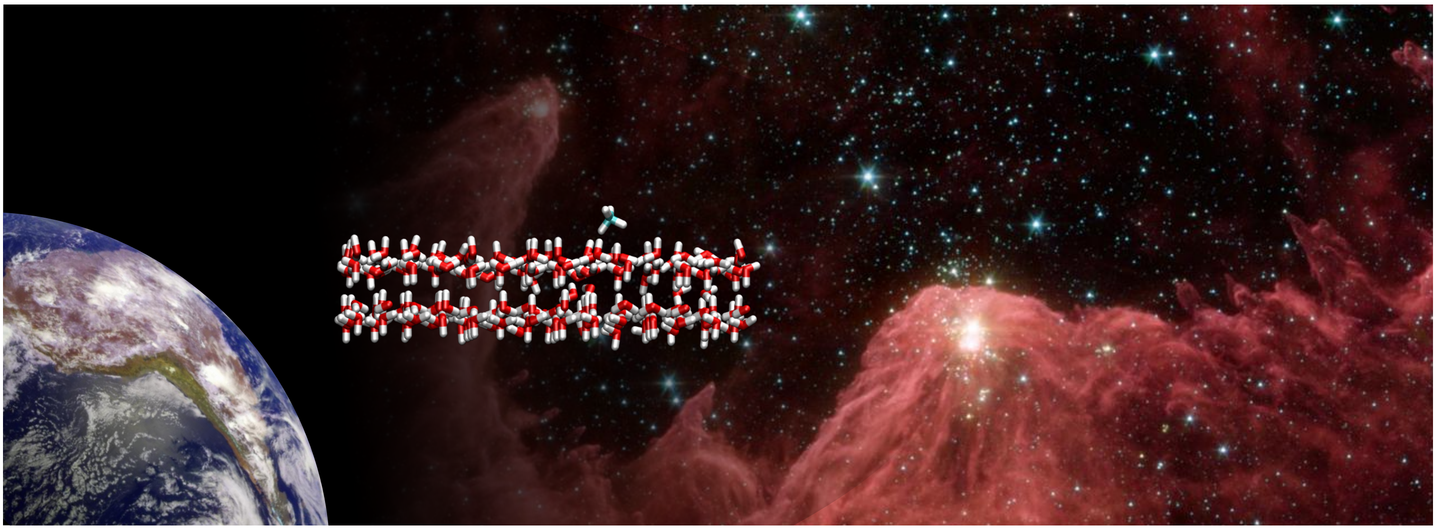
PROGRAMME AND ABSTRACTS

Astrochemistry meets Surface Science: Theoretical Frontiers

Aarhus Institute of Advanced Studies, Aarhus University, Denmark

April 5th - 8th 2022



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PROGRAMME

Tuesday April 5th:

14:00-14:15	Welcoming address	Organizers
Session 1: Recent progress and current challenges in astrochemistry and surface science (chair: Mie Andersen)		
14:15-15:15	Invited talk	Eric Herbst, University of Virginia: “Surface Chemistry in Interstellar Space”
15:15-16:15	Invited talk	Karsten Reuter, Fritz-Haber-Institut der MPG: “Challenges to First-Principles Modelling of Astro and Surface Catalysis”
16:15-16:45	Coffee break	
16:45-17:45	Intro session	1-minute presentations from all participants
17:45-19:45	Reception	

Wednesday April 6th:

Session 2: Reaction mechanisms and rate constants (chair: Zeyuan Tang)		
9:00-10:00	Invited talk	Albert Rimola, Universitat Autònoma de Barcelona: “Astrochemical reactions on dust grains. Quantum mechanical investigations and analogies with terrestrial surface chemistry”
10:00-10:30	Contributed talk	Berta Martínez-Bachs, Universitat Autònoma de Barcelona: “Formation Route of Formamide on Interstellar Water Ice Surfaces. A Quantum Chemical Investigation”
10:30-11:00	Coffee break	
11:00-11:30	Contributed talk	Joan Enrique-Romero, Universitat Autònoma de Barcelona: “A computational chemistry approach to the kinetics of radical–radical reactions on amorphous water ice surfaces”
11:30-12:00	Contributed talk	Marta Corno, Department of Chemistry, University of Turin: “Water reactivity on Schreibersite: a reservoir for prebiotic living phosphorus”
12:00-14:00	Lunch	
Session 3: Reactions of carbon-bearing molecules and PAHs (chair: Raffaele Cheula)		
14:00-15:00	Invited talk	Thanja Lamberts, Leiden Institute of Chemistry and Leiden Observatory: ”Towards molecular complexity in interstellar ices (How to marry laboratory and computational astrochemistry)”
15:00-15:30	Contributed talk	Tamar Stein, The Hebrew University of Jerusalem, Israel: “Molecular dynamics reveals formation path of benzonitrile cation formation in conditions relevant to the interstellar medium”

15:30-16:00	Contributed talk	Zeyuan Tang, Department of Physics and Astronomy - Center for Interstellar Catalysis, Aarhus University: “Dimerization of dehydrogenated polycyclic aromatic hydrocarbons on graphene”
16:00-16:30	Coffee break	
16:30-17:30	Discussion session	Moderated by Herma Cuppen with help from Albert Rimola, Thanja Lamberts, Eric Herbst and Liv Hornekær
17:30-19:30	Poster session	

Thursday April 7th:

Session 4: Structure and properties of interstellar ices (chair: Estefanía Rossich Molina)		
9:00-10:00	Invited talk	Céline Toubin, Department of Physics, Lille University: “Molecular modelling of interstellar ices”
10:00-10:30	Contributed talk	Aurèle Germain, University of Turin: “Computer Generated Realistic Interstellar Icy Grain Models: Physico-chemical Properties”
10:30-11:00	Coffee break	
11:00-11:30	Contributed talk	Jessica Perrero, Universitat Autònoma de Barcelona: “A Computational Study of Binding Energies of Astrochemically Relevant S-bearing Species”
11:30-12:00	Contributed talk	Lorenzo Tinacci, Université Grenoble Alpes: “Theoretical distribution of the ammonia binding energy at interstellar icy grains: a new computational framework”
12:00-12:30	Contributed talk	Zachary Amato, The Open University / ISIS Neutron and Muon Source: “Exploiting Neutrons to Unveil Star-Formation: Exploring Dynamical Amorphous Ice Systems”
12:30-14:00	Lunch	
Session 5: Complex materials and structure-dependent kinetics (chair: Herma Cuppen)		
14:00-15:00	Invited talk	Hannes Jónsson, Faculty of Physical Sciences, University of Iceland: “Adaptive Kinetic Monte Carlo Simulations of Long Timescale Processes at Surfaces of Solids”
15:00-15:30	Contributed talk	Mie Andersen, Aarhus Institute of Advanced Studies & Department of Physics and Astronomy - Center for Interstellar Catalysis, Aarhus University: “Combining machine learning and microkinetic modelling to treat complex reactions in surface catalysis”
15:30-16:00	Contributed talk	Raffaele Cheula, Department of Physics and Astronomy - Center for Interstellar Catalysis, Aarhus University: “Reaction mechanism and active sites of WGS and RWGS via structure-dependent microkinetic modeling and machine learning”

16:00-16:30	Coffee break	
16:30-17:30	Discussion session	Moderated by Mie Andersen with help from Céline Toubin, Hannes Jónsson, Karsten Reuter and Bjørk Hammer
19:00	Conference dinner	Pihlkjær Restaurant, Mejlgade 28 (baghuset), 8000 Aarhus C

Friday April 8th:

Session 6: Energy dissipation and non-thermal processes (chair: Joan Enrique-Romero)		
9:30-10:00	Contributed talk	Herma Cuppen, Theoretical Chemistry Department, Institute for Molecules and Materials, Radboud University Nijmegen: "Energy dissipation and restructuring in interstellar ice upon excitation of admolecules"
10:00-10:30	Contributed talk	Stefano Ferrero, Universitat Autònoma de Barcelona: "The energy dissipation process of hydrogenation reactions of atomic nitrogen on water ice surfaces"
10:30-11:00	Contributed talk	Alec Paulive, University of Virginia: "Modelling Cosmic Ray Sputtering of Interstellar Grain Ices"
11:00-11:15	Coffee break	
Session 7: Experimental aspects of astrochemistry and surface science (chair: Joan Enrique-Romero)		
11:15-12:15	Invited talk	Liv Hornekær, Department of Physics and Astronomy - Center for Interstellar Catalysis, Aarhus University: "Polycyclic Aromatic Hydrocarbons as a precursor to Molecular Complexity in Interstellar Space"
12:15-12:30	Wrap-up	Organizers
12:30-13:00	Lunch (sandwich) and departure	

ABSTRACTS

INVITED AND CONTRIBUTED TALKS

Surface Chemistry in Interstellar Space

E. Herbst[1]

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Interstellar space in our galaxy is not empty, but contains large clouds of gas and tiny dust particles as well as a rich supply of molecules, mainly organic in nature. Moreover, dense portions of these clouds are collapsing to give rise to newly-born stars and associated planets. There is a large body of evidence that that most of the molecules are formed in the clouds themselves, both via gas-phase processes and reactions on and in icy mantles covering the dust particles of silicates and carbonaceous material. Starting in the early 1970's, the detection of molecules, especially in the gas phase by rotational spectroscopy, has led to the detection of over 200 molecules ranging in size from two to nearly twenty atoms. The synthesis of these molecules in both the gas and on dust particles has been studied in detail both via theory and experiments, and by the use of giant chemical simulations in an attempt to reproduce the observations of molecules and their densities. Indeed, the chemistry that occurs can tell us much about the physical conditions in both colder regions and star-forming zones. Although gas-phase chemistry was studied first and was able to reproduce the abundances of both a large number of terrestrial-like and exotic species in the gas, it was eventually realized that significant portions of the organic molecules in the gas were synthesized on and in physisorbed layers of the ice mantle dominated by water ice. The synthesis was followed by desorption into the gas via both non-thermal and thermal processes. Infrared spectra of molecules remaining on mantles have been studied in cold regions, with the largest one methanol. The history of surface chemistry has gone through stages of increasing complexity from classical Langmuir-Hinshelwood and Eley-Rideal mechanisms to a host of newly suggested processes known as non-diffusive and three-body processes, as shown in Figure 1.[1,2] Laboratory experiments have confirmed some of these processes. Moreover, highly energized cosmic rays bombard the dust ices to form organic molecules via radiolysis. In this talk, I will give an overall view of the progress of interstellar surface chemistry with an emphasis on newly predicted mechanisms, which require more theory and experiments by surface scientists.

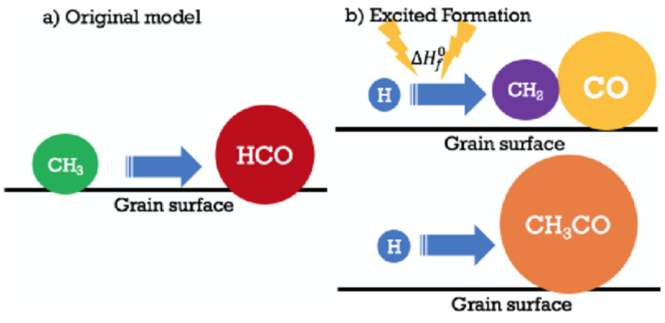

Figure 1: New Synthetic Mechanisms: a three-body process

References:

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Challenges to First-Principles Modelling of Astro and Surface Catalysis

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While at first glance worlds apart, research on heterogeneous catalysis (on Earth) exhibits an increasing overlap with research on chemical synthesis in space environments. Nanocluster and single-atom catalysts made out of abundant transition metals on low-dimensional supports are innovative systems that satisfy demands of sustainability and maximum materials efficiency in the prior field. In the latter field they are drivers for chemical space evolution that are formed by deposition on, as well as space-weathering and sputtering of mineral grains. These low-symmetry and often fluxional systems pose strong challenges to first-principles based modelling and simulation. In my talk I will survey some of these challenges and recent approaches to meet them, highlighting efforts to establish reaction mechanisms or machine-learned surrogate models for numerically efficient adsorption energetics. Particularly intriguing is the question of heat dissipation and a potential hot chemistry.

Astrochemical reactions on dust grains. Quantum mechanical investigations and analogies with terrestrial surface chemistry

A. Rimola[1], J. Enrique-Romero[1], S. Ferrero[1], B. Martínez-Bachs[1], J. Perrero[1,2], S. Pantaleone[2], C. Ceccarelli[3], N. Balucani[4] and P. Ugliengo[3]

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The Universe is molecularly rich [1]. Its chemical diversity and complexity is reflected by the *ca.* 240 molecular species detected in the gaseous phase by means of radioastronomy [2] and the different solid-state phases in the form of dust grains [3]. The presence of the gas-phase molecules cannot be explained uniquely by reactions taking place in the gas phase but chemical reactions occurring on the surfaces of grains are essential to rationalize the interstellar chemistry. However, combining astronomical observations with astrochemical modelling and laboratory experiments is not enough to fully unveil the grain surface chemistry and its contribution to the chemistry of space because they hold some intrinsic limitations [4,5,6]. Quantum chemical simulations can partly alleviate this as they provide reliable, quantitative atomic-scale information (structure, energetics, and dynamics) of chemical processes taking place on the surface of grains. This situation is somehow analogue to that in the past, *i.e.*, accurate atomistic models and characterization of their electronic structure features were very helpful to interpret complex surface chemistry experiments developed on Earth laboratories under well-controlled conditions. One of the best examples is the combined use of sophisticated surface science experimental techniques along with quantum chemical calculations to understand the relevant Haber-Bosch NH_3 synthesis [7]. This contribution aims to present the powerful potentialities of current state-of-the-art quantum chemical simulations to obtain unique, fundamental information that help improving our know-how on the interstellar grain surface chemistry, showing moreover similarities (and differences!) when the same approach is adopted for terrestrial surface chemistry purposes. To this end, examples on the modelling of realistic grain surfaces (here silicates and ices [8]), on simulations dealing with adsorption phenomena (here astrochemically-relevant species on water ice [9]) and chemical reactions (here the ethanol formation from reaction of CCH with H_2O ice [10]), and on the fate of the extra energy released in exothermic reactions (here the H_2 formation, [11]) will be presented, all in all being compared with experimental/theoretical investigations on the terrestrial amide bond formation catalyzed by silica surfaces [12].

References:

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[2] B.A. McGuire, Astrophys. J. Supp. Ser. **239**, 17 (2018).
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[5] H.M. Cuppen, C. Walsh, T. Lamberts, et al., Space Sci. Rev. **212**, 1 (2017).
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Formation Route of Formamide on Interstellar Water Ice Surfaces. A Quantum Chemical Investigation

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Interstellar formamide is a molecule of significant relevance because belongs to the group of interstellar complex organic molecules (iCOMS), which are representative compounds of the dawn of organic chemistry [1]. Moreover, formamide also plays an important role in prebiotic chemistry, not only because it contains carbon, oxygen, hydrogen and nitrogen(the four most important atoms from a biological point of view), but also because it is the simplest species containing the amide bond, the bond that joins amino acids forming peptides [2]. Due to its importance, alongside that has been detected in several star forming regions, different formation routes have been considered, both considering gas-phase reactions and processes on ice surfaces of dust grains [2]-[4]. In this contribution, the formation route of formamide starting from NH_2 and H_2CO, a synthetic route proposed to occur in the gas-phase [3], has been studied on water ice surface models in the crystalline and amorphous structural states adopting a periodic approach both for a. Potential energy surfaces have been obtained by optimizing the stationary points at the HF-3c level followed by single point energy calculations at DFT. Results indicate important differences with respect to the gas-phase synthesis due to surface effects.

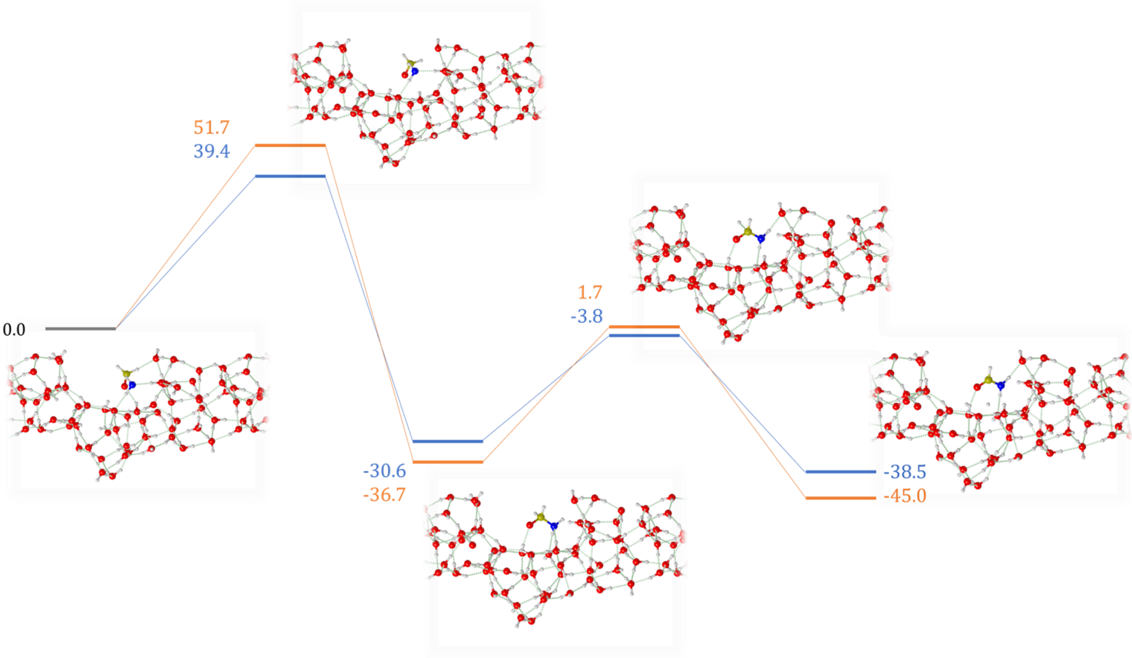

Figure 1: Potential energy surface and the corresponding stationary points of the $NH_2 + H_2CO \rightarrow NH_2CHO + H$ reaction on the amorphous slab model. Relative energy values in blue correspond to those computed at B3LYP-D3(BJ) and in orange to those at M06-2X-D3, in kJ/mol. Atom color legend: red, O; blue, N; green, C white, H.

References:

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A computational chemistry approach to the kinetics of radical–radical reactions on amorphous water ice surfaces

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The formation of interstellar complex organic molecules (iCOM) is a hot topic in current astrochemistry discussions. Understanding how these species are formed, destroyed and evolve in space is of high importance in order to predict the ultimate organic complexity reached in the interstellar medium (ISM) ([1], [2]). Two paradigms are usually invoked in the literature. The first one assumes that gas phase reactions are responsible for the formation of iCOMs after the release of simple precursors previously stored on interstellar dust grains. The second one assumes that radicals formed on in these icy mantles diffuse and react barrierlessly forming iCOMs. The latter model has gained much popularity among astrochemical models in the last years, even though some basic assumptions of the paradigm are still under debate. This is the case of the radical-radical reactivity assumption, which is extremely difficult to quantify experimentally given that radicals are short lived species.

Here we propose a complementary, and sometimes, unique alternative method: theoretical quantum chemical calculations, which can provide a precious atomistic perspective from which to study such processes (e.g. [3], [4], [5]). Thanks to this approach we showed that radical–radical reactions are not necessarily barrierless, that a competitive channel can exist involving a direct H-abstraction from one radical to the other (e.g. CH_3 + HCO → CO + CH_4) and that a radical–radical case by case study is necessary.

In this contribution, we present our latest chemical kinetics results based on the microcanonical transition state theory on the radical–radical reactivity [5]. An example is the reaction between HCO and CH_3, leading to either acetaldehyde (CH_3CHO) or CO + CH_4, on amorphous solid water ices. Additionally, we have also explored their deuterated counterparts in order to investigate the kinetic isotope effects on these reactions.

References:

[1] E. Herbst. & E. F. Van Dishoeck, ARA&A 47, 427-480 (2009).
[2] C. Ceccarelli, S. Viti, N. Balucani, et al., MNRAS 476(1), 1371-1383 (2018).
[3] A. Rimola, D. Skouteris, N. Balucani, et al., ACS Earth and Space Chemistry 2(7), 720-734 (2018).
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Water reactivity on Schreibersite: a reservoir for prebiotic living phosphorus

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Phosphorus is an element of primary importance for all living creatures, being present in many biological activities in the form of phosphate (PO_4^{3-}). However, there are still open questions about the origin of this specific element and on the transformation which allowed it to be incorporated in biological systems. The most probable source of prebiotic phosphorus is the intense meteoritic bombardment during the Archean era, few million years after the solar system formation, which brought tons of iron-phosphide materials (schreibersite) on the early Earth crust. [1] It was recently demonstrated that by simple wetting/corrosion processes from this material various oxygenated phosphorus compounds are produced. [2]

In the present work, the wetting process of schreibersite (Fe_2NiP) was studied by computer simulations using density functional theory, with the PBE functional supplemented with dispersive interactions through a posteriori empirical correction (D*0). [3,4] Therefore, the two stable (110) and (001) Fe_2NiP surfaces were used simulating different water coverages, from which structures, water binding energies and vibrational spectra have been predicted. The computed (ana-)harmonic infrared spectra have been compared with the experimental ones, thus confirming the validity of the adopted methodology and models (see Figure 1). [5,6] Moreover, water reactivity was inspected in several possible deprotonation reactions, also increasing the number of water molecules in order to lead to the formation of phosphonic and phosphoric acids and their corresponding deprotonated forms.

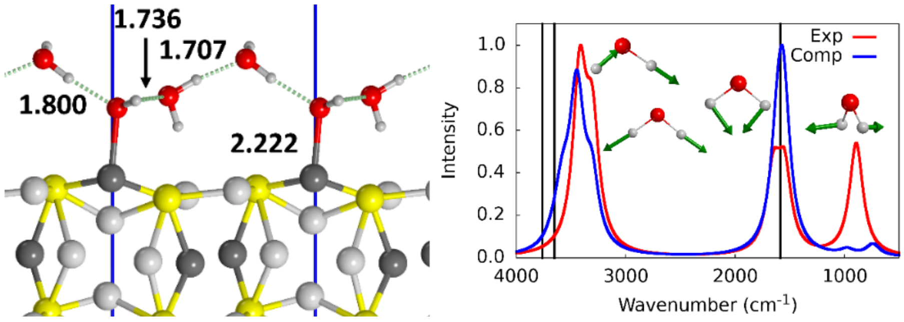

Figure 1: PBE-D*0 optimized geometry of water monolayer on the (110) Fe_2NiP surface (left) and simulated vs experimental IR spectrum (at 125 K), right. Atom color legend: H in white, O in red, P in yellow, Fe in light grey, Ni in dark grey.

References:

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Towards molecular complexity in interstellar ices (How to marry laboratory and computational astrochemistry)

Thanja Lamberts[1,2] and team
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The darkness readily observed between the stars on a clear night sky is far from empty. In fact, a large variety of molecules has been detected in the gas phase. They make up about 99% of the total mass in the Interstellar Medium (ISM). The final 1% of mass in the ISM is brought about by dust grains that once were expelled by dying stars.

I focus primarily on the cold, dense molecular medium where surface reactions lead to the build-up of ‘dirty’ ices, forming a molecular mantle covering the micron-sized dust grains. Species accrete, diffuse, and react on the surface after which they can evaporate back into the gas phase. The interplay between these processes determines which molecules are formed, where, and whether or not they are astronomically observable, either in the solid or gas phase. Confirmation or exclusion of reaction pathways is possible experimentally, however, in order to quantitatively disentangle the relative importance on realistic amorphous ices I make use of computational chemistry. This way I aim to provide coarse-grained astrochemical models with crucial input parameters, such as branching ratios, binding energies, rate constants, and energy dissipation efficiencies.

In this talk I will touch upon reactions of carbon bearing molecules, originating both from carbon monoxide [1,2] and atomic carbon [3,4], to show how an intricate interplay of reactions can lead to the formation of formaldehyde and methane, respectively. I will discuss this both from an experimental and computational point-of-view and link the various intermediates to other recent studies.

References:

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Molecular dynamics reveals formation path of benzonitrile cation formation in conditions relevant to the interstellar medium

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Understanding how complex organic molecules are formed in the harsh environment of the interstellar medium has long presented a significant puzzle to scientists. The work presented here demonstrates how aromatic molecules and aromatic nitrogen heterocycles (and nonaromatic molecules) are formed from van der Waals clusters upon ionization. Applying ab initio molecular dynamics, we demonstrate that benzonitrile cation can be formed when the clusters contain acetylene and cyanoacetylene—some of the building blocks found in Taurus Molecular Cloud-1.[1] Interestingly, benzonitrile was recently detected in Taurus Molecular Cloud-1.[2] Our results also demonstrate possible routes for forming other important compounds, including a bicyclic structure.

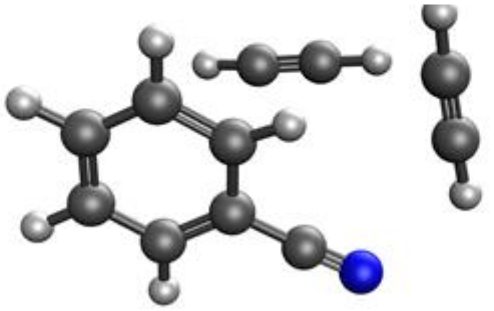

Figure 1: Benzonitrile acetylene complex.

References:

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Dimerization of dehydrogenated polycyclic aromatic hydrocarbons on graphene

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Dimerization of polycyclic aromatic hydrocarbons (PAHs) is an important, yet poorly understood step in on-surface synthesis of graphene (nanoribbon), soot formation, growth of carbonaceous dust grain in the interstellar medium (ISM). The on-surface synthesis of graphene and the growth of carbonaceous dust grain in the ISM require the chemical dimerization in which chemical bonds are formed between PAH monomers. An accurate and cheap method of exploring structure rearrangements is needed to reveal the mechanism of chemical dimerization on surfaces. This work has investigated the chemical dimerization of two dehydrogenated PAHs (coronene and pentacene) on graphene via an evolutionary algorithm augmented by machine learning surrogate potentials and a set of customized structure operators. [1] Different dimer structures on surfaces have been successfully located by our structure search methods. Their binding energies are within the experimental errors of temperature programmed desorption (TPD) measurements. [2] The mechanism of coronene dimer formation on graphene is further studied and discussed.

References:

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Molecular modelling of interstellar ices

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Heterogeneous processes are of key importance in both atmospheric and astrophysical chemistry. Significant progress has been achieved in the past decades, showing the importance of the atomistic approach to fully understand the catalytic processes in these particular environments. The description of the physical properties of atoms and molecules interacting with dust grain particles is a fundamental aspect in astrophysics to interpret observations and to refine astrochemical models [1]. The understanding of surface processes requires in particular a good description of the grain surface. Molecular dynamics (MD) approaches allow to describe amorphous or crystalline nanoscopic surfaces [2]. The obtained structures give a sample of relevant geometries for quantum level studies (QM) where the system is then cut into several parts and described with different levels of theory. By this type of approach, we are able to describe processes such as chemisorption [3], surface reactivity [4] or induced vibrational shifts [5].

In this talk, the challenges, advances and limitations of molecular scale modeling of surfaces of astrophysical interest will be discussed.

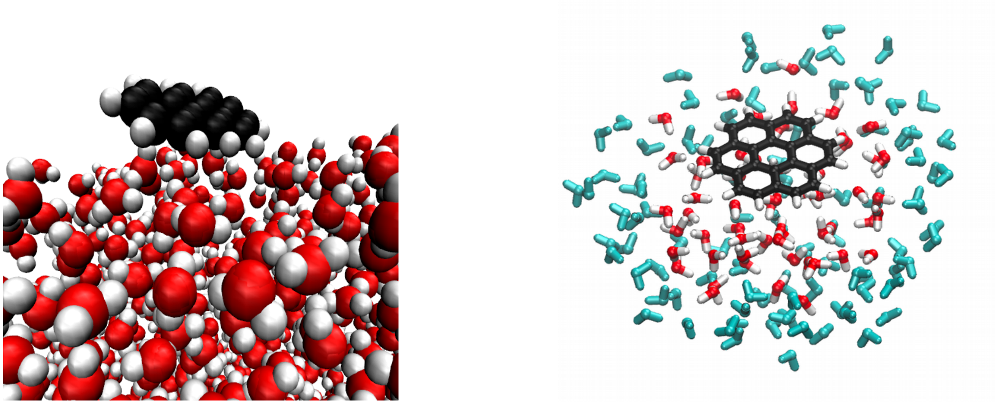

Figure: Molecular representation of water ices. On the left, adsorption of a PAH on amorphous ice obtained from classical MD simulations; on the right, division of the system into layers to be treated at different levels.

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Computer Generated Realistic Interstellar Icy Grain Models: Physico-chemical Properties

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Interstellar grains are composed by a rocky core (usually amorphous silicates) covered by an icy mantle, the most abundant molecule being H_2O followed by CO, CO_2, NH_3, and also radicals in minor quantity [1]. In dense molecular clouds, gas-phase chemical species freeze onto the grain surface making it an important reservoir of molecular diversity/complexity whose evolution brings to interstellar complex organic molecules (iCOMs). Many different models of water clusters have appeared in the literature, but without a systematic study on the properties of the grain (such as the H-bonds features, the oxygen radial distribution function, the dangling species present on the mantle surface, the surface electrostatic potential, etc.). In this work, we present a computer procedure (ACO-FROST) grounded on the newly developed semi-empirical GFN2 tight-binding quantum mechanical method [2] and the GFN-FF force field method [3] to build-up structures of amorphous ice of large size. These methods shows a very favourable accuracy/cost ratio as they are ideally designed to handle non-covalent interactions. The ACO-FROST program can be tuned to build grains of different composition, but also dirty icy grains. These icy grain models allow to study the adsorption features (structure, binding energy, vibrational frequencies, etc.) of relevant species on a large variety of adsorption sites so as to obtain a statistically meaningful distribution of the physico-chemical properties of interest to be transferred in numerical models.

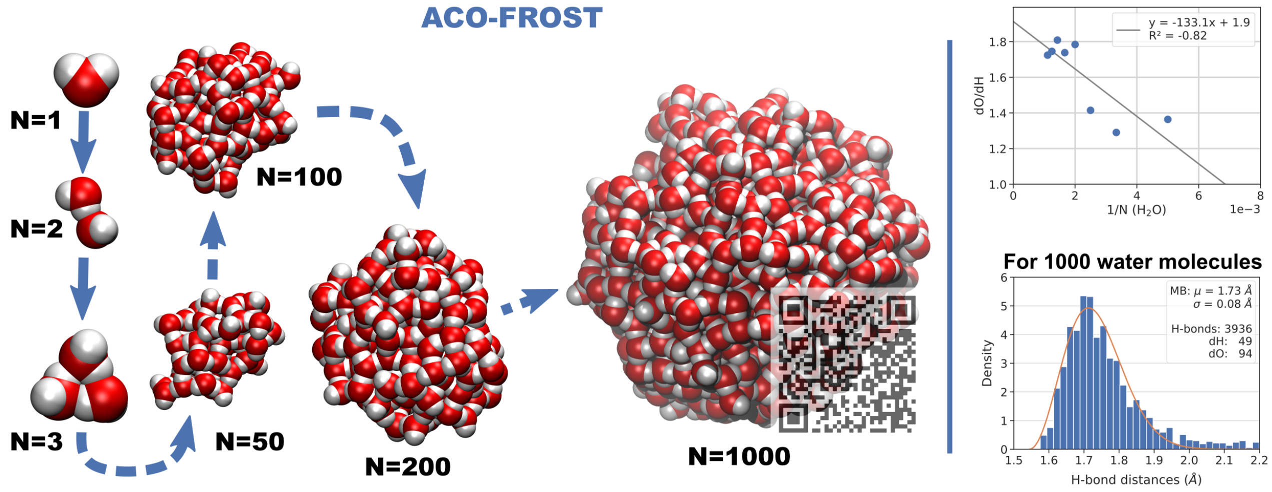

Figure 1: Left: Schematisation of the icy grain building process. Right: Ratio of dangling oxygens (dO) and hydrogens (dH) for the different grain sizes (top). H-bond length (O· · · H) distribution for a 1000 water molecules model (bottom).

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A Computational Study of Binding Energies of Astrochemically Relevant S-bearing Species

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One of the most important parameters in simulating surface chemical processes in astrochemical models are Binding Energies (BEs).[1] They determine which species enrich the gas phase and which are bound to the surface of grains. It is currently known that, in the denser and colder regions of the interstellar medium (ISM), sulphur is severely depleted in the gas phase.[2] Therefore, it has been suggested that it may be locked into the icy mantles that cover the interstellar dust particles. However, only OCS and, tentatively, SO_2, were detected in the solid phase,[3] and which could be the main carrier of sulphur is still a matter of debate.[2] To this purpose, in this work we provide the BEs of 17 sulphur-containing species. Adsorption of these species on two water ice mantles, the former modelled by the (010) surface of a proton-ordered crystalline water ice model and the latter consisting in an amorphous water ice model, has been performed. The Density Functional Theory (DFT)-based B3LYP-D3(BJ) and M06-2X functionals were used for the prediction of the structures and energetics.[4] From our study we understand that: (i) given the presence of heavy atoms, like sulphur, accounting for dispersive interactions becomes crucial for the estimation of BEs; (ii) the variety of binding sites offered by a real interstellar ice is better represented by adopting an amorphous ice model. For each species, we define a distribution with amorphous BEs where, in most cases, the upper end is covered by crystalline BE values. With the exception of few cases, both experimental and computational literature values are in agreement with our data.[1,5,6]

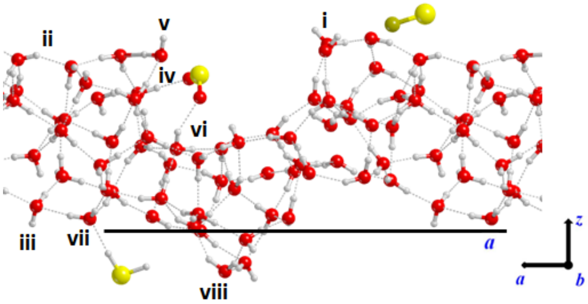

Figure 1: The periodic amorphous ice model highlighting the various adsorption sites (i-viii).

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Theoretical distribution of the ammonia binding energy at interstellar icy grains: a new computational framework

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Understanding the interaction between gas-phase species with icy grains is of paramount important to explain the chemical complexity of the Interstellar Medium (ISM) [1]. The basic quantity that rules all the chemical processes occurring on these grains (adsorption, diffusion, reaction, desorption) is the binding energy (BE) of the species at the grain surface. So far, with very few exceptions, astrochemical models have assumed single BE values for each species, which is a very strong approximation [2]. In this work, we present a new and robust computational strategy to evaluate a statistically significant BE distribution by adopting on a recently proposed amorphous solid water (ASW) cluster [3], consisting of 200 water molecules molecules. This ensures a large number and variety of adsorption sites where NH_3 (our test case) and other molecules can adsorb. The framework is based on an unbiased random and well reproducible BE site sampling. Furthermore, we propose two alternative routes for the definition of the reference structure and energy of the free icy grain, reminiscent of the way in which BEs are extracted from a temperature programmed desorption or from micro calorimetric experiments are carried out. This is relevant as water mobility due to adsorption processes may substantially alter the ice structure. Structures and frequencies are computed through the ONIOM approach [4] using a ONIOM(B97D3/aug-cc-pVTZ:xTB-GFN2) model chemistry. A final BSSE-corrected energy evaluation was carried out at ONIOM(DLPNO-CCSD(T)/aug-cc-pVTZ//B97D3/aug-cc-pVTZ:xTB-GFN2) level. The combination of such methods ensured the best cost/accuracy ratio. Figure 1 shows an example of the ONIOM adsorption sites (left) and the Machine Learning (ML) clustering analysis performed to group the BEs in two different distributions reflecting the different nature of the possible NH_3 adsorption mode.

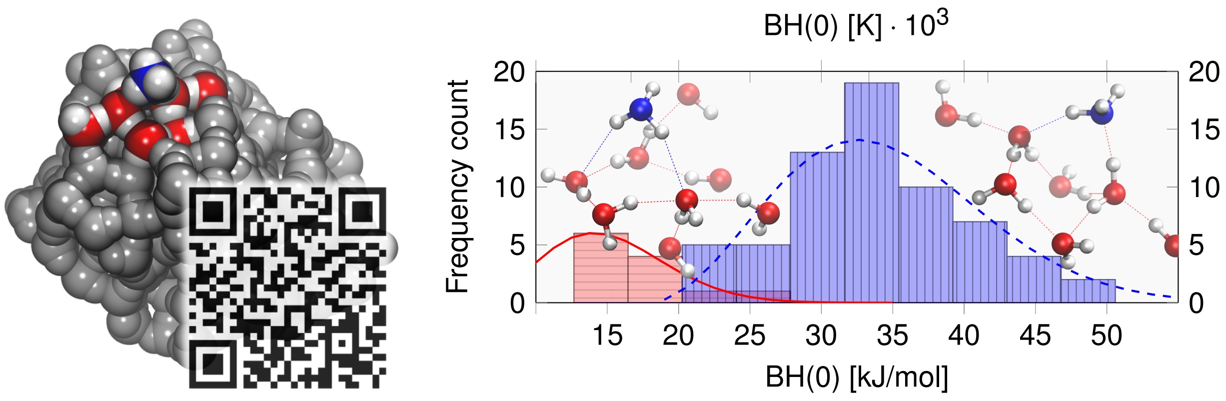

Figure 1: Left: van der Waals spheres representation of a specific NH_3 binding site: in color the ONIOM high level zone (QR code to visualize and interact with all the BE structures, through Jsmol view). Right: ML clustering analysis applied to the obtain NH_3 BH(0) (the zero point corrected BE) distribution at the icy grain.

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Exploiting Neutrons to Unveil Star-Formation: Exploring Dynamical Amorphous Ice Systems

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Interstellar ice, dominated by Amorphous Solid Water (ASW), is the largest molecular reservoir in the Universe.[1,2] In shocked regions and planet-forming disks, vapour deposition of H_2O from the gas-phase onto dust particles is the dominant formation mechanism.[2] At low temperatures, the depositions of ASW are usually very porous, allowing for a large amount of molecules to be stored within these pores. However, it seems that meta-stable interstellar ASW loses porosity as a function of time or temperature as star-formation progresses.[3,4] This porosity change is astrochemically vital as it alters the total ASW surface area. This changes the surface available for chemical catalysis; accounts for discrepancies between (observed) gas-phase and solid-state abundances of volatile interstellar molecules, and affects how icy grains might ”stick” to form the early seeds of planets and cometary nuclei.[5] To date, the issue of porosity in ASW ices remains unresolved. Our chemical physics understanding of ASW porosity evolution is unknown, and consequently inadequately modelled or accounted for in star- and planet-formation chemical models. The overarching aim of our research is thus to understand the thermally induced changes in the nano-scale physical properties and structure of these ices.

Over the past 5 years, our group has employed NIMROD and SANS2D at the ISIS second target station to study ASW growth and thermal evolution with neutrons. From our current data, it is clear that our vapour-deposited ASW exhibits both granularity and porosity- both of which evolve as a function of temperature.[6,7,8] To visualise this evolution, we have also developed molecular dynamics code, using the TIPP4P/2005 water force-field, to simulate the annealing of vapour-deposited water-ice using GROMACS. Although the system length scales are rather different, very similar trends and numerical results are found between our methods. Overall, we find drastic changes to the ice morphology are observed across the temperature range 100 to 150 K. This is set around the glass transition temperature where significant ice-network proton mobility kicks in. Such enhanced mobility results in the loss of specific surface area (SSA) and porosity; the formation of a diffuse interface and a general compaction of the ice. From our results, we have calculated the half-life for SSA decay to be around 100 hours at 77 K, 70 years at 30 K and 104 years at 10 K. Therefore, astronomical timescales would be enough to allow significant compaction and crystallisation, drastically changing our picture of ice astrophysics and processes that lead to planet formation and the basic ingredients for life.

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Adaptive Kinetic Monte Carlo Simulations of Long Timescale Processes at Surfaces of Solids

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Atomic scale processes at solid surfaces typically involve significant energy barriers as they involve transition states where bonds between atoms have ruptured before new new bonds are formed. As a result, such processes are rare events on the time scale of the vibrational motion of the atoms and direct simulation of the atomic dynamics falls orders of magnitude short of showing the relevant transitions. Instead, an approach based on transition state theory can be used to identify the mechanism and estimate the rate of the relevant transitions. On the basis of such information, the long timescale evolution of the system can be simulated. The adaptive kinetic Monte Carlo (AKMC) [1] method involves finding the mechanism and rate of possible transitions by farming out searches of first order saddle points on the energy rim surrounding the energy minimum corresponding to the current state of the system. The saddle point searches involve climbing up the energy surface without preconceived notion of possible final states [2]. Unexpected transition mechanisms can, therefore, be discovered. The method has been implemented in the EON software [3], including systematic coarse graining of the rate table (see figure), and is currently being integrated in a suite of programs for simulations of surface catalysis in the H2020 ReaxPro project.

Several applications of AKMC simulations will be described, including (1) diffusion and cluster formation of H2O molecules on ice surfaces, where admolecules and small clusters are found to reside in non-crystallographic sites, (2) metal crystal growth, where multi-atom concerted processes frequently occur and the definition of the Ehrich-Schwöbel barrier needs to be refined, and (3) diffusion of adatoms on silicon surfaces, where an indirect diffusion mechanism involving skidding along dimer rows turns out to be orders of magnitude faster than the more intuitive direct diffusion hops. The key issue for the application of AKMC is the availability of an efficient description of the atomic interactions, as direct electronic structure calculations are, for most purposes, too computationally demanding. A powerful approach based on systematic multipole expansion of the electrostatics and incorporation of quadrupole as well as dipole polarizability for the construction of molecular interaction potentials will be mentioned, as well as the popular machine learned potential energy functions.

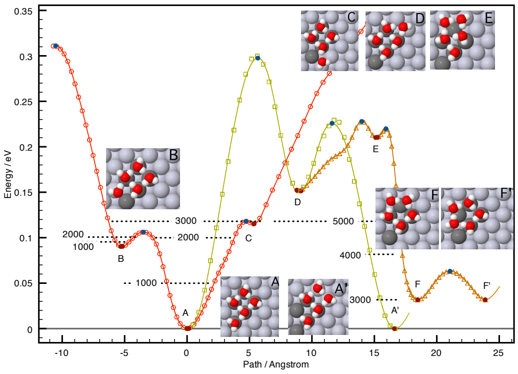

Figure 1: AKMC simulation of the diffusion of a pentamer H_2O cluster on a Pt(100) surface. From ref. [4].

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Combining machine learning and microkinetic modelling to treat complex reactions in surface catalysis

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Recently developed machine learning (ML) methods hold great promise for simultaneously reducing the computational cost and increasing the accuracy in catalysis modelling, allowing us to capture more complexity, make our models more realistic and perhaps even obtain new physical insights. In both Earth-based surface catalysis and interstellar dust grain catalysis, two dominant contributions to complexity are complex materials (e.g. metals, alloys and oxide materials, including interstellar nanosilicate dust grains) and complex reaction networks with large adsorbates that may bind to the studied surfaces in mono-, bi- or higher-dentate adsorption motifs.

In the first part of my talk, I will first present some recent work involving complex adsorbates and reaction networks. Using first principles-based kinetic Monte Carlo, we investigated selectivity trends and the role of adsorbate-adsorbate interactions for CO hydrogenation over Rh catalysts [1]. We obtained here a new theoretical understanding of recent experimental data, where large particles above 5 nm were found to be more active and selective towards methane, whereas small particles were found to less active, but more selective to acetaldehyde [2]. Subsequently, I will discuss recent work aimed at developing a ML model that is able to predict adsorption energies of the (possibly oxygenated) C1 and C2 fragments involved in this reaction network [3], which may be useful for screening broader classes of materials (e.g. alloys) for their activity and selectivity towards the more valuable C2 species such as acetaldehyde and ethanol.

In the second part of my talk, I will discuss how to extend the ML models from the well-studied transition metals to materials with a more localized and intricate electronic structure such as transition metal oxides and Mg-rich silicate clusters [4,5]. This work will also highlight physical insights into the factors controlling the reactivity of these materials, which can be revealed by analysing the obtained ML models.

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Reaction mechanism and active sites of WGS and RWGS via structure-dependent microkinetic modeling and machine learning

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The rational interpretation of the structure-activity relation in catalysis is a crucial task in the quest of engineering the chemical transformation at the molecular level [1]. In this respect, microkinetic modeling based on first-principles calculations is acknowledged to be a key tool to achieve a mechanistic understanding of the catalyst functionality. However, the effect of the complexity of the catalyst structure on activity and selectivity is neglected in state-of-the-art microkinetic models. As such, a "material gap" hinders the analysis of the underlying mechanisms at the atomic-scale level. To fill this gap, the modeling of the catalyst structure under reaction conditions is required [2]. Here, we present the development and application of a methodology for the concerted simulation of structure and activity of heterogeneous catalysts, called structure-dependent microkinetic modeling (Fig. 1), which is based on microkinetic modeling, *ab initio* thermodynamics, and Wulff construction [3-4]. As a showcase, we apply the methodology to water-gas shift (WGS) and reverse water-gas shift (RWGS) on Rh, fully characterizing the reaction mechanism with density functional theory (DFT) calculations. Then, we extend the analysis to other catalyst compositions, including single-atom alloys (SAAs), by the application of machine learning techniques and linear scaling relations.

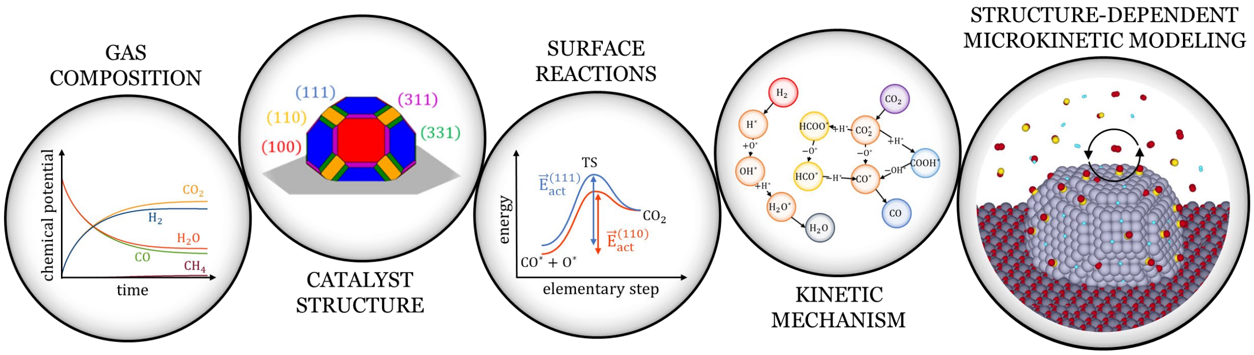

Figure 1: Schematic representation of the steps of structure-dependent microkinetic modeling.

Our analysis on WGS and RWGS on Rh makes it possible to rationalize that, far from equilibrium, the two systems not only follow different reaction pathways but also show a different "identity" of the active sites. Indeed, WGS occurs mainly on the sites of the Rh(111) facet, whereas RWGS proceeds on the sites of Rh(100). Reaction path analyses point out that WGS follows either an oxygen-assisted or a carboxyl-mediated mechanism, where the rate-controlling step (RCS) is the H_2O^* dissociation on Rh(111). RWGS, instead, proceeds through the CO_2^* decomposition to CO* and O*, which is the RCS on Rh(100), in agreement with experimental reaction orders [4]. The microkinetic investigation of WGS and RWGS on other transition metals and SAAs allows rationalizing how the kinetic mechanism and the catalytic activity change with the catalyst composition, paving the way toward the rational catalyst design for these two industrially relevant catalytic processes.

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Energy dissipation and restructuring in interstellar ice upon excitation of admolecules

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Dust particles covered by icy mantles play a crucial role in the formation of molecules in the Interstellar Medium (ISM). It is on 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. Complex organic molecules are formed through an intricated 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 (CO2, H2O and CH4) on top of a water ice surface. We consider different types of excitation such as translational, rotational, and/or vibrational excitation. This leads to a generalize expression for non-thermal desorption which is then included in an astrochemical model and the results are compared against astronomical observations.

The energy dissipation process of hydrogenation reactions of atomic nitrogen on water ice surfaces

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In the colder (10-20K) regions of interstellar medium, the icy surfaces of interstellar grains serve as solid state supports for chemical reactions[1][2]. Among the plausible roles of these surfaces, that of third body is advocated, in which the formation energy of surface reactions can be dissipated among the grain causing the stabilization of the product[3]. This energy dissipation process is poorly understood at the atomic scale and it can have a tremendous impact on astrochemical surface processes like chemical desorption and diffusion[4][5].

In this work, we studied the formation of NH_3 via successive H-addition to atomic nitrogen on crystalline and amorphous ice surfaces. We first characterized the potential energy surfaces of the hydrogenation reactions and possible competitive processes (i.e., H abstractions) using static quantum chemical calculations. Subsequently, the partitioning of the nascent energy released by the hydrogenation reactions between the newly formed species and the surface has been elucidated by means of *ab initio* molecular dynamics (AIMD) simulations.

Results indicate that the H-additions on N are largely favorable reactions at 10 K, being barrierless and exhibiting large negative reaction energies, as opposed to the competitive H-abstractions, which are either endothermic or present high activation energies. AIMD simulations show that such favorable nascent energies are, in large part, quickly absorbed by the ice surfaces and their dissipation can be accelerated by mechanisms involving an H exchange between the surface and the newly formed species (Figure 1).

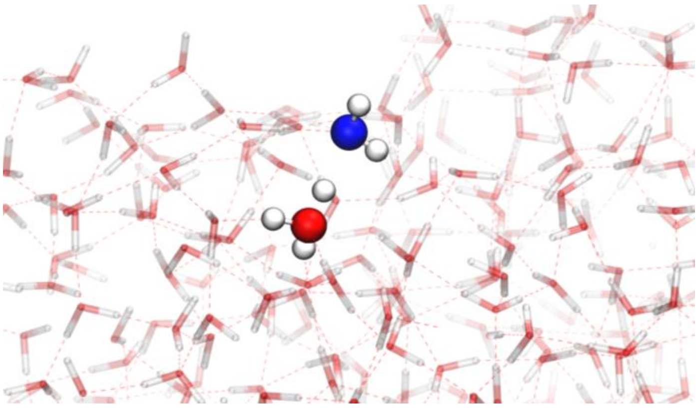

Figure 1: $H_3O(+)NH_2(-)$ complex formation on an amorphous ice surface.

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Modelling Cosmic Ray Sputtering of Interstellar Grain Ices

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In the Interstellar Medium (ISM), the formation and detection of complex organic molecules (COMs) has been facilitated by fast surface reactions occuring on physisorbed ices on the surface of grains. However, in cold dark clouds, such as TMC-1, thermal desorption of many COMs is inefficient because of the lack of thermal energy to overcome binding energies [1]. Non-thermal desorption methods, such as reactive desorption and photodesorption [2] are therefore important explanations for the gas-phase detection of many COMs that are primarily formed through grain ice surface reactions in colder environments of the ISM. We discuss theories of sputtering off of grain ices [3,4], a non-thermal desorption process, based on the ejection of water ice, carbon dioxide ice, and a simple mixed ice for implementation into rate-equation based models of the ISM. We derive the rate coefficients of sputtering from stopping power cross sections, cosmic ray fluxes, and sputtering yields. The rates of sputtering are generally higher for carbon dioxide and mixed ice based sputtering, partially due to larger yields. This results in enhanced desorption rates for all grain species in our model. This increase is followed by increased gas phase abundances for molecules produced in efficient grain reactions, such as methanol (CH_3OH) and methyl formate ($HCOOCH_3$). Notably, some species with efficient gas phase destruction pathways, such as acetaldehyde (CH_3CHO), see less of an increase in gas-phase abundances, in models with sputtering, compared to other molecules. These results suggest that sputtering is an efficient, non-specific method of non-thermal desorption that should be considered as an important factor in future chemical models.

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Polycyclic Aromatic Hydrocarbons as a precursor to Molecular Complexity in Interstellar Space

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Interstellar space harbours a surprising chemical complexity in spite of the extremely low temperatures and pressures that characterize it. This chemical complexity is thought to be catalyzed by interstellar nanoscale dust grains and large carbonaceous molecules such as the Polycyclic aromatic hydrocarbons (PAHs). PAHs are ubiquitous in interstellar space, however, their impact on interstellar chemistry is still not thoroughly understood. Theoretical calculations and experimental measurements show that PAHs react readily with atomic hydrogen to form superhydrogenated species - e.g. PAH molecules like pentacene and coronene can be fully superhydrogenated with one excess H atom pr. carbon atom via H atom addition. Once super-hydrogenated, PAH molecules can act as catalysts for molecular hydrogen formation and may participate in further reactions towards formation of a variety of hydrocarbon molecules. When functionalized with O or N atoms or with these species substituted into the carbon skeleton the PAH may well act as precursors for a much wider set of complex organic molecules. In the talk I will present scanning tunneling microscopy and temperature programmed desorption measurements of hydrogen and deuterium addition reactions on a selection of PAHs molecules with focus on resulting stable superhydrogenation configurations and cross-sections and isotope effects for the initial H and D addition reactions. Density Functional Theory calculations provide insights into the underlying principles that guide the hydrogen functionalization pathways. Furthermore, I discuss the IR spectra and fragmentation of functionalized cationic and protonated PAHs as obtained from infrared multiphoton dissociation spectroscopy measurements performed at the FELIX light source and discuss reactions towards more complex species via hydrogenation of pentacene-quinone and fragmentation of functionalized PAHs.

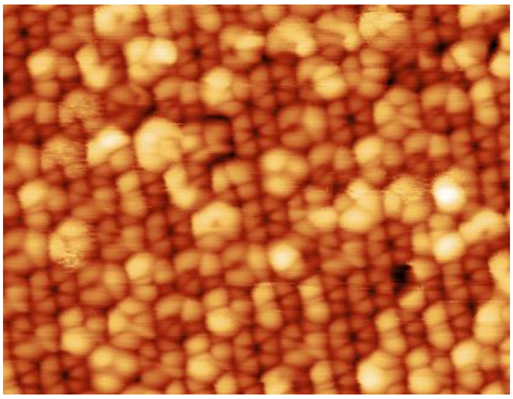

Figure 1: STM image of superhydrogenated coronene molecules on a graphite surface.

ABSTRACTS

POSTERS

Vibrational Energy Dissipation in Carbon Monoxide ices: A Tale of Four Isotopes

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Ices rich in carbon monoxide are believed to play a key role as carbon reservoir and they are chemically linked to the production of complex organic molecules (COMs) within interstellar clouds (*i.e.*, [1]). These COMs are oftentimes observed in the gas-phase, even for those without efficient gas-phase reaction networks, similar to the case of methanol [2]. As such, these COMs are thought to form on grain surfaces and subsequently desorb. However, thermal desorption is negligible for large molecules at the cold temperatures of interstellar clouds (10 K). Therefore, other potential desorption mechanisms have been proposed, such as cosmic-ray-induced desorption [3], or chemical desorption [4]. The latter has garnished significant support by atomistic simulations [6, 7]. Most studies on energy dissipation have so far been performed on water-rich ices, and, therefore, we focus here on pure CO ice clusters.

We simulate the energy dissipation of a vibrationally excited, stretched, CO molecule on (surface) or in (subsurface) a CO ice cluster. The same simulation is repeated substituting the excited $^{12}C^{16}O$ molecule for $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$. Simulations used in this study were performed using the Atomic Simulation Environment (ASE) [8], and the CO-CO pair potential described by van Hemert et al. We present dissipation timescales for all isotopes and discuss their differences. We also present an analysis on the effect of exciting a surface versus subsurface molecule.

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Prebiotic chemistry on mineral surfaces

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Interstellar space accommodates a vast variety of materials. Among these are minerals which constitute the exteriors of rocky planets, meteorites and interplanetary dust particles. Within this group, phyllosilicates and layered double hydroxides are of particular interest. These minerals form under low-temperature water-rich conditions and have been shown to exhibit the ability to concentrate and protect small organic molecules through adsorption onto their surfaces [1]. Moreover, they can act as templates and catalysts for selective polymerisation reactions between adsorbed species. [2,3] These characteristics suggest they might have played a key role in the prebiotic reactions that led to the emergence of the first biomolecules.

The mineral-molecule interactions are governed by the mineral composition, surface charge distribution and particle morphology. In order to understand and validate potential reaction mechanisms, it is, therefore, crucial to elucidate the relationship between of these factors on the adsorption and reactivity of organic molecules.

Classical molecular dynamics simulations can be used to study adsorption characteristics of biomolecules and their precursors on mineral surfaces at an atomistic level. In particular, this methodology permits the construction of sufficiently large systems and can, therefore, deliver an accurate representation of heterogeneity of mineral structures.

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Global atomistic optimisation enhanced by local surrogate model

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This work implements a Gaussian Approximation Potential [1] using SOAP [2] descriptors as the surrogate model used for structure relaxations and structure selection in a global structure search setting. The model is trained on-the-fly based on structures selected in a lower confidences bound acquisition function using the uncertainty of the model. The use of a local model has several benefits compared to the previously adopted global GPR model in the GOFEE algorithm [3], such as the possibility to transfer solutions to smaller problems into the optimisation for larger systems. Furthermore the model will extrapolate better beyond already discovered structures due to the local nature of the model, which will lead to better exploration of the search space and thus faster convergence.

The optimisation of the DFT energy of C_5H_5N, where the global minimum is the heterocyclic molecule pyridine, is explored. A clear improvement when substituting the global GPR model for the local model is found. A further increase in performance is gained by transferring the C_4H_5N pyrrole structure into the search for pyridine. This exemplifies the power of the local model, where the search convergence greatly improves when biased with the knowledge of the global minimum of the smaller molecule.

The optimisations are performed in the AGOX [4] code and the local surrogate model is implemented in this code using the DScribe package [5] for the SOAP descriptors.

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The Effect of Cluster Size on the Intra-Cluster Ionic Polymerization Process

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Polyaromatic hydrocarbons (PAHs) are widespread in the interstellar medium (ISM). The abundance and relevance of PAHs call for a clear understanding of their formation mechanisms, which, to date, have not been completely deciphered. Of particular interest is the formation of benzene, the basic building block of PAHs. It has been shown that the ionization of neutral clusters can lead to an intra-cluster ionic polymerization process that results in molecular growth.[1-3] *Ab-initio* molecular dynamics (AIMD) studies in clusters consisting of 3–6 units of acetylene modeling ionization events under ISM conditions have shown maximum aggregation of three acetylene molecules forming bonded $C_6H_6^+$ species; the larger the number of acetylene molecules, the higher the production of $C_6H_6^+$. These results lead to the question of whether clusters larger than those studied thus far promote aggregation beyond three acetylene units and whether larger clusters can result in higher $C_6H_6^+$production. In this study, we report results from AIMD simulations modeling the ionization of 10 and 20 acetylene clusters. The simulations show aggregation of up to four acetylene units producing bonded $C_8H_8^+$.[4] Interestingly, $C_8H_8^+$ bicyclic species were identified, setting a precedent for their astrochemical identification. Comparable reactivity rates were shown with 10 and 20acetylene clusters.

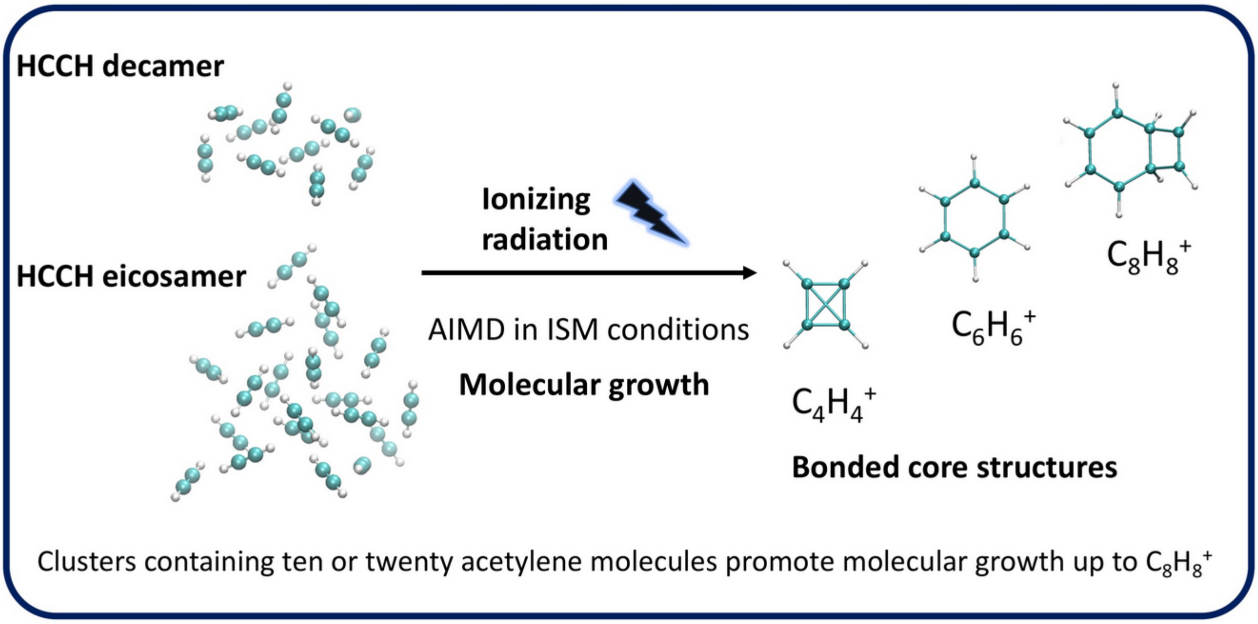

Figure 1: Pure acetylene clusters form bonded structures of up to eight carbons upon ionization.

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Water Ice Nanoclusters
on Pristine and Functionalised Graphite

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In cold regions of the interstellar medium (ISM) icy mantles will form on the surface of dust grains where they act as heterogeneous catalysts for the formation of complex organic molecules (COMs) [1]. In recent years, however, descriptions of how icy mantles form and interact with highly porous grains [2][3], have been challenging the often depicted layer-by-layer "onion model" growth. Even in cold environments of the ISM, arguments are put forward suggesting partly ice-covered grains with exposed bare grain surfaces. The grains are complex and have porous structures themselves, stressing the importance of the grain-ice interface. Diffusion, adsorption, and possible reaction barrier characteristics are influenced by the structure of the ice and grain surface [4][5], which may impact the catalytic effects on COM production.

To examine how water clusters form on interstellar dust grain surfaces during the early stages of ice growth, we use a low-temperature scanning tunnelling microscope (LT-STM) functioning at 5 K. Sub-monolayer coverages of water were deposited onto both pristine and oxygen functionalized graphite at different temperatures to map the variations in clustering and growth of water ice as the surface conditions change.
Presented in Figure 1 is an STM image of water ice clusters grown at 40 K via molecular deposition on a pristine graphite surface. Diffusion limited aggregation (DLA) [6] growth is visible from the fractal structure of the clusters, both near step edges and for individual nucleation sites. Oxygen functionalization of the graphite surface drastically changes the water mobility and act as anchoring sites for nucleation. STM offers a unique look into non-heat-treated, water ice nanoclusters formed under controlled conditions.

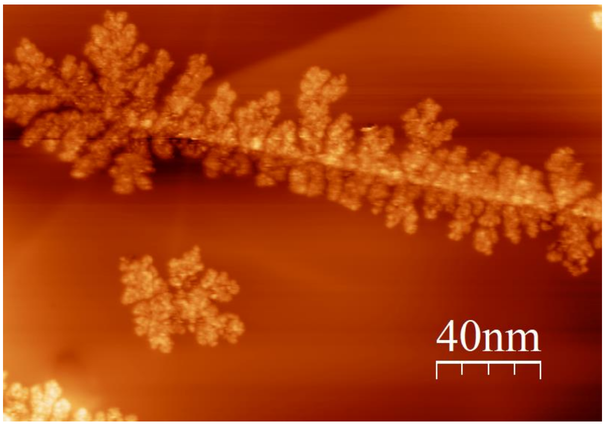

Figure 1: LT-STM image obtained at 5 K of water ice clusters on HOPG (4.5 V, 15 pA). The image shows a cluster on the terrasse of HOPG and aggregation of water along a step-edge on the HOPG surface.

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Searches for stable nano-sized silicates clusters in the interstellar medium

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In this study we present a density functional theory (DFT) study of two types of nano-sized magnesium-rich silicate clusters, namely pyroxene, $(MgSiO_3)_N$, and olivine, $(Mg_2SiO_4)_N$. Using an evolutionary search method [1], the most stable structures with N running from 2 to 8 have been identified. The found structures are compared to previously reported global energy minimum (GM) structures [2]. In the case of olivine with N=4, a new, highly stable GM has been identified and characterized. By restarting the searches for different GMs, we investigate how the performance of the searches can be improved by transferring results from completed searches into on-going searches for larger values of N. Using the role-model method [3] together with smaller clusters, we find the GMs for larger clusters using a smaller number of DFT evaluations and with higher fidelity. The study aims to establish a database of possible structural motifs of small nano-sized silicate clusters in the interstellar medium.

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Effects of curvature on the hydrogenation of a PAH

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Polycyclic aromatic hydrocarbons (PAHs) account for 5-20% of the interstellar carbon abundance [1] and are, as such, expected to play an important role in the physics and chemistry of the interstellar medium (ISM). It has been demonstrated that hydrogenation of PAHs can lead to superhydrogenated species and formation of H_2 [2,3]. Most studies have focused on planar PAHs, although curved PAHs are likely present in the ISM as well, as bowl-forming mechanisms are observed in the photochemistry of PAHs [4] with curved species having been proposed as intermediate steps in the formation of fullerenes [5].

Curvature is expected to modify the reactivity of PAHs. Therefore, we here present first results comparing the reactivity towards H addition of the curved PAH corannulene, $C_{20}H_{10}$, to that of the similarly sized planar PAH coronene, $C_{24}H_{12}$. Temperature programmed desorption measurements were used to characterise the superhydrogenation of the PAH following H atom exposure, with products identified by quadropole mass spectrometry.

Corannulene is found to have a significantly higher cross-section for the first H addition, demonstrating the potential importance of curved species as catalysts in the ISM. Surprisingly, a superhydrogenated species with an odd number of added H atoms shows comparable and sometimes even greater stability than the most dominant even addition species which is not observed for previously studied neutral PAHs. And, also in contrast to other PAHs, the fully superhydrogenated corannulene is not produced to any significant amount. Such contrasting results for similar species demonstrate the remarkable differences in the reactivity along the hydrogenation sequence for curved and planar PAHs.

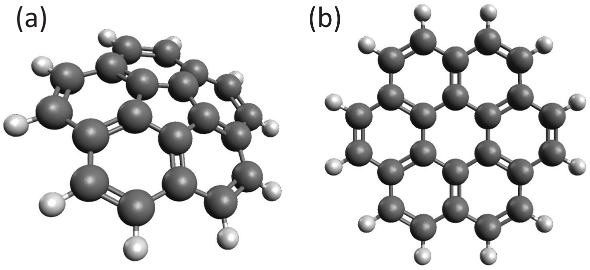

Figure 1: (a) Corannulene and (b) coronene

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Predicting Binding Energies of Astrochemically Relevant Molecules via Machine Learning

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Models describing the formation, destruction, and survival of molecules in astrophysical environments often require binding energies between surfaces of dust grain particles and astrochemically relevant molecules as parameters[1,2]. One of the key methods to determine these is through temperature-programmed desorption experiments. However, experiments are time-consuming and the focus often has to be limited to the scientifically most impactful systems. With the large number of recently detected molecules in the interstellar and circumstellar medium[3], this inevitably means that some of them are not studied. Furthermore, certain molecular species are difficult to work with, either because they are unstable, highly reactive, toxic, or simply challenging to deposit onto a surface.

The aim of this work[4] is to instead use machine learning (ML) to predict the binding energies for new molecules and thereby provide a tool for astrochemists to use as an alternative to experiments. A sketch of the employed approach is shown in Figure 1. First, a collection of astrochemical molecules and their binding energies on specific surfaces has been compiled from the analysis of literature research papers regarding temperature-programmed desorption. Second, the data has been assigned molecular features e.g. atoms, functional groups and other molecular properties. If the surface coverage is below monolayer, the surface is included as well as a category. Third, a ML model of the type Gaussian Process Regression has been trained on the collected data. Finally, the model is used to predict the binding energies of new molecules. When testing on 8 molecules left out from the training data, the predictions show an average deviation of 11% compared to the experimental values.

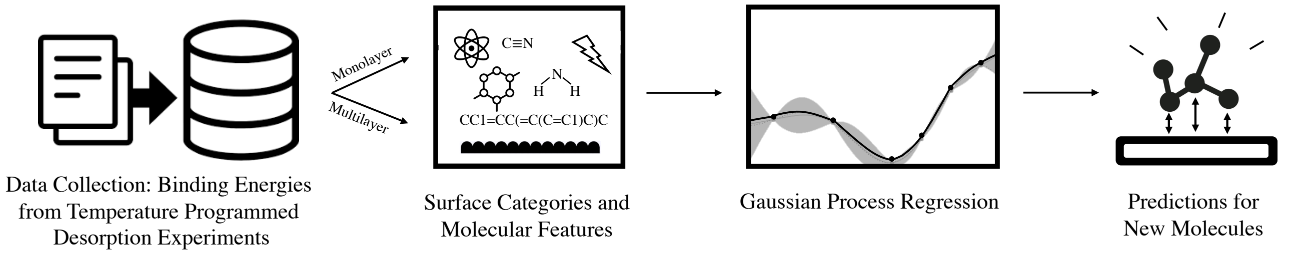

Figure 1: Schematic overview of the work

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Isomerization of Hydrogen Cyanide and Hydrogen Isocyanide in a Cluster Environment: Quantum Chemical Study

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In this work we study the isomerization of hydrogen cyanide (HCN) and hydrogen isocyanide (HNC). The isomers are omnipresent in the interstellar medium (ISM), and the ratio between them has been studied extensively, as it serves as an indicator of the physical conditions in different areas of the ISM. The above-mentioned isomers are also important from an astrobiological point of view, as they are thought to be precursors of organic molecules such as adenine. We focused upon the chemistry that occurs upon ionization of pure HNC clusters by using quantum chemistry calculations and *ab-initio* molecular dynamics (AIMD) simulations. Upon ionization of HNC clusters, $HCNH^{+} \cdots CN$ is formed, and this formation is accompanied by HNC-to-HCN isomerization. Furthermore, the cluster environment and the network of hydrogen bonds plays a central role in the isomerization process and the stabilization of the clusters. In contrast to HNC clusters, we show that isomerization of ionized HCN clusters can occur only for the larger clusters. In particular, we show that upon ionization of the cluster, it is possible to form an aminonitrile cation. We propose a barrierless route for the dimerization of the aminonitrile, forming diaminonitrile, a known precursor of amino acids and nucleobases.

Kinetic Isotope Effect for Hydrogen and Deuterium on Coronene

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Polycyclic aromatic hydrocarbons (PAHs) are a group of molecules that have been identified widely within the interstellar medium (ISM) [1]. They are believed to account for between 5% and 20% of all available carbon and play an important role in astrochemistry [2]. Therefore, understanding how PAHs react with atoms and molecules is of interest when trying to understand the chemical evolution of the ISM. Of particular interest is how these molecules react with hydrogen, the most abundant element in the ISM and its isotope, deuterium. Coronene is a PAH that consists of seven carbon rings and when exposed to hydrogen atoms can be superhydrogenated. This has been investigated by depositing coronene onto a Highly Oriented Pyrolytic Graphite (HOPG) surface which is a laboratory dust grain analog making it astrochemically relevant.

The monolayer of coronene has been exposed to hydrogen or deuterium produced by an atomic beam source. The atoms were cooled through collisions with the walls of a quartz nozzle attached to the source. The effects of the hydrogenation were then investigated using temperature programmed desorption and scanning tunneling microscopy techniques, where it has been found that the reaction cross-section differs between hydrogen atoms and deuterium atoms. For hydrogen this cross-section was σ_{H} = 0.040Å^2 and for the deuterium it was σ_{D} = 0.164Å^2. This suggests that there is a kinetic isotope effect that is entangled in hidden reaction pathways that are difficult to directly observe. The ratio ($\sigma_{\mathrm{H}}/\sigma_{\mathrm{D}}$) of this kinetic isotope effect for coronene is 0.24 which is different to the ratio for graphene of 0.62 [3].

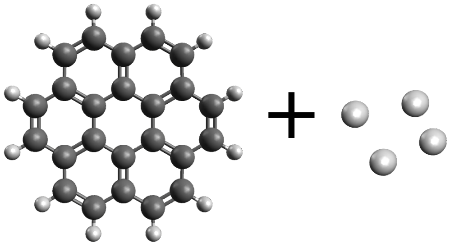

Figure 1: Coronene ($C_{24}H_{12}$) + Hydrogen/Deuterium

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