach to observe all molecular phases.

The James Webb Space Telescope (JWST) is an infrared-optimized observatory with a 6.5m-diameter segmented primary mirror and instrumentation that provides wavelength coverage of 0.6-28.5 microns, sensitivity 10X to 100X greater than previous or current facilities, and high angular resolution (0.07 arcsec at 2 microns) and low-moderate spectral resolution (R~100-3000) [1,2]. It offers multiple capabilities through 4 science instruments including: imaging, spectroscopy (slit, IFU, grism/prism), coronography, and aperture mask interferometry. JWST spectral range covers numerous astrochemically relevant species in both the gas and solid phase, including the vibrational modes of ices. With comparable angular resolutions, JWST can probe regions where ALMA is identifying COMs to determine their origins. JWST is currently on schedule to launch in October of 2018 and will operate 5+ years after commissioning.

The Stratospheric Observatory for Infrared Astronomy (SOFIA) provides imaging and spectroscopic capabilities at wavelengths from 0.3-1600 microns, operating at 37,000+ ft, which is above 95% of atmospheric water vapor [3]. The observatory offers capabilities that include photometric, spectroscopic, and polarimetric observations. SOFIA provides access to the far-infrared as well as high spectral resolution that current space-based facilities do not offer. This is significant for studies of water and other molecules, including COMs, throughout the ISM.

This presentation will provide an overview of these telescopes and briefly introduce current efforts for the next generation of space-borne observatories. Examples of ground-breaking observations in Astrochemistry will be highlighted.

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Adsorption of PAHs on interstellar ice viewed from molecular dynamics

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Polycyclic Aromatic Hydrocarbons **(PAHs)** have had an astrophysical interest since they were proposed, in the mid-eighties, to be the carriers the Aromatic Interstellar Bands **(AIBs),** a set of infrared (IR) emission bands observed in the [3 - 15 μm] range in many regions of the interstellar medium (ISM). PAHs would also be potential candidates to carry the Diffuse Interstellar Bands **(DIBs)**, which are weak absorption bands measured between 0.38 and 1.3 μm on the extinction curve of our galaxy. Besides, PAHs are likely to play a role in the chemistry of the ISM as, for instance, they would form stable complexes with iron, thus contributing to the iron depletion from the gas phase of the ISM. In molecular clouds, some gases are condensed on dust particles and form ice mantles essentially made of water. PAHs may also condense on/in these ices and contribute to the complex grain chemistry [1]. This heterogeneous chemistry plays a fundamental role in presence of the adsorbed 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 codeposition [3] of PAH and water are achieved at the Institut des Sciences Moléculaires (ISM, Bordeaux). In connection with these experiments, we are modeling PAHs interacting with various icy environments using a multi-method approach. The aim is to identify a configuration that could best describe the experiments and provide quantitative indications on the effect of the environment on the IR spectra.

The most relevant configurations obtained within the MD/FF approach are then taken as starting conditions for new trajectories (see fig 1). We run on-the-fly Born Oppenheimer MD simulations, the electronic structure being described explicitly within the Density Functional based Tight Binding (DFTB) scheme. The efficiency of DFTB allows to run simulations of sufficient duration so as to derive the IR spectra. Results on the effects of the icy environment on the PAH's IR spectra will be presented. Our **multi-scale multi-method** approach allows us to identify coupled modes between PAH and water for a wide range of frequencies.

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REACTIVITY OF HYDROGEN ON NANOSILICATE GRAINS: THE ROLE OF SILICATE STOICHIOMETRY AND CHEMISORBED WATER

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Dust plays a crucial role in the chemical evolution of the ISM by catalyzing molecule formation and, through scattering strong interstellar radiation, preventing molecular photodissociation in denser regions. Via lab characterization of pristine material and astronomical observations, the general properties of dust particles in various environments have been reasonably well discerned. Fitting the observed spectra with a combination of lab spectra of materials of different crystallinity, shape, size and composition gives valuable insight into the possible identity of dust particles in space.

We present a complementary approach to understanding the formation, structure and reactivity of small silicate dust grains based on a bottom-up (i.e. from an atomistic and electronic level) computational modelling [1]. Crucially, our approach is independent of assumptions based on bulk materials properties, is not limited to any particular chemistry or specific thermodynamic conditions, and provides a solid basis for subsequent kinetic modelling for longer timescales associated with larger dust particle species.

Specifically, we show how our approach can provide detailed and quantitative insights into the reactivity of ultra-small silicate dust grains (nanosilicates) with respect to their role as ice condensation nuclei [2] and their role in H_2 formation and dissociation [3,4] and. We also report on computed IR spectra of our nanosilicate species. A large part of this work was accomplished through the STSM: "Reactivity of hydrogen on large magnesium silicate clusters".

Figure 1: Intermediate steps during the formation/dissociation of molecular hydrogen catalyzed by a hydroxylated nanosilicate dust grain.

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MECHANISMS OF SIO OXIDATION: IMPLICATIONS FOR DUST FORMATION

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The SiO molecule has been observed in the interstellar medium and in stellar outflows and is believed to be important for the formation of interstellar dust [1-6]. It is also found in terrestrial environments such as the upper atmosphere (from meteoric ablation) [7], in combustion of silicon compounds [8] and in industrial silicon production processes [9]. SiO can react with oxygen-bearing species, such as OH, to form SiO_2. Molecular SiO_2 will readily condense to solid silica particles at sufficiently high concentrations (in sufficiently dense media). SiO can also condense directly to form clusters, and through a series of reactions with different species form silicate dust [3-5]. There is a lack of experimental data on the elementary reactions involved in SiO oxidation, with a few exceptions [10], and computational chemistry techniques are essential in providing mechanistic insight and estimates of the rates of reaction [10,11]. I will present results on oxidation reactions of SiO, in particular with OH, O_2, and H_2O, and their implication for the formation of solid particles. This work was initially motivated by studies on formation of silica dust particles in silicon industry [9], and it serves as an illustration of the mutual benefit of research on seemingly very different topics.

We have applied a combination of electronic structure theory calculations, both coupled cluster [CCSD(T)] and density functional theory (DFT), with dynamics simulations and statistical rate theories in order to obtain high accuracy in calculated reaction kinetics and thermodynamics. The calculations are performed for a wide range of pressures and temperatures, reflecting the very different environments in which these reactions occur. I will discuss under which physical conditions the oxidation and condensation processes are important, from a thermodynamic and kinetic point of view. Results also show that the M06 density functional is an excellent choice for calculating kinetics and thermodynamics of processes in Si-O-H systems.

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THEORETICAL STUDY OF HNCO FORMATION AT LOW TEMPERATURE FROM N AND CO IN PRESENCE OF WATER

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A great number of complex organic molecules (COM) have been detected in space, in the interstellar medium as well as on meteorites or comets. As such their formation in astrophysical environments is a challenging question. An increasing interest is thus devoted to their possible formation routes, starting from reactions involving atomic elements or very simple diatomic molecules in order to step by step increase the molecular complexity. In this context, special focus is given on the [H,N,C,O] family, the simplest species containing the four basic elements involved in all biomolecular compounds. Four isomers correspond to this generic sequence in the energy order HNCO<HOCN<HCNO<HONC [1] and the three lower-energy species have been observed in different regions of space. Several gas phase models have been proposed, in particular for the formation of the isocyanic acid HNCO isomer [2, 3]. However gas-grain chemical models appear to be crucial to attempt to reconcile the different observations [4]. The combination of theoretical approaches and laboratory experiments is indeed quite necessary to shed some light on these processes.

Laboratory experiments have recently been performed to understand further the formation mechanism of HNCO at very low temperature, in presence of water. First experiments involving N and CO on water ices have shown the possible formation of HNCO [5]. In addition, matrix isolation techniques were used to characterize unstable species and intermediates along the formation reaction scheme [6] and various pathways could be proposed. In the present study, we have investigated all possible pathways leading to the formation of isocyanic acid from atomic nitrogen and CO, in presence of H_2O molecules, both from a structural and energetic point of view [7]. Theoretical calculations are performed at hybrid DFT, double hybrid DFT and CCSD(T) levels of theory in order to get the most accurate results, and meanwhile to compare their ability to describe energy barriers. These reactions involving atomic nitrogen, the models considered here have to deal with different spin states increasing significantly the complexity of the calculations.

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CHARACTERIZATION OF THE HNO MOLECULAR SYSTEM AND STUDY OF THE O+NH→N+OH REACTION

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The rate of the reaction O (^{3}P) + NH (X $^3\Sigma^-$) → N (^{4}S) + OH ($^2\Pi$) ; ΔE = -21.9 kcal/mole, at low temperatures, has different estimates in different databases. This reaction, which might play an important role in the cycle of water formation, can occur on different Potential Energy Surfaces (PESs) with different spin states according to the Wigner-Witmer spin orbital correlation rules [1].

The collision between O(^{3}P) and NH (X $^3\Sigma^-$) gives rise to 27 PES, one with A' symmetry and two with A'' symmetry at C_s configurations, each one of these can be a singlet, a triplet or a quintet spin state. On collinear geometries the A' and one A'' PESs correlate with $^1\Pi$, $^3\Pi$ or $^5\Pi$ degenerate states presenting a Renner Teller crossing. The other ^{1}A'' and ^{3}A'' PESs correlates with a $^1\Delta$, $^3\Sigma$, which have lower energy than the Π states at short distances. As quintet state saddle-point is collinear corresponding to the $^5\Pi$ degenerate state, the other 5A'' has never been studied. For each spin state, the two A'' surfaces do not cross at C_s configurations, avoided cross, but they do cross at collinear geometries, where there is a Ian-Teller crossing line between the Π and the Σ or Δ states.

The product H(^{2}S) + NO ($^2\Pi$) (henceforth referred to as products 1) correlates with the singlet or triplet surfaces (both A' and A''). The second A'' surface correlates with an excited NO molecule. On the singlet surface correlates to a $^2\Delta$ state and, on the triplet surface, it correlates to a NO molecule in the $^2\Sigma$ state.

The products N(^{4}S) + OH($^2\Pi$) we are interested in, (henceforth referred to as products 2) only correlate with the triplet and quintet states.

On the ^{1}A', ^{1}A'' and ^{3}A'' PESs there are no barriers for other of the reactions but there is an internal barrier, lower than reactants and products 2 energies, connecting the HNO and NOH minima. Note that the relative position of these two minima depends on the spin state. For the HNO minima the singlet state has lower energy, but for the NOH minima the triplet state is the lowest. Although the reactions to form products 1 or 2 are exothermic, products 1 have lower energy and can be produced in reactions through these 3 PESs. On the ^{3}A'' the reaction to form products 2 proceeds throughout the internal barrier before dissociation. It has been proposed that products 2 are 5% of the products on this surface.

The ^{3}A' PES does not correlate with the HNO or NOH minima and is repulsive. It has not been considered for the studies of these reactions. The saddle point is in collinear configurations and estimated to be 11.7 kcal/mol on the $^3\Pi$ PES.

It's relevant that the $^5\Pi$ PESs which can produce products 2 throughout a collinear saddle point. The estimated barrier is 5.6 kcal/mole and the rate constants computed using Transition State Theory, are significant at high temperatures. We remark that the electronic probability of reactants

enter these PESs is 10/27, comparing with 2/27 to react through the two singlet surfaces or 3/27 to enter the ^{3}A'' PES.

To our knowledge there are no PESs for the ^{3}A', ^{5}A' and both ^{5}A'' PESs far from collinearity.

In this work we present preliminary results for the dynamics of the reaction O (^{3}P) + NH (X $^3\Sigma^-$) $\rightarrow$ N (^{4}S) + OH ($^2\Pi$) on the available PESs for the ^{3}A' state. We present quasiclassical trajectory [2] results at temperatures between 5 and 100 K computed on the PESs of Schatz and co-workers [3] and the most recent PES of Guo and co-workers [4].

In regard to the two quintet surfaces, ^{5}A' and ^{5}A'' [5,6], they are restricted to particular configurations of the system and are not suitable for reaction dynamic studies. Further work is needed to study the reaction rate in this state.

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H_2O_2 (a,^{3}A) - An important molecular system
New potential energy surface

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The reactions of an oxygen atom in its ground (^{3}P) and first excited (^{1}D) states, resulting from the incidence of solar radiation on stratospheric ozone (Hartley band), with a water molecule play an important role on the modelling of atmospheric chemistry and ozone depletion cycle [1]. These reactions and their reverse reactions, the reaction between two hydroxyl radicals, are relevant for the chemistry of combustion processes [2]. The triplet state of H_2O_2 assumes special relevance on the studies the combustion reactions of O_2 and H_2. In this work, we describe a new potential energy surface (PES) for the first excited triplet state of the hydrogen peroxide, H_2O_2 (a,^{3}A). This new H_2O_2 PES aim to accurately reproduce all the different dissociation channels in accordance to the Wigner-Witmer rules, namely, O(^{3}P) + H_2O, OH + OH, O_2 ($^3\Pi$) + H_2 and H + HO_2. We have computed a large amount of ab initio energies using the MOLPRO 2009.1 set of programs [4]. The open-shell coupled cluster theories (RCCSD) was used with perturbative triples corrections (RCCSD(T)) as defined by R. J. Bartlett et al. [5]. In our calculations, the geometry is optimized using aug-cc-pVXZ (X=T,Q) basis sets and extrapolated to basis set limit using results from five zeta basis set (aug-cc-pV5Z) with RCCSD-F12 level calculation. They also account for the electrostatic dipole-dipole interaction between two OH ($^2\Pi$) fragments. Using the PES for the different reaction fragments, the H_2O PES [6] and the HO_2 PES[7], and the ab initio points computed extrapolated to basis set limit, we are able to build a PES for the lowest triplet state of H_2O_2. We present the characterization of transition structures on the H2O2 lowest triplet state. Dynamical studies of the O(^{3}P)+H_2O and OH($^2\Pi$)+OH($^2\Pi$) reactions on this new PES are the next step of this work.

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THEORETICAL STUDY OF THE HOOH (X, ^{1}A) POTENTIAL ENERGY SURFACE

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Many reactions involving hydrogen and oxygen have attracted widespread attention due to their overwhelming importance in chemistry [1,2]. In the present work, attention has been focused on the singlet potential energy surface of the H_2O_2 system.

The construction of this PES is crucial to the study of the dynamics of the $O(^1D)$ + H_2O $(X,^1A_1)$ reaction, which plays an important role in the stratospheric chemistry mainly in the ozone degradation processes through the OH/HO_2 catalytic cycle [3], as well as in combustion processes. Besides that, the study of the H_2O_2 system is driven forward by the knowledge of the existence of the hydrogen peroxide on the surfaces of Europa, Gaymede and Callisto (icy satellites) with concentrations of about 0.3% by weight. H_2O_2 has also been proposed as a precursor molecule to generate molecular oxygen on the surfaces of Ganymede and Europa.

This new DMBE H_2O_2 PES, based on a 3x3 matrix, accurately reproduces all the different dissociation channels in accordance to the Wigner-Witmer rules, namely, $O(^1D)$ + H_2O → OH + OH, O_2 $(^1\Delta)$ + H_2 and H + HO_2 [4]. It has been obtained by fitting more than 35 thousand *ab initio* energies computed using the aug-cc-pVTZ and aug-cc-pVQZ basis sets and extrapolated to basis set limit [5]. It also accounts for the electrostatic dipole-dipole interaction between two OH ($^2\Pi$) fragments.
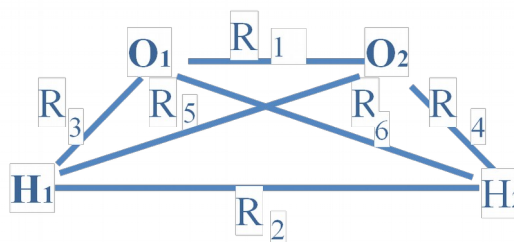
The Potential Energy Surface must be symmetric to permutation of the two oxygen atoms or the two hydrogen atoms. In this case, the R_1 and R_2 distances keep the same, but the R_3, R_4, R_5 and R_6 distances will exchange according to a permutation group isomorphic to the D_2 symmetry point group. These distances constitute a base for:

(A₁) ρ_1= 1/2 (R_3 + R_4 + R_5 + R_6)
(B₁) ρ_2= 1/2 (R_3 + R_4 - R_5 - R_6)
(B₂) ρ_3= 1/2 (R_3 - R_4 + R_5 - R_6)
(B₃) ρ_4= 1/2 (R_3 - R_4 - R_5 + R_6)

Since the PES must belong to the A_1 representation, the integrity basis is given as ρ_1; ρ_2^2; ρ_3^2; ρ_4^2; $\rho_2\rho_3\rho_4$. Using R_1 and R_2 and this integrity basis we are able to build a polynomial totally symmetric to permutations of identical atoms.

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PARTITION FUNCTION CONVERGENCE STUDY FOR RELIABLE ISM MOLECULAR ABUNDANCE RATIOS

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Determination of Interstellar Medium (hereafter, ISM) molecular and/or isotopic abundance ratios toward different star-forming regions gives strong insight into the formation mechanism of ISM species (i.e. on the chemistry and the involved processes). Nevertheless, to derive accurate ISM molecular/isotopic ratios, we need to be confident with the intensity calculation of the molecular species at different temperatures. Indeed, the isotope ratio accuracy depends on the spectroscopic determination of transition frequencies, assignments, and line strengths together with the partition function approximation considered.

A convergence study of the partition functions within a range of temperatures that are representative of star-forming regions is presented here for the following molecules: methyl formate, acetic acid, acetonitrile, methyl mercaptan and isocyanic acid. This study has allowed us to determine more accurate and more reliable ISM molecular and/or isotopic abundance ratios (see, e.g., Refs. [1, 2, 3]), which are expected to be relevant in Astrochemistry.

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REACTIVITY OF CH_3^+ WITH BUT-2-YNE USING REACTION MONITORING WITH SYNCHROTRON RADIATION

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The methyl carbocation is ubiquitous in astrophysical environments ranging from the interstellar medium (ISM) to terrestrial and planetary atmospheres, cometary comae, etc. In the ISM, CH_3^+ reactivity with simple molecules needs to be included to model cloud chemistry at elevated temperatures (e.g. hot cores), or inner regions of protoplanetary disks [1]. CH_3^+ is one of the key ions in the atmosphere of Titan [2], where it is responsible for formation of complex hydrocarbons [3].

Although methyl cation reactivity with saturated and unsaturated hydrocarbons up to C_3 have been investigated in the past (with CH_4, C_2H_6, C_3H_8, C_2H_4 and C_2H_2) reactions with larger hydrocarbons are almost non-existent. In particular, the reactions with methyl substituted acetylenes (i.e. propyne C_3H_4, and but-2-yne C_4H_6) are expected to be relevant for the growth of complex hydrocarbons in Titan's atmosphere, where they are proposed as responsible for the couples of ions ($C_4H_7^+$/ $C_4H_5^+$ and $C_5H_9^+$/$C_5H_7^+$) observed by the Ion Neutral Mass Spectrometer on board of the Cassini probe [4].

Here we report on the reaction of CH_3^+ with but-2-yne C_4H_6 by measuring absolute reactive cross sections and branching ratios as a function of collision energy using both the home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) at Trento and the CERISES-apparatus, installed on the DESIRS beamline of the synchrotron radiation source SOLEIL. While in the first set-up the methyl cation is generated with an uncontrolled amount of internal excitation, in the other one direct VUV photoionization with synchrotron radiation of methyl radicals is used to produce CH_3^+. The latter method opens the way to investigation of the effect of internal degrees of freedom (vibrational) on CH_3^+ reactivity. Experimental results are interpreted under the light of a theoretical study of product formation mechanisms using DFT methods (with optimizations followed by CCSD(T) single-point energy calculations). The most abundant ionic products are $C_4H_6^+$ and $C_4H_5^+$ resulting from charge transfer and H^- transfer processes, while the third most abundant product is $C_3H_5^+$ plus C_2H_4, formed via a complex mediated mechanism. Most relevant for the growth of complex organic species on Titan is the detection of a minor channel attributed to $C_5H_7^+$ and formed by H_2 elimination from a stable intermediate.

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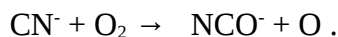[4] A. Ali, E.C. Sittler Jr, et al. Planet. Space Sci. **87**, 96-105 (2013)

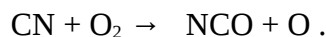# FORMATION OF ANIONS BY RADIATIVE ELECTRON ATTACHMENT

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We will discuss the formation of the molecular anions by radiative electron attachment. More specifically we will discuss the formation of NCO-, which is a stable anion and has been identified in astrophysical ice (see [1]). The mechanism of its formation is still under debate (see e.g. [2] and [3]).

Recently Yurtsever et al. (see [4]) have explored various mechanisms for its formation. One suggested pathway is the molecular reaction

$$CN^- + O_2 \rightarrow NCO^- + O \,.$$

In the same publication the authors have studied also the formation of the neutral NCO molecule by the reaction

$$CN + O_2 \rightarrow NCO + O \,.$$

This reaction could be followed by radiative electron attachment (REA)

$$NCO + e^- \rightarrow NCO^- + photon$$

and form the anion NCO-. Reaction rates for this second step are still unavailable. We will present some estimates and will compare the two proposed formation pathways of the NCO- anion.

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NUCLEATION OF SILICON CARBIDE CLUSTERS IN AGB STARS

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Dust is ubiquitous in the Universe and plays a crucial role in astrophysical environments. Dust impacts the synthesis of complex organic molecules in molecular clouds, the wind-driving of evolved stars and the formation of asteroids and planets [1]. The presence in pristine meteorites and spectral fingerprints indicate that dust formation takes place in the highly dynamic and turbulent atmospheres of Asymptotic Giant Branch (AGB) stars. However, the chemical pathways that lead to nucleation and the thermodynamic conditions are not fully understood.

One of the major dust components is silicon carbide (SiC). In the bulk phase, SiC exists in about 250 crystalline forms. Its most commonly encountered structures are hexagonal α-SiC and cubic β-SiC which are the only types found in meteorites [2]. However, the properties of clusters with sizes below 50 nm differ significantly from bulk properties. Quantum and surface effects of these small particles lead to non-crystalline structures, whose characteristics (geometry, atomic coordination, density, energy) may differ by orders of magnitude, compared to the bulk material. Thus, a bottom-up approach, starting with prevalent molecules in the gas phase (e.g. SiC, SiC2) and successive growth to clusters by molecular (addition) reactions, seems to be suitable. Such a method has been applied for silicate dust clusters of enstatite and forsterite stoichometry [3]. The number of possible structural isomers increases exponentially . The investigation of large clusters is therefore computationally demanding. In order to reduce the computational effort, as well as the number from thousands of possible structural isomers, we use several semi-classical optimisation techniques. They include molecular dynamics such as simulated annealing and Monte-Carlo simulations [4,5], applying semi-classical Tersoff-type potentials taylored for SiC [6].

Once pre-optimised, the candidate structures are further optimized on the quantum level of theory. As a result, structure-specific infrared spectra, vibrational frequencies, rotational constants, and zero-point-energies can be extracted. In addition, we are interested in the cluster properties:
At which size clusters tend to arrange crystal lattice and transit to the bulk phase?
Do the clusters exhibit atom-specific separation (segregation)?
What spectral fingerprint individual clusters calculated vibrational modes and how do they compare with (circum-)stellar observations?
Could the clusters account for the 11.3 µm feature - commonly attributed to SiC dust – for and unidentified infrared bands in the 3-13 µm range?

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Building Carbon Bridges on and between Fullerenes in Helium Nanodroplets

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Ever since the discovery of fullerenes by Kroto et al. [1] and even more since the recent laboratory confirmation of fullerene presence in the interstellar medium [2], fullerene formation and reaction schemes have been subject of a lively debate. Here we report the observation of sequential encounters of fullerenes with C atoms in an extremely cold environment. The experiments were performed with helium nanodroplets at 0.37 K doped with C_{60} molecules and C atoms derived from a novel, pure source of C atoms. They were subsequently exposed to electrons at a controlled energy and investigated using a high resolution time-of-flight mass spectrometer. The mass spectra revealed the formation of carbenes of the type $C_{60}(C :)n$ with n up to 6. Bridge-type bonding of the C adatoms to form the known dumbbell $C_{60}=C=C_{60}$ was also observed.

To interpret the experimental findings, we employed density functional theory calculations at the B3LYP/6-31g(d) level that elucidated the carbene character of the $C_{60}(C :)n$ species and their structures.

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The low-lying vibronic spectrum in the $X\ ^2\Pi_u$ state of the C_5^- ion computed variationally

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Carbon clusters (C_n) have been of great interest in interstellar, plasma, and combustion chemistry for over three decades. Especially interesting is the C_5^- ion in its ground electronic $X\ ^2\Pi_u$ state that exhibit Renner-Teller coupling. In this work, the vibronic spectrum is computed variationally with a simple model for *ab initio* handling of the Renner-Teller effect in molecules with linear equilibrium geometry and with arbitrary number of nuclei [1]. The model assumes that the electronic state is well separated from the other electronic states; the harmonic approximation is applied; the coupling between the bending and stretching vibrational modes is neglected. The kinetic energy operator for infinitesimal bending vibrations is applied, the spin–orbit operator is assumed in the phenomenological form, and the asymptotic (linear limit) electronic wave functions are used in matrix representation of the kinetic energy operator. Our approach, and particularly the computer program we wrote, can be applied without modifications to molecules with any number of nuclei provided that not more than three bending modes are simultaneously excited (the usual case). When necessary, the program can easily be extended to encompass larger number of exited modes.

We study systematic crossings of the potential surfaces split upon bending vibrations and their effect on the magnitude of the non-adiabatic matrix elements. Contrary to the situation with tetra-atomic molecules [2] we are not able to determine easily all possible crossing points. Thus, we consider several cases: planar geometries, and several special non-planar geometries. Our results are compared with the corresponding second order perturbative calculations [3].

We present the low-lying K = 0, 1, 2, and 3 vibronic energy levels and the vibronic levels correlating with the four lowest-lying zeroth-order (neglected both vibronic and spin–orbit couplings) bending levels, calculated in various approximations (assuming the vibronic coupling but neglecting the spin–orbit one and vice versa, and finally taking into account both of them). The mixing of the vibronic levels that correlate with different zeroth-order bending levels begins already at the third (1, 0, 0) and the fourth (1, 0, 1) zeroth-order level. We show also the bending levels correlating with a zeroth-order level in which all three bending modes are excited (1, 1, 1). The discrepancies between the variational and perturbative results do not exceed 20 cm^{-1}. The error margin is in general somewhat larger than in the case of tetra-atomic, and particularly triatomic molecules. The reason for this is that the density of the vibronic levels in five-atomic species is larger, causing greater number of cases where the zeroth- and first-order vibronic levels lie close to one another, with a consequence that the second-order perturbative handling of the problem becomes lesser reliable.

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A THEORETICAL STUDY OF THE CN+C_2H_4 REACTION

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Nitrogen-containing organic species are ubiquitous in interstellar medium and in some planetary atmospheres. One of their possible sources is the reaction of cyano radicals, CN, with unsaturated hydrocarbons. Of particular interest to the chemistry and photochemistry of the atmosphere of Titan is that both CN and ethene, $CH_2=CH_2$ are known to be present there. Their reaction may be the origin of numerous nitrogen-containing organics, including the polymers constituting the organic aerosols observed in the atmosphere of this moon of Saturn. The kinetics and the branching ratios for this reaction is an important piece of the puzzle of Titan's atmospheric chemistry.

The reaction has been studied experimentally in a wide range of temperatures not only at near 25 K of astrochemical interest but also at higher ones (up to740 K), since the reaction is part of the mechanism of combustion in N-containing flames [1,2]. In crossed beam experiments [3-5], in addition to getting information on the dynamics of the reaction, identification of the products was also possible. The major product was found to be C_2H_3CN which is formed in an exothermic channel, but at higher energies, C_2H_3NC, an essentially thermoneutral product was also observed.

In the latter papers, quantum chemistry was also used to explore the potential energy surface and RRKM calculations were also performed in order to understand the experimental observations. There were four intermediates and two reactions channels identified, being separated from each other by seven transition structures. The primary products may be C_2H_4CN and C_2H_4NC, and the rate of the reaction and the final product ratio will be determined by which of them is formed preferentially. The transition state theory calculations possible with the simple transition-state theory calculations using the information on the stationary points of the potential energy surface can not answer the question which of the primary products is formed more efficiently. For this, dynamical simulations are appropriate.

Quasiclassical trajectory calculations are performed on a potential energy surface calculated on the fly using density-functional theory. The preliminary results available so far indicate preferential formation of C_2H_4CN in the primary step.
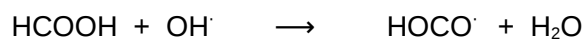
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GLYCINE IN THE INTERSTELLAR MEDIUM: FORMATION OF THE HOCO INTERMEDIATE

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One pathway for the formation of glycine in the interstellar medium could be the recombination of the HOCO radical with the aminomethyl radical. The HOCO radical can be formed by a hydrogen abstraction from formic acid [1], which is found in the interstellar medium.

$$HCOOH + OH^{\cdot} \longrightarrow HOCO^{\cdot} + H_2O$$

The calculation of reaction rates at the low temperatures of dark clouds requires consideration of atom tunneling. We present reaction rate constants including atom tunneling obtained with the instanton method [2].
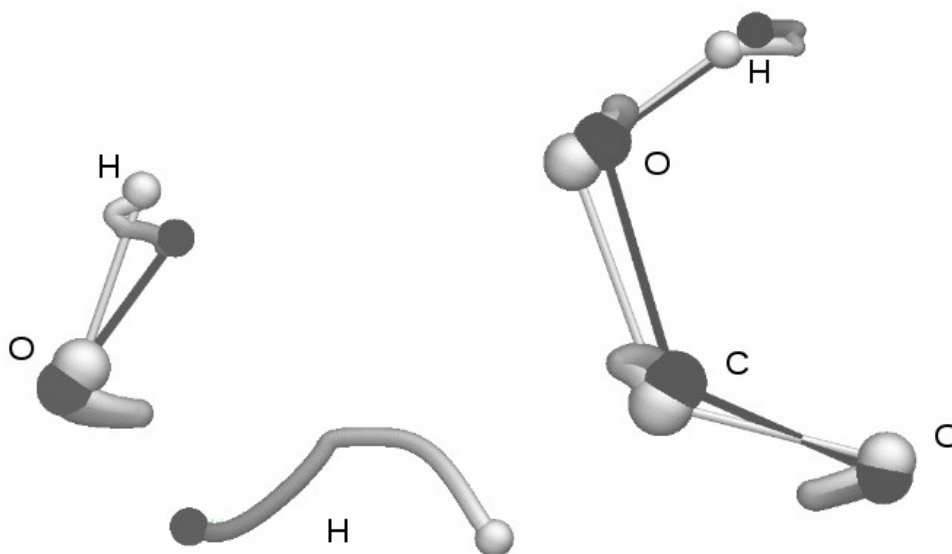

Figure 2: IRC for the reaction from formic acid and OH radical (white) to H_2O and HOCO radical (black).

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PHOTOCHEMISTRY OF PAH IN WATER ICE AND OF PAH:WATER COMPLEXES. REACTION MECHANISMS AND ASTROPHYSICAL IMPLICATIONS.

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Polycyclic aromatic hydrocarbons (PAHs) are believed to contribute to both the Diffuse Interstellar Bands (DIBs) and the Unidentified/Aromatic InfraRed Bands (UIR/AIBs) widely observed along interstellar lines of sight. In star forming regions, PAHs in the solid and gas phases play key roles in the chemical evolution. Several groups have shown that PAHs in water ices react, upon UV irradiation, to produce oxygenated species [1,2,3].

We present the results of a recent experimental and theoretical study of the PAH:water system. FTIR and UV-visible spectroscopies have been used to investigate the photo- reactivity of coronene and pyrene with water molecules at low temperatures in both argon matrices and in solid water ices. Classical molecular dynamics were used to construct an ice surface, upon which the adsorption of PAH molecules was studied. Ab-initio (DFT, DFTB) calculations of water:PAH clusters have been used to study intermolecular interactions and the effect of the argon matrix on such aggregates.

We show that PAH:water systems are highly photoreactive, producing oxygenated products after short UV irradiation times. We also show that the presence of a water ice is not necessary to catalyse the PAH:water reaction, but rather that small water clusters (n << 6) can react with PAH molecules to form alcohols and quinones, suggesting a reaction mechanism via a charge transfer Rydberg state rather than via an ionized PAH. Calculations performed on PAH:water systems involving water clusters and water ices support the conclusion that the orientation of the PAH compared to the water molecules is a key factor controlling the photo reactivity pathway. Both the matrix and water ice environments favour water reaction with the edges of PAH molecules.

These results suggest that oxygenated PAHs could be formed in dense clouds with low water abundances, where there is low energy UV field and where water does not condense onto grain surfaces in the form of an icy layer.

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Potential energy surface and kinetics of the H$_2$CO + OH reaction

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H$_2$CO has been found to be highly abundant in the interestellar medium, and is one of the simplest of the so called complex organic molecules (COMs)[1]. Its chemistry at low temperature is of paramount importance and in this work we focus on the study of H$_2$CO + OH $\rightarrow$ HCO + H$_2$O reaction, being this the only open channel at low temperatures. Highly accurate *ab initio* calculations have been done for this reaction, in good agreement with previous calculations on the stationary points of the potential[2]. An analytic full dimension description of the potential energy surface is obtained by fitting to a large set of *ab initio* points. Preliminary results on the kinetics of the reaction are presented, based on classical dynamics calculations.

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LiH$_2$ - An important molecule in interstellar chemistry
Long range Theoretical Study

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The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe [1,2]. The reaction LiH + H → Li + H$_2$ is considered to contribute to LiH depletion, while the hydrogen-exchange reaction LiH + H → LiH + H leads to the retention of LiH in this process.

In this work we report our recent studies on the long-range interactions between the reactants of those reactions. For the LiHH system, the main contribution for the long-range interactions is the dispersion interaction. To modeling the dispersion interaction, the parallel and perpendicular values of the polarizabilities, α, for the diatomics (H-H and Li-H) have been calculated and fitted (see figure 1).
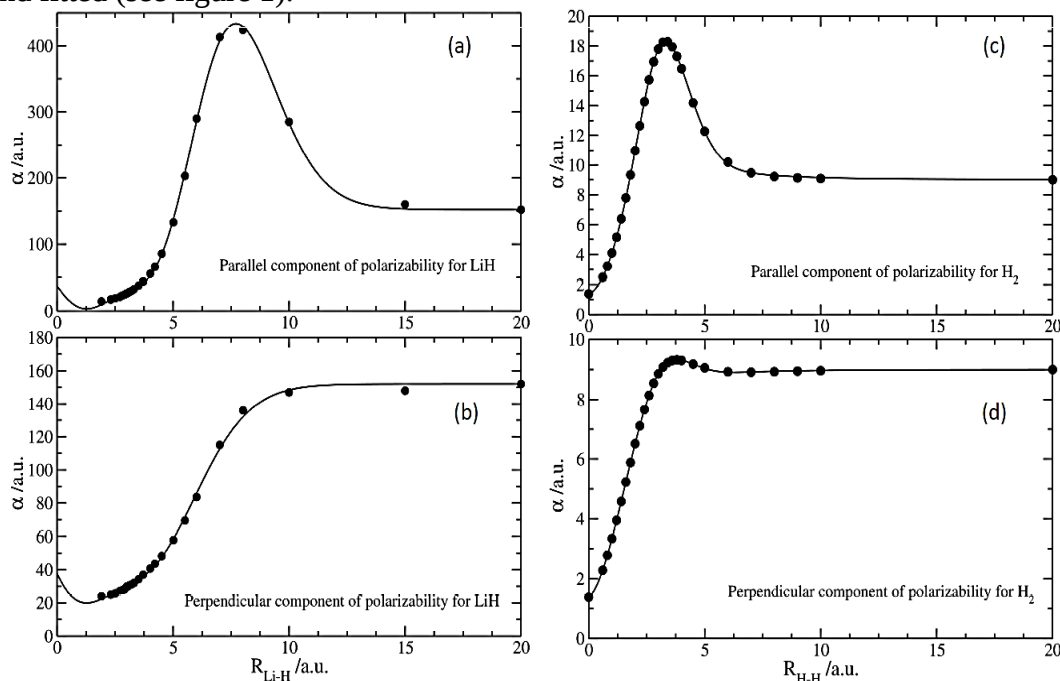

Figure 1: Parallel and perpendicular components of polarizabilities, α, for LiH ((a) and (b)) and H$_2$ ((c) and (d)). Solid lines are the functional form fit to the ab initio calculations (solid dots).

The dispersion interaction coefficients C$_6$ can then be computed as C$_8$ and C$_{10}$ have been semiempirically estimated from C$_6$ using a universal correlation. The total dispersion interaction will be computed as a function of C$_n$ and inter-atomic distances [3].

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CO$_2$ ICES IN QUIESCENT DARK MOLECULAR CLOUDS

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Carbon dioxide (CO$_2$) is an important component of the interstellar ice with an abundance of 15-25 % with respect to H$_2$O and is believed that dust grain surface chemistry plays an important role in CO$_2$ formation [1]. We have performed laboratory experiments to study the formation of CO$_2$ after ion irradiation of astrophysical relevant ice mixtures. These laboratory spectra have been used to fit the profile of the CO$_2$ bending mode band observed at about 15 µm (660 cm^{-1}) by Spitzer Space Telescope [2, 5] in the line of sight of background sources.

From a qualitative point of view good fits to observations are obtained by considering either three or four laboratory components. From a quantitative point of view a better result is obtained with four components that is when the spectrum of CO$_2$ formed after ion irradiation of CH$_3$OH is added to the fitting procedure. These results support the hypothesis that energetic processing of icy grain mantles can be an efficient means by which CO$_2$ is formed in the quiescent dark cloud regions; moreover it indirectly suggests the presence of CH$_3$OH in icy grain mantles in the quiescent cold regions.

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A PRIMORDIAL ORIGIN FOR MOLECULAR OXYGEN IN COMETS

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Last fall, Bieler et al. (*Nature*, 2015) [1] reported the detection of O_2 in comet 67P/Churyumov-Gerasimenko (67P hereafter) by the *Rosetta* spacecraft with a surprisingly high abundance of 3.7 ± 1.5 % w.r.t. H_2O ice. This makes O_2 the fourth most abundant species in cometary comae (after H_2O, CO and CO_2). Inspection of old mass spectrometry data from *Giotto* for comet Halley suggests that 67P is not the only comet rich in O_2, but that this is a common property [2]. This result has attracted huge interest from planetary scientists, astronomers and the press worldwide. The Rosetta team argued convincingly that O_2 must be of primordial nature, i.e., coming from the interstellar cloud from which our solar system formed. However, interstellar O_2 gas is notoriously difficult to detect and has only been observed in one potential precursor of a solar-like system, rho Oph A [3].

Here, the chemical and physical origin of O_2 in comets is investigated using sophisticated astrochemical models [4]. Three origins are considered: i) in dark clouds, ii) during forming protostellar disks, and iii) during luminosity outbursts in disks. The dark cloud models show that O_2 ice is efficiently formed, reaching the abundance level seen in comets, only when the H/O ratio is low, limiting the conversion of O_2 ice into water for physical conditions. Reproduction of the observed abundance of O_2 and related species, HO_2, H_2O_2, and O_3, in comet 67P/C-G, requires a low diffusion-to-binding energy ratio (< 0.6), a small reaction barrier (~ 300 K) for the surface reactions destroying O_2, and a low H/O ratio facilitated by a high initial fraction of gas-phase atomic oxygen, a high total density, and a low cosmic ray ionisation rate ($< 10^{-17}$ s^{-1}). A temperature of 20 K, slightly higher than the typical temperatures found in dark clouds, also enhances the production of O_2. Disk models show that O_2 can only be formed in the gas phase in intermediate disk layers, and cannot explain the strong correlation between O_2 and H_2O in comet 67P/C-G. However, any primordial O_2 ice can survive transport into the comet-forming regions of protoplanetary disks. Luminosity outbursts driven by accretion variability can entrap disk-formed gas-phase O_2 into the ice mantle and help explain its strong association with water ice; however, other volatile species, CO and N_2, are also trapped, in contradiction with observations towards 67P/C-G. Taken together, the models presented here favour a dark cloud (or ``primordial'') origin for O_2 in comets, albeit for dark clouds which are warmer and denser than those usually considered as solar system progenitors.

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THEORETICAL MODELS FOR INTERSTELLAR CARBONACEOUS DUST AND ICY MIXTURES

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Solar system objects like outer planets, their satellites, comets and asteroids contain a carbonaceous structure often covered by ices of different composition. The carbonaceous content is assumed to be formed by hydrogenated amorphous carbon (HAC). The surface ices are made of frozen H_2O, CH_4, CH_3OH, NH_3 and others. Our goal in this work is to make theoretical models using quantum chemical tools, like ab initio and DFT methods, for the structure of the carbonaceous core and for mixtures of ices with various compositions, and predict their spectra, aiming to match the space observations. We present in this communication a summary of the recent calculations performed in our group on these subjects.

Based on the recent literature [1,2], we have constructed two different models for HAC particles, designated as rings and chains (RC) and substituted graphite (SG) according to their chemical composition and structure (Figure 1). Calculations with varying density values allow proposing structures with low density, in the range of 0.75 to 1 g cm^{-3} as the most likely constituents of the experimental HAC samples [3].

The New Horizons mission has provided infrared spectra on a range of locations of the surface of Pluto and Charon, showing the variety of composition of different spots. The spectra reveal the general abundance of CH_4 ice in Pluto, mixed with CO, N_2 and other hydrocarbons, and also the presence of H_2O at some specific points [4]. In our work we generate amorphous mixtures of H_2O and CH_4 of the desired composition and optimize their structure searching for the minimum of their potential energy surface. The corresponding structure (Figure 2) is taken to calculate the harmonic vibrational spectrum, and as a starting point for a molecular dynamics simulation, which will yield also the prediction of the near-IR spectrum.
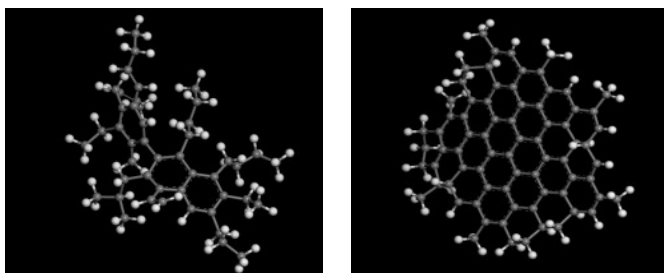

Figure 1. *HAC models used for the simulation: RC (left, [1]) and SG (right, [2])*
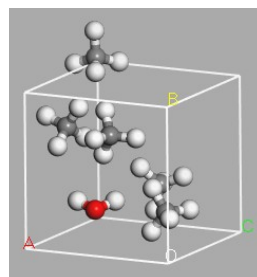

Fiure 2. *Relaxed amorphous structure for a 5:1 CH$_4$/H$_2$O mixture.*

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ATMOSPHERIC PRESSURE PLASMA ASSISTED DEPOSITION OF CARBONACEOUS INTERSTELLAR DUST ANALOGS

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Dust grains, mostly composed of carbonaceous and silicate materials, constitute about 1 % of the interstellar medium (ISM) total mass. Although the nanometer and micrometer-sized solid particles distributed in the ISM play an important role for astrophysical processes, their formation, evolution, nature, distribution and structure is still under investigation. For this reason, various studies have been devoted to the production of deposits which serve as analogs to the interstellar material (e.g. hydrogenated amorphous carbon) in order to gain an accurate and deep understanding of observed phenomena. In recent years, plasma deposition techniques have became appropriate methods to obtain laboratory analog of interstellar dust under controlled conditions. In this study we investigated the deposition and characterization of the carbonaceous compounds growth on various substrates by using a high power dielectric barrier discharge (DBD). Helium, hydrogen and hydrocarbon gases (C_nH_{2n+2}, n= 1 - 4) were employed as main plasma working gas, active gas and precursor gases. A comparative characterization of plasma gas phase and of materials was performed. The carbonaceous materials properties were investigated by spectroscopic (FTIR, Raman, XPS) and microscopic techniques (SEM). Information about the plasma species involved in the growth process was obtained by Mass Spectrometry and FTIR measurements. In addition, we compared our experimental results with astronomical data. The IR spectra of plasma polymerized carbonaceous material pointed many similarity with the astronomical spectra, including the aliphatic sp^3-C-H stretching at 3.4 μm and the aliphatic sp^3-C-H bending at 6.8 μm and 7.2 μm, as can be seen in Figure 1. A. Scanning electron microscopy studies revealed the formation of inhomogeneous aggregates of micron and submicron sized grains (Figure 1. B).
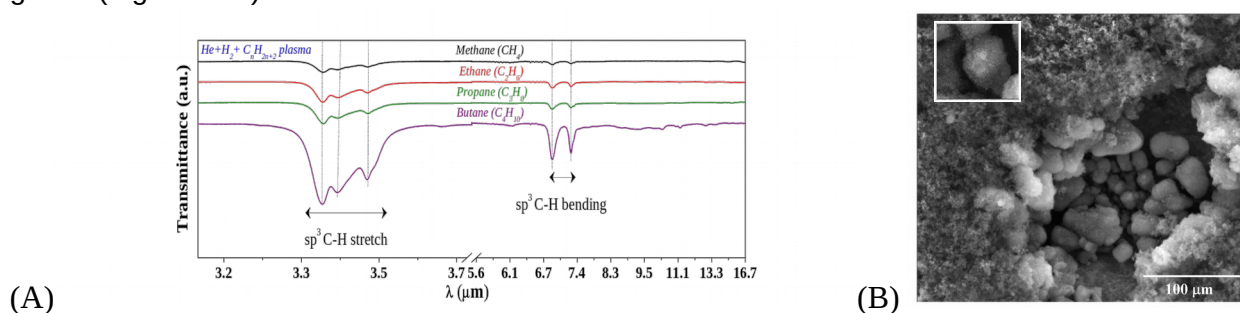

(A) (B)

Figure 1: (A) IR spectra of carbonaceous deposits synthesized using a DBD reactor onto NaCl substrates. (B) SEM image of 'fluffy' deposit growth on flexible carbon substrates from methane. *Parameters*: positive HV pulses with 5.7 kV amplitude, 1 kHz and 400 ns width, atmospheric pressure, 10 % C_nH_{2n+2}, + 89 % He + 1 % H_2.

KINETIC MODEL FOR CHEMICAL REACTIONS IN CH_4-N_2 MIXTURE WITH OXYGEN CONTAINING ADMIXTURES FOR STUDY OF PREBIOTIC ATMOSPHERES

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We developed kinetic model for prebiotic atmospheres for chemical reaction in N_2 + CH_4 mixture. The content of CH_4 was set to 2%, the total pressure was set to 101 kPa and the gas temperature to 300 K. It was assumed that 2% of nitrogen was dissociated to nitrogen atoms in the ground state, the CH_4 was fully dissociated into 90% of CH_3 and 10% of CH_2. This was taken as initial conditions for the calculations and the kinetic equations were solved numerically for time from 0 to 10 s.

The kinetic model uses the set of chemical reactions and their rate coefficients from Loison et al [1]. In this model 189 different particle types and 986 chemical reactions was taken into account. Also reaction with oxygen and oxygen containing species were involved in the model, although the calculations were performed firstly without any oxygen. The initial conditions were as described above. The calculations were also repeated with different initial conditions (different concentrations of nitrogen atoms, CH_3 and CH_2 radicals). The different initial conditions resulted in small changes in the product concentrations, however, the main discrepancies between the model and experimental results were not solved. Also the calculation with initial nonzero oxygen concentration was performed.

It follows from these results that the surface reaction (e.g. on electrode surfaces) are important and these reactions could explain the increased ammonia concentrations observed in the experiment. Finally the results from different experiments with discharges in N_2 + CH_4 mixtures were compared with our results. It was found that our results are in agreement with the results of Ramirez el al [2], who used corona discharge. At corona discharge the surface reaction should not play important role and thus the agreement between model and experiment is better.

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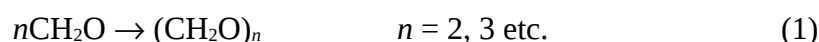
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FRAGMENTATION OF DEPROTONATED GLYCOLALDEHYDE IN THE GAS PHASE AND

RELEVANCE TO THE FORMOSE REACTION

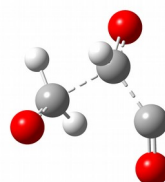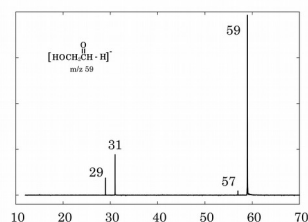Osamu Sekiguchi and Einar Uggerud*

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The formose reaction,[1], formally:

$$n\text{CH}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n \qquad n = 2, 3 \text{ etc.} \qquad (1)$$

has been invoked[2] to explain prebiotic formation of carbohydrates, a source for metabolic energy, as well as the key genetic molecule RNA; in particular because both formaldehyde and glycolaldehyde are among the almost 200 compounds that have been identified in interstellar space).[3]

From gas phase reactivity studies employing tandem mass spectrometry,[4] the unimolecular dissociation of the corresponding base of glycolaldehyde has been probed under conditions of collisional activation. Three reactions were observed in order of decreasing abundance; loss of CO, CH_2O, and loss of H_2. Detailed reaction mechanisms for each of the three reactions were obtained by quantum chemical calculations, and the reaction characteristics and energetics were found to be in good agreement with experimental observations.

The relevance of these findings to the formose reaction and possible interstellar formation of carbohydrates from formaldehyde is discussed. It is concluded that the critical C–C bond forming reaction between two formaldehyde molecules to give the glycoladehyde is unlikely to occur in the gas phase via a route involving the free formyl anion, thereby precluding a key pathway for interstellar formation of carbohydrates. Likewise, a previous investigation of the protonated forms of glycolaldehyde and glyceradehyde ruled out a proton catalyzed alternative.[5,6] Therefore, an alternative formation reaction is suggested.

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PEPTIDE BOND FORMATION IN THE INTERSTELLAR MEDIUM

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The fundamental building blocks of life could have been created in space and transported to Earth via comet collisions. More complex macromolecules could have then been formed from those initial organic precursors and later intelligent life developed. For life to begin complex molecules are needed which consist of smaller constituents for instants sugars, fatty acids, nucleic acids and amino acids. The latter are vital for our existence and can create peptide bonds when fusing together. The two molecules have been detected in the interstellar medium which have the aforementioned bond, namely formamide and acetamide[1]. Through the study of the creation of the amide bond we can gain insight on how higher peptides can be formed in the vacuum of space.

We evaluated the reaction pathways which yield different molecules with a peptide bond, in the interstellar medium using the Gaussian 09[2] program suite, employing MP2 (full) method[3] with the Aug-CC-pVTZ basis set[4]. We calculated the reaction enthalpies and Gibbs free energies of the reaction pathways under the conditions in interstellar space (temperature, pressure). The analysis of the reactions where NH_4^+ and CH_5^+ are formed via the collision of appropriate molecules with H_3^+ were also conducted. We also checked whether evaluated reactions were barrier free and performed an analysis of the corresponding potential energy surfaces of the transition thus creating correspondent energy profiles of the reaction pathways.

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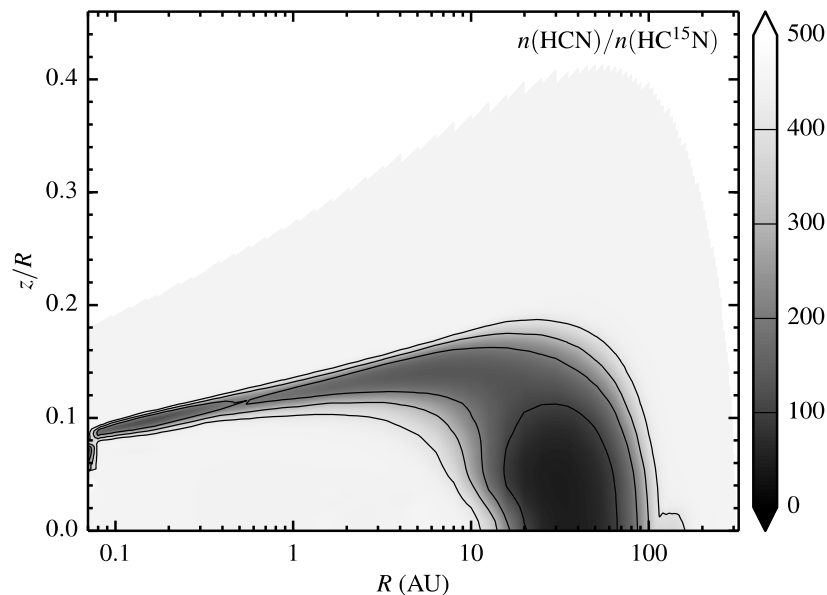# NITROGEN ISOTOPE FRACTIONATION IN PROTOPLANETARY DISKS

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Isotopes offer a powerful means to study the physical and chemical history of the solar system. The two stable isotopes of nitrogen – ^{14}N and ^{15}N – show a range of abundance ratios from 440 in the Sun to 270 on Earth and down to 150 in comets. In order to explain these values, we must trace nitrogen isotope fractionation along the entire process of forming a low-mass star and its planetary system. We will summarize previous work on pre- and protostellar cores, and present new observations [1] and chemical models [2] of protoplanetary disks. The dominant fractionation mechanism is self-shielding of N_2, similar to what has long been known to happen for CO. Low-temperature chemical fractionation does not contribute to the ^{14}N/^{15}N ratio in disks. The average abundance ratio of $HC^{14}N$ to $HC^{15}N$ in our models [2] agrees well with the measurement of 200±100 from ALMA observations of the Herbig Ae star MWC 480 [1].

Abundance ratio of $HC^{14}N/HC^{15}N$ in a typical disk model [2]. The initial ratio is 450. Darker shades of gray indicate stronger fractionation of ^{15}N, consistent with measurements in the solar system and ALMA observations of the Herbig Ae star MWC 480 [1].

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REACTION DYNAMICS OF THE LiH + H REACTIONS

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The lithium chemistry has received a great attention in recent years due to the importance that LiH molecules and its ionic variants can have in the primordial universe[1]. The reaction LiH + H → Li + H2 is considered to contribute to LiH depletion, while the hydrogen-exchange reaction LiH + H → LiH + H leads to the retention of LiH in this process.

In this work we report our recent reaction dynamics calculations of the title reactions using classical trajectory methods and accurate quantum dynamic calculations.
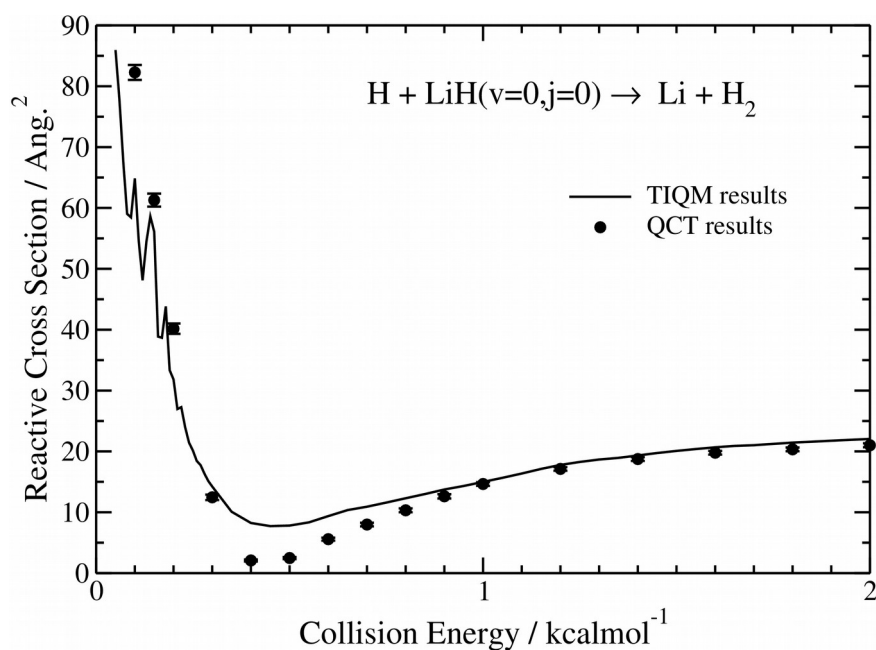

Figure 1: Integral cross sections as a function of collision energy for the depletion reaction

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WG3 - Non thermal desorption from cold surfaces

Program

08h30	J.H. Fillion	Introduction
08h45 - 09h15 (25+5)	H. Linnartz	Vacuum UV Photodesorption and Photochemistry of interstellar Ice Analogues
09h15 - 09h35 (20+5)	G. Munoz-Caro	Photon-induced desorption of astrophysical ice analogues: ice temperature dependence and release of photoproducts during irradiation
09h35 - 10h00 (20+5)	M. Bertin	UV photodesorption of intact molecules and of photofragments from small organics ices
10h00 - 10h30 (25+5)	S. Andersson	MECHANISMS OF SIO OXIDATION: IMPLICATIONS FOR DUST FORMATION
10h30 - 11h00		$C_8H_{10}N_4O_2$ b^re_ak
11h00 - 11h30	E. Dartois	Swift heavy ion modifications of astrophysical water ice
11h30 - 12h30	all participants	Discussion on Photon- and Cosmic Ray- induced desorption - possibility for participant to address open questions (3 slides max)
12h30 - 14h00		$L_uNC_h = f(CH_3(CH_2)_nCOOH + C_nH_{2n}O_n + C_8H_{10}N_4O_2)$
14h00 - 14h30 (25+5)	M. Alducin	Recombinative desorption induced by femtosecond laser pulses
14h30 - 15h00 (25+5)	M. R. S. McCoustra	Photons, Electrons and Cosmic Rays... A Common Story
15h00 - 15h30 (25+5)	H. Zacharias	Laser-induced desorption from doped ices by XUV free-electron laser pulses
15h30 - 16h00 (25+5)	S. Koehler	Low-Energy Electron-Induced Reactions in Amorphous Solid Water
16h00 - 16h30		$C_of^fe_e$ B^re_ak
16h30 - 17h30	all participants	General discussion on molecular processes with possibility for participant to address open questions (3 slides max)
17h30 - 18h30	all participants	Free discussion and discussions around posters
18h30 - 18h45		Conclusion of the workshop

Vacuum UV Photodesorption and Photochemistry of Interstellar Ice Analogues

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Upon vacuum UV irradiation interstellar ice constituents can photo-desorb, photo-dissociate and/or photo-react. Over the last 10 years a substantial number of highly sophisticated experiments and theoretical studies have been performed to characterize these processes quantitatively. All this work has resulted in photo-desorption rates, detailed information on the underlying molecular processes, dissociation branching ratios and chemical networks, providing pathways towards molecular complexity in space. No doubt that much progress has been realized in this period, specifically, as the resulting numbers have shown to be important to interpret astronomical observations and as input in astrochemical models.

It also has become clear that this type of studies is far from trivial. Whereas there exists very good qualitative agreement between experiments performed in different groups and/or different methods, clear mismatches have been reported when it comes to the exact numbers, characterizing photo-induced cryogenic solid state processes. Their origin is likely to be found in the rather high dependency on relatively small changes in the used experimental settings, e.g. the spectral emission pattern of vacuum UV lamps in combination with the wavelength dependency of for example photodesorption, or in response to different ice deposition techniques.

This talk acts as an introduction to today's WP3 meeting, reviewing the state-of-the-art, summarizing the challenges and concludes with some suggestions for future directions, including explicitly astronomical applications.

Photon-induced desorption of astrophysical ice analogs: ice temperature dependence and release of photoproducts during irradiation.

Guillermo M. Muñoz Caro[1], **Rafael Martín Doménech**[1], **Gustavo A. Cruz Díaz**[1,2], **Yu-Jung Chen**[3]

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Energetic photons and ions impinging on icy grains likely contribute to the observed gas phase abundances toward very cold regions. Several studies reproduced CO ice irradiation with UV in the laboratory because this molecule is not directly dissociated at photon energies below 11 eV, which leads to an efficient photodesorption that can be measured by the decrease of its infrared absorption band. The linear decrease of the CO photodesorption yield as a function of ice deposition temperature is intriguing and cannot be explained by variations in the ice density or optical properties, since they are only observed above 20 K.

Other molecular ice components are, either efficiently photodissociated, or not active in the infrared: CH_3OH, CO_2, O_2, CH_4, NH_3, etc. Their photon-induced desorption is two or more orders of magnitude lower than that of CO, but also their photoproducts are found to desorb during irradiation. The desorption of photoproducts follows two different patterns: a) an increasing desorption up to a maximum as the concentration of the product grows in the ice bulk, and b) a constant desorption that results from photochemical processes on the ice surface, leading to the desorption of fragments or molecules. In our presentation we will open the debate of CO photodesorption dependence on the physical ice properties, and discuss the two desorption patterns of photoproducts observed during CH_3OH ice irradiation and the $H_2O:CH_4$ ice mixture, the latter is presented in the poster of R. Martín-Doménech.

UV photodesorption of intact molecules and of photofragments from small organics ices

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2. LCP (UMR 8000), CNRS, Université Paris-Sud, F-91405 Orsay, France
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The photodesorption, i.e. the desorption of molecules induced by the UV photoprocessing of the molecular icy mantles of grains, is often considered as an important non-thermal process for explaining the gaseous molecular abundances in some of the coldest regions of the ISM (disks, edges of clouds...). Past experimental studies of the photodesorption process have given many results for several simple ices (CO, H_2O, CH_3OH, CO_2...). However, for some cases, the absolute photodesorption rates varied from a study to another. For some others, the rates were found surprisingly constant at about 10^{-3}-10^{-4} molecules/photon for a collection of condensed species, whose properties are significantly different (adsorption energies, UV absorption cross sections, mass, dissociative behaviors...).

Conducting energy-resolved experiments at the synchrotron SOLEIL, we have these last years focused our studies on UV photodesorption in the 7 - 13.6 eV range, and obtained for the first time energy-resolved photodesorption rates for a collection of small molecules such as CO, N_2, O_2 and CO_2 [e.g. 1-3]. These studies have highlighted the importance of an indirect desorption processes, mediated by the excitation of co-adsorbed CO in mixed ices, which as a consequence makes the photodesorption rates very dependent on the ice composition. Recently, we have focused our photodesorption studies on condensed methanol CH_3OH and formaldehyde H_2CO, which are both organics detected in the gas phase of the cold ISM.

Our recent results on the photodesorption of methanol and formaldehyde will be presented. The predominant role of the UV-photochemistry in the solid organics will be emphasized, together with the role of the CO-mediated indirect process in the case of CO-organics mixed ices. For the H_2CO ices, this photochemistry promotes the intact molecule desorption by the production of excited CO fragments in the solid phase [4]. On the contrary, the photodissociation of solid methanol prevents its photodesorption as an intact molecule, which has been found very low as compared to what was previously considered. Instead, the photoprocessing is dominated by the desorption of its direct photofragments such as CH_3, OH, H_2CO, H_3CO and CO [5], therefore enriching the gas phase in reactive radicals.

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Photodesorption of water from interstellar ices: interplay between simulations and experiments

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The interaction of UV photons with ice-covered dust grains in interstellar space is important in the chemical and physical processing of interstellar matter. Photodissociation of water molecules in the solid state produces reactive radicals that react to form more complex molecules. In addition, the absorption of UV photons leads to desorption of molecules and in cold regions, where thermal desorption is insignificant, this process controls the ratio of molecules in the gas phase and the solid state.

In this talk, I will give an overview of our current understanding of the basic mechanisms of water photodesorption based on recent experimental and theoretical studies. In particular, I will present results from molecular dynamics simulations on these processes, performed by ourselves and others, and their interplay with experimental studies to increase the qualitative and quantitative understanding of photodesorption processes. I will also discuss some future research opportunities from a molecular simulation point of view.

Swift heavy ion modifications of astrophysical water ice.

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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 complex evolution under 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 cosmic ray particles that produces new species via radiolysis processes, but first affects their structural changes and induces molecules and radicals desorption from these grains. Theses cosmic rays can be simulated in the laboratory for a better understanding of astrophysical processes. The high-energy cosmic rays component (just below or above 100 MeV/u) irradiation was so far only scarcely simulated experimentally. Nevertheless, there is a clear need to study the interaction of high energy cosmic rays with ices, since their energy deposit on dust grains and ice mantles is expected to be important. In particular, the physical state of the ice is extremely important in many respects for astrophysicists, to allow in particular surface physicist to perform experiments on realistic surfaces for a better understanding of interstellar chemistry. This talk will be dedicated to describe the evolution, in an astrophysical context and based on laboratory experiments, of the ice physical state and focus on sputtering, resulting from the interactions with swift ions.

Recombinative desorption induced by femtosecond laser pulses

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Femtosecond laser pulses have proven to be very efficient in promoting reactions at metal surfaces that cannot be initiated by thermal activation.

The wavelength and intensity of the laser pulse determine if a reaction starts as a direct excitation of the adsorbate or, on the contrary, if it is an indirect mechanism in which the substrate efficiently absorbs the laser energy to subsequently release it on the adsorbates. The latter is precisely the mechanism that better accounts for reactions induced by UV/vis lasers on metal surfaces. In this talk I will focus on such kind of photodesorption processes and present recent results on the desorption of molecular O_2 from Ag(110) as well as on the recombinative desorption of H_2, D_2 and HD from Ru(0001). These two systems will allow us to extract information on how the desorption yields are affected by the chemisorption properties and by the presence of additional adsorbates

Photons, Electrons and Cosmic Rays… A Common Story

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This short talk will try to piece together from various directions a common story in relation to non-thermal processes in and on ices promoted by various mechanisms. At the core of the this story rests the unique ability of water ice to support long-lived excitons.

Laser-induced desorption from doped ices

by XUV free-electron laser pulses

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The interaction XUV and VUV radiation with doped molecular ices on grains is important for light-assisted association or dissociation reactions in or on these ices, particularly in accretion disks and the photon dominated regions of interstellar clouds [1]. Important insights into the non-thermal desorption kinetics of CO from pure CO [2] and $CO:N_2$ ice mixtures [3] have been obtained through electronically resonant excitation using quasi-cw synchrotron radiation. For probing the underlying molecular dynamics of bond formation or breaking, as well as the desorption process itself, femtosecond duration pulses are required. We therefore used XUV pulses from the free-electron laser FLASH in Hamburg to irradiate various molecular ices and ice mixtures. Neutral products were state selectively detected by REMPI while ionic desorption products were directly detected by a linear time-of-flight mass spectrometer. For all experiments an XUV photon energy of $h\nu = 40.8$ eV was used to simulate the action of the HeII resonance line. The ices were held at a temperature of $T = 18$ K.

Here we will report on the first preliminary results for the desorption of neutral CO from a multilayer CO ice. CO was detected state selectively by (2+1) REMPI via the B $^1\Sigma \leftarrow$ X $^1\Sigma$ band. It is found that the CO rotational excitation is quite low with a rotational temperature of about $T_{rot} \sim 160$ K. On the other hand vibrationally excited CO molecules were detected yielding a hot vibration with a vibrational temperature in the range of $T_{vib} \sim 1500$ to 2000 K. This leads to the preliminary conclusion that desorption proceeds via a short-lived CO anion intermediate. As the bond distance in CO^- is very different from the neutral carbon monoxide, this leads to vibrational excitation after the electron jumps back to the remaining ice, leaving a neutral CO to desorb.

We also investigated the system of mixed methane and deuterated water ice. The thickness of the molecular ice layer was about 13 nm, which permits a portion of the incident radiation to reach the graphite substrate. Besides simple fragments from both parent ice species, methane association reaction products up to $C_3H_x^+$ have also been observed. The most striking observation is the appearance of $C_nH_x^+$ clusters with up to n = 11. For the desorption of these clusters a highly nonlinear dependence of the yield (m ~ 5) on the desorption laser intensity is found. This highly nonlinear yield allowed a measurement of the initial dynamics by two-pulse time-correlated desorption. A preliminary analysis shows a width of the desorption yield of about 1.5 ps (FWHM), with the peak delayed by less than 500 fs. This points to an electronic process for the primary step, as expected at these photon energies.

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Low-Energy Electron-Induced Reactions in Amorphous Solid Water

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The low energy electron-stimulated reduction and oxidation reactions of CO sandwiched between layers of amorphous solid water (ASW) were investigated for various film thicknesses and electron fluences.

Layered water/CO films were grown on a Pt substrate by first depositing a thick ASW layer, followed by a single monolayer of CO, which was capped by a thick ASW layer. The films were irradiated with 100 eV electrons, and the concentration of reactants and products was monitored using temperature-programmed desorption and reflection absorption IR spectroscopy.

The reduction intermediates and products HCO, H_2CO, H_3CO and CH_3OH were detected, as well as CO_2 from the oxidation channel. CO concentration profiles as a function of electron fluence were simulated using a simple Monte Carlo model that tracks H atoms through the ice lattice.

The results support an H atom migration mechanism, with H atoms diffusing through the film and taking part in the reduction of CO. It appears that H atoms diffuse deeper within the film than OH radicals, the latter of which are responsible for the oxidation pathway.

Posters

M. Domenech	UV photoprocessing of an H_2O:CH_4 ice analog: two observed patterns in the desorption of photoproducts
R. Dupuy, Bertin, G. Féraud, C. Romanzin, P. Jeseck , L. Philippe, T. Putaud, X. Michaut, and J.-H. Fillion	UV photodesorption of CH_4 from pure and CO-rich ices

UV photoprocessing of an H$_2$O:CH4 ice analog: two observed patterns in the desorption of photoproducts.

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Photodesorption of molecules is one of the non-thermal desorption mechanisms invoked to explain the gas-phase abundance of certain species toward cold regions in the interstellar medium. Photodesorption from ices whose components cannot be directly dissociated by UV photons is thought to take place through an indirect mechanism usually known as Desorption Induced by Electronic Transitions (DIET). However, photodissociation in ices can trigger other desorption mechanisms.

We present UV-irradiation experiments of a binary water-rich ice mixture (H$_2$O:CH4). Photon-induced formation of CO, CO$_2$, CH$_3$OH, and H$_2$CO was observed. The contribution from different mechanisms to the photon-induced desorption of some of the photoproducts was evidenced by the observation of two different patterns for the evolution with fluence of their photodesorption yields during the experiments.

In particular, the photodesorption yield of CO exhibited an increasing desorption as its concentration in the ice grew. This photodesorption is probably driven by an indirect mechanism, like the DIET mechanism, that is able to induce photodesorption of the products accumulated in the ice and subsequently exposed to the surface. On the other hand, H$_2$CO desorbed with a constant yield during UV-irradiation. This could be explained by an inmediate desorption right after their formation on the ice surface, probably thanks to the excess energy in the parent photofragments after dissociation by a UV photon.

UV photodesorption of CH$_4$ from pure and CO-rich ices

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In cold and dense regions of the interstellar medium (ISM), molecules are found either in gas phase or accreted at the surface of insterstellar dust grains. UV irradiation of the ice mantle of these grains is the motor for a rich solid-phase chemistry, but also provides a non-thermal pathway for the desorption of molecules. This photodesorption process is believed to account for a significant part of the gas-to-ice abundance ratio of some molecules. In recent years, laboratory studies have aimed at determining absolute photodesorption rates of molecules commonly found in the ISM (CO, H$_2$O, N$_2$, CO$_2$...) and at understanding the underlying desorption mechanisms.[1][2][3]

Here we report an experimental study of the photon-induced desorption of CH$_4$, one of the most abundant molecules in ice mantles. We obtained the energy-resolved photodesorption rates between 7 and 13.6 eV for both a pure, thick CH$_4$ ice and for CH$_4$ deposited on top of a thick CO ice. The latter confirms results from a previous study [1] that showed the ability of CO to induce desorption of other molecules, significantly changing the energy-resolved profile and overall photodesorption yield of CH$_4$ compared to the case of the pure ice.

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