Chemical Evolution of Cosmic Matter

703. WE-Heraeus-Seminar

23 – 25 October 2019
Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Subject to alterations!

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de.

Scope of the 703. WE-Heraeus-Seminar:

The seminar will focus on laboratory investigations to understand the fundamental steps of chemical matter evolution in our cosmos. The meeting is motivated by the advent of new telescope facilities operating in the microwave- and infrared region and featuring ultrahigh angular resolution and breathtaking sensitivity. This opens up new insights into processes leading to the formation and evolution of molecules in stellar environments that are otherwise inaccessible. The seminar brings together an international group of experimentalists, theoreticians and astronomical observers with expertise in gas-phase and solid phase species, interpretation of molecular spectra, structure and possible formation and destruction mechanisms. Furthermore, an important aim of the seminar is to intensify the existing collaborations between the various already active working groups and to integrate new groups into the network. In particular, excellent speakers which are experts of their fields will give introductory talks at the PhD level which intend to inspire young researchers for the highly interdisciplinary field of chemical evolution.

Scientific Organizers:

Prof. Dr. Thomas Giesen	E-mail t.giesen@physik.uni-kassel.de
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Introduction

Administrative Organization:

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Registration:

Jutta Lang (WE-Heraeus Foundation) at the Physikzentrum, reception office Tuesday (17:00 h – 21:00 h) and Wednesday morning

Door Code:

(Key symbol button) 2 7 0 3 #

For entering the Physikzentrum during the whole seminar

Program

Program

Tuesday, 22 October 2019

17:00 – 21:00	Registration	
from 18:30	*BUFFET SUPPER / Informal get together*	

Wednesday, 23 October 2019

07:30	*BREAKFAST*	
09:00 – 09:10	Thomas Giesen	**Introduction**

Chair: Alexey Potapov

09:10 – 10:00	Stephan Schlemmer	**The boon and bane of high-resolution spectroscopy**
10:00 – 10:50	Luca Dore	**The role of the submillimeter-wave spectroscopy in astrochemistry**
10:50 – 11:10	*COFFEE BREAK*	
11:10 – 12:00	Olivier Pirali	**Far-infrared spectroscopy of astrophysical molecules using synchrotron radiation**
12:00 – 12:50	Thomas Schultz	**CRASY: Correlated mass-rotation spectra of heterogeneous samples**
12:50	**Conference photo** (in the foyer of the lecture hall)	
13:00	*LUNCH*	

Program

Wednesday, 23 October 2019

Chair: Stephan Schlemmer

14:30 – 15:20	Satoshi Yamamoto	**Chemical evolution and its diversity in disk forming regions**
15:20 – 16:10	Arnaud Belloche	**Molecular complexity in the interstellar medium**
16:10 – 16:30	*COFFEE BREAK*	
16:30 – 17:20	Aurore Bacmann	**Complex organic molecules in cold dark cores – progress and challenges**
17:20 – 18:10	Markus Röllig	**PDR modelling review**
18:10 – 19:30	**Round table**	
19:30	*DINNER*	

Program

Thursday, 24 October 2019

07:30	*BREAKFAST*	

Chair: Cornelia Jäger

09:00 – 09:50	Harold Linnartz	**From small to tall: Molecular complexity in interstellar ices**
09:50 – 10:40	Farid Salama	**The chemical evolution of cosmic carbon: Laboratory studies with the COSmIC facility**
10:40 – 11:00	*COFFEE BREAK*	
11:00 – 11:50	Ewen Campbell	**Electronic spectroscopy of molecular ions of astrochemical interest**
11:50 – 12:40	Melanie Schnell	**A multi-spectroscopic approach to reveal the astrochemistry of polycyclic aromatic hydrocarbons**
12:40	*LUNCH*	
14:30 – 14:45	Stefan Jorda	**About the Wilhelm and Else Heraeus Foundation**

Chair: Friedrich Wyrowski

14:45 – 15:35	Tomasz Kamiński	**Shock chemistry and rare isotopologues around eruptive stars**
15:35 – 16:25	Javier Goicoechea	**Chemistry in UV-irradiated interstellar clouds**
16:25 – 16:45	*COFFEE BREAK*	
16:45 – 19:00	**Poster session**	
19:30	*HERAEUS DINNER at the Physikzentrum (cold & warm buffet, free beverages)*	

Program

Friday, 25 October 2019

07:30	*BREAKFAST*	

Chair: Harold Linnartz

09:00 – 09:50	Christina Puzzarini	**Rotational spectroscopy, quantum chemistry and the astrochemical challenges**
09:50 – 10:40	Svitlana Zhukovska	**Destruction and re-formation of grains in an inhomogeneous interstellar matter**
10:40 – 11:00	*COFFEE BREAK*	
11:00 – 11:30	Guido Fuchs	**High-resolution spectra of small molecules and the astronomical search for them in late-type stars**
11:30 – 12:00	Alexey Potapov	**Chemistry on the surface of cosmic dust grains**
12:00 – 12:30	Thomas Giesen	**Wrap-up, poster awards**
12:30	*LUNCH*	

End of the seminar *and FAREWELL COFFEE /* ***Departure***

Please note that there will be **no** *dinner at the Physikzentrum on Friday evening for participants leaving the next morning.*

Posters

Posters

1.	Prudence Ada Bibang	**Radioresistance of complex organic molecules in solid phase**
2.	Benjamin Arenas	**Combining high-resolution millimeter-wave rotational spectroscopy with electrical discharge for astrochemical reactions**
3.	Mélisse Bonfand	**The complex chemistry of young high-mass star forming regions**
4.	Stefan Brackertz	**1) Symmetries of CH_5^+** **2) From lines to states without a model**
5.	Alexander Breier	**High-resolution microwave spectroscopy of radioactive molecules: Mass-independent studies of AlF, AlO, TiO, and FeO**
6.	Héctor Carrascosa de Lucas	**Photon-induced desorption of larger molecules from a pure CH_4 ice**
7.	Kuntal Chatterjee	**Deciphering the elusive structure of the fragment ions of a probable interstellar biomolecular building block: The case of pyrimidine**
8.	Pragya Chopra	**The ultrafast dynamics of polycyclic aromatic hydrocarbons upon ionization using XUV radiation at 30.3 nm**
9.	Ko-Ju Chuang	**The solid-state formation of complex organic molecules from dust fragment analogues (C_2H_2)**
10.	Michael Debus	**Retrieval of laser frequency comb repetition rate and carrier envelope offset frequency from an interferogram**
11.	Petr Dohnal	**Experimental study of isotope effect in reaction of $O^+(^4S)$ ions with H_2, HD and D_2**
12.	Sérgio Domingos	**Clusters of chiral PAHs — with and without H_2O**
13.	Otto Dopfer	**Structural, vibrational, and hydration properties of a protonated interstellar aromatic molecule: The case of benzonitrile**

Posters

14.	Eileen Döring / Daniel Witsch	**High-resoultion IR spectrum of TiO and its isotopologues**
15.	Yurii Dumin	**Magnetically-stimulated diffusion of Rydberg atoms in the cosmic environment**
16.	Christian Endres	**Rate coefficients for NH_3-He collisions: First results from pump-probe chirped-pulse experiments**
17.	Sasan Esmaili	**Extraterrestrial origin of life: How the building blocks of life may form in space**
18.	Diksha Garg	**Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy of Phenanthrene in different charge and dehydrogenated states**
19.	Marius Hermanns	**Chirped pulse mmwave spectroscopy of complex molecules**
20.	Bettina Heyne	**Chirped-pulse microwave spectroscopy of complex molecules**
21.	Vadym Ilyushyn	**Methyl mercaptan and its most abundant isotopologs: Global modelling of $v_t = 0, 1, 2$ torsion-rotation spectrum at millimeter and submillimeter wavelengths**
22.	Matin Kaufmann	**Building-up of a precision spectrometer using a REMPI detection scheme**
23.	Sergiy Krasnokutskiy	**Fullerene oligomers and polymers as carriers of unidentified IR emission bands**
24.	Holger Kreckel	**Astrochemical studies at the Cryogenic Storage Ring**
25.	Heather Lewandowski	**Cold and controlled reactions of ions and molecules**
26.	Donatella Loru	**Unravelling the formation of substituted polycyclic aromatic hydrocarbons in the interstellar medium by plasma sources**

Posters

27.	Birgitta Müller	**Spectroscopic signature and optical constants of interstellar ice analogues**
28.	Holger Müller	**Considerations for and recent developments of the Cologne Database for Molecular Spectroscopy (CDMS)**
29.	Guillermo Muñoz Caro	**X-ray versus UV irradiation of H_2O:CO:NH_3 ice mixtures leading to complex organic molecules**
30.	Markus Nötzold	**Quantum state-dependent reactive collisions of OH^- with ultracold Rubidium in a hybrid trap**
31.	Fabian Peterß / Thomas Büchling	**Infrared cavity ringdown spectroscopy of molecules in supersonic jets**
32.	Robert Radloff	**Geometry and optical properties of astrochemically relevant silicon carbide clusters**
33.	Štěpán Roučka	**Analysis of $N^+ + H_2 \rightarrow NH^+ + H$ reaction endothermicity by experimental study of isotope effects and the reverse reaction**
34.	Gaël Rouillé	**Experimental study of diamond formation in astrophysical environments**
35.	Philipp Schmid	**Spectroscopic study of the protonated amine $CH_3NH_3^+$**
36.	Dmitry Strelnikov	**IR/NIR spectroscopy of astronomically relevant fullerene derivatives**
37.	Akemi Tamanai	**Experimental molecular emission spectroscopy: Adopting an ALMA-type cartridge receiver**
38.	Nadine Wehres	**Emission spectroscopy using heterodyne receivers**
39.	Robert Wild	**Reaction studies of astrophysically relevant anions**
40.	Max Winkler	**Probing RNA stability and formation in simulated prebiotic environments on the early Earth and in Space**

Abstracts of Lectures

(in alphabetical order)

Complex organic molecules in cold dark cores – progress and challenges

A. Bacmann[1]

[1]*Institut de Planétologie et d'Astrophysique de Grenoble, Grenoble, France*

Among the exciting results of the past decade in astrochemistry is the discovery that molecular complexity is ubiquitous in the molecular interstellar medium. In particular, and against all expectations, complex O-bearing molecules once thought to be characteristic of hot core chemistry have also been found in prestellar cores. In these sources, the very low temperatures (10 K) exclude thermal processes as invoked in hot cores as possible molecular formation mechanisms, so that their presence has remained a puzzle. While a wealth of ideas have emerged to account for complex molecule formation in such environments, quantitative agreement with observed abundances is still lacking: so far, no consensus has yet been reached as to which formation mechanism – gas-phase or on grain surfaces - is dominant. In this presentation, I will give an overview of what we know (and what we don't) about the chemistry of complex organic molecules in prestellar cores, highlighting observational, experimental and theoretical progress and challenges.

Molecular complexity in the interstellar medium

A. Belloche[1]

[1] *Max-Planck-Institut für Radioastronomie, Bonn, Germany*

The search for complex organic molecules (COMs) in the interstellar medium (ISM) has revealed species of ever greater complexity. It is in part motivated by the presence of COMs in comets, whose origin may go back to the early phases of the formation of our Solar System. This search in the ISM relies on the progress made in the laboratory to characterize the rotational spectra of COMs. Our understanding of the processes that lead to molecular complexity in the ISM builds on numerical simulations that use chemical networks fed by laboratory and theoretical studies. The advent of ALMA and NOEMA has opened a new door to explore molecular complexity in the ISM. Their high angular resolution reduces the spectral confusion of star-forming cores and their increased sensitivity and bandwidth allows the detection of low-abundance molecules that could not be probed before. The complexity of the recently-detected molecules manifests itself not only in terms of number of atoms but also in their molecular structure. I will discuss these developments and present some recent results on complex organic molecules derived from the EMoCA, ReMoCA, and CALYPSO interferometric surveys.

Electronic spectroscopy of molecular ions of astrochemical interest

E. K. Campbell[1]

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One of the most versatile techniques available, at present, to obtain the spectra of cold molecular ions is based on ion storage in a cryogenic radiofrequency trap. Over the last few years, parallel activities in several research groups have pushed the temperature of these devices to their lowest limits. Routine tagging of virtually any cation with helium atom(s) has led to a relatively straightforward route to obtain gas phase spectroscopic information on buffer gas cooled molecular ions.[1] Moreover, a new sensitive method for detecting the absorption of a photon emerged.[2] In this talk I will highlight some of our experimental work on the fullerenes[3] and analogues and related molecular species of putative astrochemical interest,[4] and discuss the implications. Time permitting, I will also describe some of our current activities which involve combining non-standard methods for the synthesis and characterisation of complex molecular ions, and present some preliminary results on carbon cations C_n^+ that had thus far evaded spectroscopic investigation in the gas phase.

References

[1] Gerlich, J. Chin. Chem. Soc. **65**, 637-653 (2018).
[2] Chakrabarty *et al.*, J Phys. Chem. Lett., **4**, 4051-4054 (2013).
[3] Maier & Campbell, Int. J. Mass Spectrom., **434**, 116-122 (2018).
[4] Campbell & Maier, ApJ, **850**, 69 (2017).

The role of the submillimeter-wave spectroscopy in astrochemistry

L. Dore[1] and M. Melosso[1]

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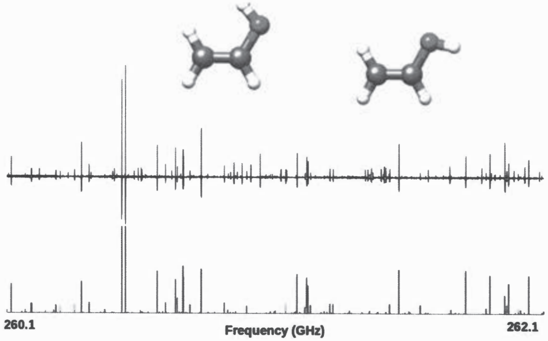
"Astrochemistry is the study of the abundance, formation, and chemical reactions of atoms, molecules, and ions and how they interact with radiation in both the gas and condensed phases in solar systems and in the interstellar medium." [1] Therefore, one of its topics is gathering spectroscopic information supported by laboratory-based studies. Moreover, "approximatively one-half of the total luminosity and 98% of the photons emitted since the Bing Bang fall into the submillimeter and far-infrared." [2] These two premises point to the importance of gas-phase submillimeter spectroscopy for astrochemistry.

Recent studies in Bologna include the spectroscopic characterization of a wide class of species: small nitrogen-containing species (NH, NH_2, NH_3, HC_3N) and their deuterated isotopologues, pre-biotic molecules (aminoacetonitrile, ethanimine, cyanomethanimine), and Complex Organic Molecules (vinyl alcohol, ethylene glycol).

An accurate knowledge of rotational energy levels is the first step toward the astronomical identification and the derivation of molecular abundances of these species in the interstellar medium.

Figure Portion of the rotational spectrum of Vinyl Alcohol. [3]



References

[1] L. Wang, c&en **90**, 39 (2012)

[2] P.H. Siegel, IEEE Trans. MW Th. Tech. 50, 910 (2002)

[3] M. Melosso, B. A. McGuire, F. Tamassia, C. Degli Esposti, and L. Dore, ACS Earth Space Chem. **3**, 1189 (2019)

High-resolution spectra of small molecules and the astronomical search for them in late-type stars

Guido W. Fuchs

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At the end of their stellar lives many evolved stars, such as low and intermediate mass asymptotic giant branch (AGB) stars and the more massive red super giants, are rapidly losing mass via strong stellar winds. These winds are one of the major sources of molecules and dust in the universe. The molecules found are composed of refractory materials like metal atoms, carbon or silicon and are believed to be crucial for dust formation. In our laboratories we study the gas-phase spectra of these kinds of molecules via high resolution infrared spectroscopy. Our experimental setups will be presented and examples of the investigated molecules, like TiO, Al2O and C3, will be discussed. Furthermore, with new infrared instruments on telescopes like IRTF, Gemini North or VLT spectrally highly resolved observation s (R > 80 000) can be performed towards late-type stars, like VY Canis Majoris, o-ceti (Mira) and others. The potentials and challenges of our latest high-resolution IR observations will be presented and discussed.

Chemistry in UV-irradiated interstellar clouds

J. R. Goicoechea[1]

[1]*Instituto de Física Fundamental, CSIC, Madrid, Spain*

Far-UV photons (FUV, $E < 13.6$ eV) from massive stars regulate, or at least influence, the dynamics, heating, ionization, and chemistry of most of the neutral ISM (HI and H_2 clouds). Investigating the interaction between FUV radiation and interstellar matter (molecules, atoms, and grains) thus plays a central role in Astrochemistry. Indeed, it contributes to a better understanding of a broad range of environments in which similar physical and chemical process operate (diffuse clouds, the interface between HII regions around massive stars and their parental dense cloud, planetary nebulae, starburst galaxies, etc.) all generically known as “photodissociation regions” (PDRs).

The chemistry of PDRs depends on the propagation and attenuation of stellar FUV photons into the cloud. Different physical processes and chemical reactions control the molecular composition as a function of cloud depth. Traditionally considered to be too harsh environments to host a rich chemistry, modern-day observations using multi-wavelength techniques and broad-band spectrometers do show a distinctive (photo)chemistry. Specific “PDR molecules" are the molecular ions CF^+, CO^+, HOC^+, CH^+, SH^+, OH^+ or H_2Cl^+ ions (some of them extremely reactive). Their formation routes often represent the first steps of interstellar chemistry. The list of molecules detected in prototypical PDRs such as the Horsehead Nebula or the Orion Bar steadily increases. It ranges from well-known radicals (*e.g.,* C_2H, CN, OH, HCO), heavier ions (such as l-C_3H^+) involved in the formation of small hydrocarbons (*e.g.,* C_3H_2 and C_3H), isotopologues and isotopomers (*e.g.,* ^{13}CCH, $C^{13}CH$, DCN and HNC), to PAHs and complex organic molecules (COMs, *e.g.,* CH_3CN, HCOOH, CH_2CO, etc.). Explaining the presence of COMs in PDRs is particularly challenging, and opens new avenues for grain surface and ice-mantle desorption studies.

The emission from the above species not only reflects subtle excitation and chemical processes (photoreactions, state-to-state reactions with FUV-pumped vibrationally excited H_2, fractionation reactions, photo-erosion of grains, etc.), also they trace the steep variations in the gas properties (physical and FUV-illumination conditions, ionization fraction, etc.) as a function cloud depth. In this contribution I will review our on-going modelling and observational efforts (with ALMA, Herschel and the IRAM 30m telescope) to characterize the chemistry of PDRs.

Shock chemistry and rare isotopologues around eruptive stars

T. Kamiński[1,6], K. M. Menten[2], R. Tylenda[1], K. T. Wong[3], J. M. Winters[3], A. A. Breier[4], Th. F. Giesen[4], A. Karakas[5], N. A. Patel[6]

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Red novae, a newly-recognized group of eruptive variable objects, are optical manifestations of merging non-compact stars that may be observed in real time. They represent transients erupting at luminosities intermediate between those of classical novae and supernovae. In red nova eruptions, stellar coalescence produces circumstellar environments particularly rich in molecular gas and dust. ALMA, NOEMA, and SMA interferometers have recently revealed the complexity of the cool remnants of such events, including their spatio-kinematic structure and a rich molecular inventory of peculiar molecular and isotopologic composition. The submillimeter observations have provided, for the first time, the masses dispersed during the merger events and revealed bipolar outflows, which strongly constrains hydrodynamic models of progenitor common-envelope systems and violent stellar mergers. Additionally, detailed studies of chemical composition of red-nova remnants have yielded many surprises and include the detection of complex organic molecules and the first observation in space of a "radioactive molecule", ^{26}AlF. Some of these observations suggest that complex molecules might have formed in shock-excited gas rather than on ice. There are numerous similarities between the merger remnants and some pre-planetary nebulae (PPNe) and it is possible that some objects classified as PPNe are indeed old merger remnants. Although rare, merger remnants may thus contribute to the Galactic chemical evolution.

From small to tall: molecular complexity in interstellar ices

H. Linnartz[1]

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Observational studies reveal that complex organic molecules (COMs) can be found in various objects associated with different stages along the star formation process. The identification of COMs in prestellar cores, *i.e.*, environments in which thermally induced chemistry can be excluded and radiolysis is limited by cosmic rays and cosmic ray induced UV-photons, is particularly important as this stage sets up the initial chemical composition from which ultimately stars and planets evolve.

Recent laboratory results demonstrated that molecules as complex as glycolaldehyde and ethylene glycol are efficiently formed on icy dust grains *via* non-energetic atom addition reactions between accreting H atoms and CO-molecules, a process that dominates surface chemistry during the 'CO-freeze out stage' in dense cores. This work [1-3] will be shortly reviewed as a starting point to demonstrate that a similar mechanism can result in the formation of the biologically relevant molecule glycerol - $H_2C(OH)(HCOH)CH_2OH$ – a sugar alcohol necessary for the formation of membranes of modern living cells and organelles [4]. Our experimental results are fully consistent with a reaction scheme in which glycerol is formed along a chain of radical-radical and radical-molecule interactions between various reactive intermediates produced upon hydrogenation of CO ice or its hydrogenation products.. Extending on the results obtained in these studies, the new laboratory findings presented here will show that the proposed reaction mechanism holds much potential to form even more complex species, specifically when injecting other radicals into the chemical network [5].

References

[1] H. Linnartz, G. Fedoseev, S. Ioppolo, Int. Rev. Phys. Chem. **34**, 205 (2015).
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Far-infrared spectroscopy of astrophysical molecules using synchrotron radiation

O. Pirali[1,2]

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Our team exploits the synchrotron radiation extracted by the AILES beamline of SOLEIL synchrotron facility to study different families of molecules in the far-IR and THz spectral range. We have developed several experimental set-ups which, together with the high resolution Bruker interferometer of the beamline, allow to record rotationally resolved spectra of a large number of molecules of astrophysical relevance. In addition, our recent progresses in mixing synchrotron radiation with different laser sources allows us to consider interesting prospects for sub-MHz resolution spectroscopy in this part of the electromagnetic spectrum [1].

References

[1] J.-F. Lampin et al., Optics Letters, in press (2019)

Chemistry on the Surface of Cosmic Dust Grains

Alexey Potapov

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Astrochemistry is a hot topic in the last decades due to the detection of complex organic molecules (COMs) in astrophysical environments such as cold interstellar molecular clouds and hot protostellar molecular cores as well as in comets and meteorites. One hypothesis about the source of organic compounds, which could serve as the basis of life on Earth, is their formation in the interstellar medium (ISM) and delivery to early Earth on board of meteorites. Dust grains play a central role in the physics and chemistry of practically all astrophysical environments. They influence the thermal properties of the medium by absorption and emission of stellar light, provide surfaces for efficient chemical reactions responsible for the synthesis of a major part of important astronomical molecules from simple ones such as H_2 and H_2O to COMs, and they are building blocks of planets.

The role of dust grains in surface reactions includes: i) direct participation of functional groups and atoms and ii) catalytic effect. In my talk, I will discuss laboratory experiments devoted to both cases with the focus on recent results obtained in our group. For the first time, we have demonstrated that the bombardment of bare carbon grains by O and H atoms at low temperatures causes the formation of CO molecules, with their further hydrogenation leading to the formation of formaldehyde. The formation of H_2CO, a direct precursor of methanol, is an indication for an alternative route of COM formation in the ISM – grain surface processes. For the first time, we have put in evidence the catalytic role of the dust surface studying the $CO_2 + 2NH_3 \rightarrow NH_4^+NH_2COO^-$ thermal reaction on silicate and carbon grains. Surface catalysis on grains accelerates the kinetics of the reaction studied in the temperature range of 60 - 80 K as compared to molecular solid. A faster kinetics, on this particular reaction or other ones, especially radical-radical reactions, should have a great impact on the astrochemical modelling involving surface chemistry.

Rotational Spectroscopy, Quantum Chemistry and the Astrochemical Challenges

Cristina Puzzarini[1]

[1]*Department of Chemistry "Giacomo Ciamician", Bologna, Italy*

The discovery in the interstellar medium of molecules showing a certain degree of complexity, and in particular those with a prebiotic character, has attracted great interest. A complex chemistry takes place in space, but the processes that lead to the production of molecular species are a matter of intense discussion, the knowledge still being at a rather primitive stage. Understanding the chemical evolution of the universe is one of the main aims of Astrochemistry, with the starting point being the knowledge whether a molecule is present in the astronomical environment under consideration. The astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence in the astronomical environment under consideration. However, the interpretation of astronomical detections in terms of chemical evolution is not at all straightforward.
By means of selected examples, it will be shown that challenges in astrochemistry [1] can be successfully overcome by combining state-of-the-art computational spectroscopy approaches [2] with experiment in the field of rotational spectroscopy. Two topics will be mainly addressed: the determination of accurate spectroscopic signatures to guide future astronomical observations [3-4] and the investigation of feasible reaction mechanisms leading to the formation of interstellar molecules [5-6].

References

[1] M. Biczysko, J. Bloino, C. Puzzarini, WIREs Comput. Mol. Sci. **8**, e1349 (2018)
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[5] D. Skouteris, N. Balucani, C. Ceccarelli, F. Vazart, C. Puzzarini, V. Barone, C. Codella and B. Lefloch, Astrophys. J. **854**, 135 (2018)
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PDR Modelling Review

M. Röllig[1]

[1]*Universität zu Köln, Köln, Germany*

The interaction between active massive star formation and the ambient interstellar medium (ISM) is one of the hot topics in modern astrophysics. Feedback from young massive stars is one of the major candidates to regulate the star formation efficiency down to the observed values, e.g. in the Milky Way. The study of photon dominated regions (PDRs) is at the center of this research. PDRs are the portion of the ISM where the physical and chemical conditions are governed by the FUV photons from nearby massive stars [1]. A detailed understanding of the relevant physical and chemical processes in PDRs is key in interpreting observations of PDRs and in deriving the local conditions.

Numerical models of PDRs are important tools to develop a deeper understanding of the relevant chemical and physical processes. I will provide an overview over the fundamentals of numerical PDR modelling [2] and present a number of recent applications that demonstrate how these models can be applied in astrophysical research [3].

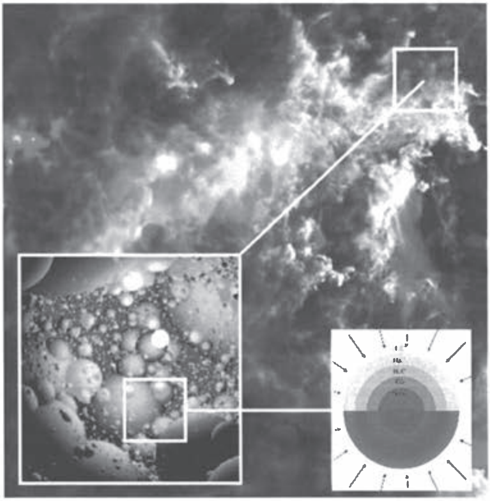

Fig 1: Numerical modelling concept of clumpy PDRs using the KOSMA-τ model.

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The Chemical Evolution of Cosmic Carbon: Laboratory Studies with the COSmIC Facility

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Cosmic dust plays an essential role in our understanding of the chemical and physical evolution of the universe. Our understanding of cosmic dust relies on a combination of astronomical observations (either remote or on extraterrestrial dust samples), astrophysical modeling and laboratory studies of realistic analogs of cosmic dust grains. The COSmIC facility was developed at NASA Ames to study the evolution of cosmic carbon from circumstellar outflows to interstellar clouds to planetary atmospheres in the laboratory [1]. COSmIC stands for "Cosmic Simulation Chamber" and is dedicated to the study of neutral and ionized molecules and grain particles under the low temperature and density conditions that are required to simulate space environments. COSmIC integrates a variety of instruments that allow generating, processing, and monitoring simulated space conditions in the laboratory. It is composed of a Pulsed Discharge Nozzle (PDN) expansion that generates a plasma in a free supersonic jet expansion, coupled to high-sensitivity, complementary in situ diagnostic tools used for the detection and characterization of the species present in the expansion: Cavity Ring Down Spectroscopy (CRDS) and fluorescence spectroscopy systems for photonic detection and an orthogonal Reflectron Time-Of-Flight Mass Spectrometer (oReTOF-MS) for mass detection.

Recent advances achieved in laboratory astrophysics using COSmIC's laboratory data in synergy with observational data will be presented. These results include the formation of dust grains and aerosols from gas-phase molecular precursors in environments as varied as circumstellar outflows of late AGB stars [2] and planetary atmospheres [3] and the evolution of our understanding of the diffuse interstellar bands (DIBs) with applications to the ESO Diffuse Interstellar Bands Large Exploration Survey (EDIBLES [4, 5]). Plans for future laboratory developments and techniques to study the evolution of cosmic carbon molecules and grains (including NIR-MIR CRDS, laser induced fluorescence (LIF) and incandescence (LII)) will also be addressed as well as their astronomical applications.

Acknowledgements: The authors acknowledge the support of NASA SMD/APRA, SSW programs and the technical support of R. Walker and E. Quigley at NASA ARC.

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The Boon and Bane of High-Resolution Spectroscopy

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Interstellar molecules are identified primarily through their fingerprint-like rotational spectra. In quiescent sources molecular line centers are determined at accuracies below 1 MHz at THz frequencies. Consequently related laboratory spectra shall be recorded at accuracies better than 10^{-7}. Taking spectra of weak transitions, e.g., for molecular ions is extremely challenging when large fractions of THz spectra are desired. I will discuss an approach we are following in Cologne which is based on action spectroscopy in traps where first low resolution spectra (~cm^{-1}) are taken especially in the infrared using pulsed lasers like nanosecond OPOs or the free electron laser facility FELIX [1]. These studies are followed by higher resolution infrared spectra where sub-MHz accuracies are feasible with the use of a frequency comb for energy calibration. Based on these studies rotational spectra can often be predicted with high confidence such that the scanning range can be reduced substantially. Recent examples and future wishes shall be discussed in this talk.

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A multi-spectroscopic approach to reveal the astrochemistry of polycyclic aromatic hydrocarbons

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Diksha Garg, Jason Lee, Melanie Schnell
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Polycyclic aromatic hydrocarbons (PAHs) are of great interest for its potential central role in astrochemistry. It is assumed that they contain up to 20% of the galactic carbon and help make up the composite of ice grains. They are also considered to be at the heart of a rich chemistry in space, for example by acting as catalysts. To unravel the various aspects of their impact in astrochemistry, we perform a multi-spectroscopic approach covering large areas of the electromagnetic spectrum.

The structures and intermolecular interactions of PAH-water complexes are investigated using high-resolution chirped-pulse rotational spectroscopy in our lab and infrared spectroscopy using the Free-Electron Laser (FEL) FELIX in Nijmegen in the gas phase. With this work, we aim at understanding interactions between PAHs themselves and water. Another motivation is to learn how an ice layer begins to form on a PAH surface. Recently, we extended our studies to chiral helicenes. Discharge experiments with PAHs and other astrochemically relevant molecules as precursors generate new PAH-related species that we can then characterize spectroscopically.

To study PAH photophysics, we use the Hamburg FEL FLASH and perform ultrafast XUV-UV/IR pump-probe experiments, with ionization and dissociation as competing pathways and synchrotron experiments at SOLEIL to study the ionization potentials of PAH clusters. In a first successful beamtime, we investigated structural changes of PAHs in different charge and dehydrogenation states of the three-ring PAH phenanthrene using Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy and the endstation PIPE at the synchrotron PETRA III in the 280 eV to 320 eV energy range (to cover the carbon K edge). In comparison with quantum-chemical calculations, it will be particularly interesting to understand how the structures change upon stepwise removal of individual H atoms, and if folding and thus a first step towards fullerenes is observed.

In my presentation, I will provide an overview of our research activities on PAHs and discuss some of the latest results.

CRASY: Correlated Mass-Rotation Spectra of Heterogeneous Samples

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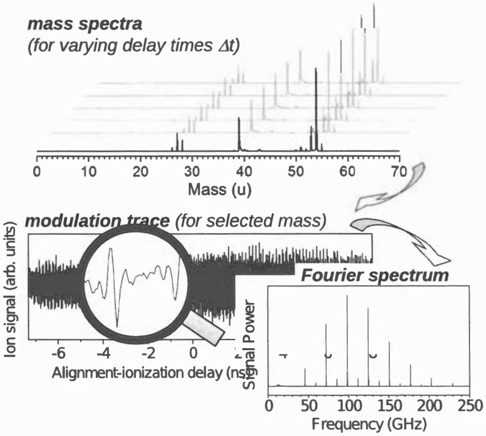
The majority of molecular samples are inherently heterogeneous: natural or synthesized samples are rarely of pure structural, isomeric, or isotopic composition. Spectra for impure samples show averaged signals for all sample components and are often insufficient to resolve signals for individual sample components. Would it not be nice if we could mark each sample component before the measurement?

We develop correlated rotational alignment spectroscopy (CRASY) to perform this feat. Mass-CRASY data resolved 10 naturally occurring carbon disulfide isotopologues [1] and correlated cationic fragments to their neutral precursor species [2].

Mass-CRASY achieved single-MHz rotational resolution over a spectral range of 500 GHz [3], an order-of-magnitude better resolved than preceding Raman spectra [4]. Rotational spectra are calibrated in a time-domain equivalent to frequency comb spectroscopy [3].

Future experiments will analyze increasingly complex heterogeneous samples. Assignment of isotopic heterogeneity will allow de-novo structure analysis and to observe static and kinetic isotope effects. Novel reactive species will be characterized in pyrolized molecular beams. For biomolecular tautomers, we aim to identify tautomer-specific electronic structure and photochemical reaction dynamics.



Mass-CRASY measurements: ***Mass spectra*** (top) are measured at multiple time-delays delays Δt between a pump and probe laser pulse. For each mass, the temporal ***ion signal modulation*** (bottom left) reflects wave packet interference between rotational states populated by the pump pulse. A Fourier transformation of the modulation signal reveals the ***rotational spectrum*** (bottom right) correlated to the mass.

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Chemical Evolution and Its Diversity in Disk Forming Regions

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In the formation of sun-like protostars, a disk structure forms around a newly formed protostar and evolves into a protoplanetary disk and eventually to a planetary system. Along this physical process, chemical composition of the interstellar gas also evolves into that of planetary materials. For thorough understandings of the origin of the Solar System, it is of fundamental importance to elucidate detailed processes of the chemical evolution. By extensive use of the state-of-the-art radio telescopes including Atacama Large Millimeter/submillimeter Array (ALMA), we are studying the chemical process and its diversity associated with the disk formation. Some highlights are summarized as follows:

(1) Chemical composition in star forming clouds is much more complex than ever thought. Fairly 'complex' organic species such as $HCOOCH_3$, CH_2OHCHO, and NH_2CHO as well as highly unsaturated organic molecules (carbon-chain molecules) such as C_2H, $c\text{-}C_3H_2$, and C_4H are detected in star forming cores. Interestingly, the chemical composition is found to be different from object to object [1,2].
(2) The above chemical diversity is found to be delivered to the vicinity of the protostars, where protoplanetary disks are being formed. Thus, the chemical diversity will be inherited to protoplanetary disks, and eventually to planetary systems [3-5].
(3) Chemical composition drastically changes in the transition zone from the infalling-rotating envelope to the disk structure. Some specific molecules are found to trace specific physical parts just like 'a molecular marker'. This fact, in turn, allows us to study the physical structure of the disk forming regions [3-6].

These results provide us with new insight into the material origin of the Solar System, and more systematic studies are in progress.

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Destruction and re-formation of grains in an inhomogeneous, evolving interstellar matter

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Observations indicate that properties of interstellar dust vary strongly across the interstellar gas phases. We address these changes with models of dust evolution in an inhomogeneous, multiphase interstellar medium (ISM) using high-resolution hydrodynamic simulations of the local Milky Way [1, 2, 3]. We find that the observed distribution of interstellar element depletions of Si and Fe results from the interplay between efficient sputtering of grains in supernova blast waves and subsequent re-formation of dust by accretion of gas species in the cold, neutral medium. I will discuss what recent simulations tell us about physical conditions, main processes, and timescales of dust destruction and growth in the ISM. I will also present constraints for sizes and composition of iron and silicate grains from dust evolution modeling.

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Abstracts of Posters

(in alphabetical order)

Radioresistance of complex organic molecules in solid phase

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Ices are omnipresent in cold regions in space on, e.g surfaces of planets and their satellites, transnepunian objects, dust grains and comets. Although such ices are mainly formed from small molecules (e.g water, carbon oxides, nitrogen, methane) larger complex organic molecules (COMs) may be present. To give an example, a plethora of molecules (among them glycine and several aromatic molecules) have been detected by ESA'S Rosetta mission on comet 67P/Churyumov-Gerasimenko. Ionizing radiation (UV photons, electrons, ions from cosmic rays or solar wind) induces several physico-chemical processes such as radiolysis and subsequent formation of new molecules including COMs. Organic molecules have been and are constantly being delivered from space to Earth by e.g. micrometeorites and thus may have contributed to the emergence of life. In order to determine the survival time of complex molecules in space environment, it is necessary to study their radiation resistance.

At CIMAP (Caen, France) using different beam lines of the GANIL facility and at GSI (Darmstadt, Germany), the interaction of swift highly charged heavy ions with astrophysical ices was studied in a wide projectile energy range from keV to GeV. We study the radiation resistance of COMs by in situ Fourier transform infrared absorption spectroscopy. The evolution of the chemical composition with projectile ion fluence allows to deduce the corresponding destruction cross section of COMs.

We present results on radiosentivity of COMs such as nucleobases and pyridine. Mixtures of pyridine and water were irradiated at different concentrations of pyridine at low temperature (15K). We report the apparent destruction cross section as a function of pyridine concentration. Pure pyridine is found to be more radiation resistant than pyridine mixtures with low concentrations (<50% of pyridine).

Combining High-resolution Millimeter-wave Rotational Spectroscopy with Electrical Discharge for Astrochemical Reactions

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Electrical discharge sources have been used extensively for the generation of molecular ions, radicals, and long chain unsaturated hydrocarbons, which have subsequently been discovered to be present in the interstellar medium (ISM) [1]. We have used a discharge source to produce a number of medium-sized, astronomically relevant, neutral organic molecules from multi-component mixtures. We aim to use this information to infer reaction pathways from the mixture components to the discharge products. These pathways could then be applied to astronomical environments, such as molecular clouds. The products are characterised with our segmented chirped-pulse Fourier transform millimeter-wave spectrometer, which has been previously applied in our room-temperature studies of cyanides and alcohols [2]. We will concentrate here on the discharge products of mixtures of molecules already detected in the ISM, such as aldehydes in mixture with the nitrogen-containing molecules acetonitrile and ammonia. Any newly-observed species in our spectra can be assigned with rest frequencies and rotational parameters already suitable for interstellar searches with millimeter-wave radio telescopes, such as the Atacama Large Millimeter/submillimeter Array. Results from our experiments will allow us to better consider reaction pathways towards complex organic molecules in extra-terrestrial environments.

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The complex chemistry of young high-mass star forming regions

M. Bonfand[1,2], **A. Belloche**[2], **R. T. Garrod**[3], **K. M. Menten**[2], **H. S. P. Müller**[4], **T. Csengeri**[1] **and S. Bontemps**[1]

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Interstellar complex organic molecules (COMs) were first detected toward so called hot cores around high-mass protostars. The high temperatures that prevail in these regions boost the gas-phase chemical complexity via thermal desorption of complex species from dust-grain surfaces. To understand the key processes leading to the formation of the numerous COMs detected toward hot cores, the physical conditions in which complex species form need to be well constrained. Here we take advantage of the high sensitivity and high angular resolution provided by ALMA to investigate the physical and chemical structure of the envelope of young high-mass protostars.

Combining the analysis of the 3 mm imaging line survey Exploring Molecular Complexity with ALMA (EMoCA [1]) and astrochemical models we led the first detailed comparison of the chemical composition and physical structure of four hot cores embedded in Sagittarius B2(N) [2]. Given its exposure to the extreme environment of the Galactic center region, Sgr B2(N) is an excellent target to study the impact of environmental conditions (cosmic-ray ionization rate, external radiation field, and minimum dust temperature during the pre-stellar phase) on the production of COMs [3].

Such investigations focused on hot cores show that they exhibit a great diversity in their chemical composition and physical structure. Among the 35 sources targeted by the Search for high-mass Protostars with ALMA up to Kiloparsec Scales project (SPARKS, [4]), G328.2551-0.5321 shows the first observational evidence for larger densities of COMs detected toward accretion shocks within the envelope than the radiatively heated compact region toward the protostar and the accretion disk [5]. G328.2551-0.5321 is thought to be chemically young, representing an earlier evolutionary stage compared to classical hot cores. It is an excellent target to study the chemical evolution of hot cores, as well as the origin of chemical differentiation.

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Symmetries of CH_5^+

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The spectra of protonated methane, CH_5^+, have eluded any analytical description so far. However, in 2015 Schmiedt et al. used group theoretical considerations to understand why the separation of molecular rotation and vibration fails for CH_5^+ [1]. The authors proposed a five dimensional superrotor model overcoming these problems [2]. They succeeded in describing the experimental energies reasonably well [3, 4] but the associated symmetry labels are in conflict with those of the numerical calculations of Wang et al. published in 2016 [5]. Fábri and Császár recently calculated level energies also in accordance with the experimental results using a new model based on graphs connecting the large number of equivalent minima on the potential energy surface [6].

We present some results and some ideas about the relations between all these approaches that appear, at a first glance, to be very different. These results include:

- Schmiedt et al. argued that there cannot exist equivalent rotations for the permutations of CH_5^+ as $\mathbf{S}_5$ is not isomorphic to any subgroup of $SO(3)\times\{E,E^*\}$. With the help of the results of Fábri and Császár we found a geometric explanation of this insight.
- Also by group theory Schmiedt et al. argued that SO(4) cannot be used to describe CH_5^+. Using the fact that SO(4) is isomorphic to $SU(2)\times SU(2)$ we show that this statement has an geometric explanation, too.
- A group theoretical explanation of the work of Fábri and Császár results in a splitting of $\boldsymbol{S}_5=\boldsymbol{S}_4\times\boldsymbol{S}_2$ associated with an ordinary equivalent rotation for the $\mathbf{S}_4$ part. This gives some clues to the interpretation of the SO(5) superrotor symmetry proposed by Schmiedt et al.
- The description of CH_5^+ using the overarching SO(5) group is equivalent to a replacement of its 5 protons by a 5-dimensional quasi-particle "living" on a sphere. Relating the symmetry labels of this quasi-particle to the CH_5^+-motions remains an open question to date.

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From Lines to States without a Model

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The fundamental Ritz combination principle [1] originally found for atoms has also been applied to molecules as a method to reconstruct the energy states from measured lines without relying on any model Hamiltonian. In 2006 Nesbitt and coworkers [2] proposed to apply it to protonated methane, CH_5^+, which was first done in 2015 [3] and extended in 2017 [4] by our group. Currently, we are elaborating this method to a universal, easy to use tool which can be used for arbitrary spectra as there is a broad field of potential applications:

- First step of understanding of molecular spectra for which not even a zero order Hamiltonian exists (as for CH_5^+ in 2015)
- Separation of mixed spectra consisting either of spectra of different molecules (i.e. from an experiment in a discharge tube) or spectra consisting of subspectra originating from different nuclear spin species (i.e. para- and ortho-$He\text{-}H_3^+$)
- Preprocessing for the assignment of rich experimental spectra to analytical models or numerical data

The challenges in generalizing the method to arbitrary molecules, solutions for most of these challenges and first results will be discussed.

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High-resolution microwave spectroscopy of radioactive molecules: mass-independent studies of AlF, AlO, TiO, and FeO

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Astrophysical observations of radioactive isotopes, like ^{26}Al, ^{44}Ti, or ^{60}Fe, provide insight into the nucleosynthesis of stellar cores [1]. The detection of characteristic γ-photons which are released during radioactive decay are used to map their spatial distribution on large scale [2]. In general, the assignment to certain stellar objects fails due to limited sensitivity, exceptions are the nearby supernovae remnants Cas A and SN1987A [3,4] for which the radioactive decay of ^{44}Ti was detected.

An alternative approach is the observation of molecules containing radioactive isotopes. Radio-telescope facilities, like ALMA, can identify these species via their rotational transitions. In the outer atmosphere of late type stars, the molecular condensation starts with simple diatomic particles containing refractory elements.

The astrophysical detection of diatomic radioactive molecules requires highly accurate rotational transition frequencies, which are obtained from laboratory measurements of their stable counterparts using mass-independent Dunham parameterization [5].

In this work, systematic studies are presented for ^{26}AlF, ^{26}AlO, ^{44}TiO, and ^{60}FeO, as most promising tracers of nucleosynthesis in stellar environments, based on high-resolution measurements on the rotational transitions of their abundant stable isotopologues (^{27}Al, $^{46-50}$Ti, ^{54,56}Fe).

A global data analysis reveals the experimentally derived molecular structure beyond the Born-Oppenheimer (BO) limit for the first time. Based on this analysis, the rotational transitions of the radioactive molecules are determined with high accuracy at the sub-MHz level, which enables their unambiguous identification in stellar environments. Possible candidate stellar sources will be discussed.

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Photon-induced desorption of larger molecules from a pure CH_4 ice

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At the low temperatures found in the interior of dense clouds and circumstellar regions, along with H_2O, CO, CO_2, or CH_3OH, the IR features of CH_4 have been observed on icy dust grains [1]. Ultraviolet (UV) photons induce different processes in ice mantles, affecting the molecular abundances detected in the gas-phase.

The aim of this work is to understand the processes that occur in a pure CH_4 ice mantle submitted to UV irradiation. We studied photon-induced processes for the different photoproducts arising in the ice upon UV irradiation by using a continuum emission hydrogen lamp.

Experiments were carried out in ISAC, an ultra-high vacuum chamber equipped with a cryostat and a F-type UV-lamp able to reproduce the conditions present in dense clouds and the secondary UV-field. Infrared and UV spectroscopy were used to monitor the solid phase, while quadrupole mass spectrometry served to monitor the gas phase. These techniques were used during the formation, irradiation and warm-up of the ice.

Direct photodesorption of pure CH_4 was not observed. UV photons form $CH\cdot$ and $H\cdot$ radicals, leading to photoproducts like H_2, C_2H_2, C_2H_4, C_2H_6, and C_3H_8. Evidence for the photodesorption of C_2H_2 and photochemidesorption ([2], and references therein) of C_2H_6 and C_3H_8 is found, the latter species is so far the largest molecule found to photochemidesorb. $^{13}CH_4$ experiments were also carried out to confirm the reliability of these results.

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Deciphering the elusive structure of the fragment ions of a probable interstellar biomolecular building block: The case of pyrimidine

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Pyrimidine (Pym), a N-containing heterocyclic molecule, is one of the fundamental building blocks of the genetic materials DNA and RNA. The prebiotic chemistry concerning the formation of Pym and its subsequent evolution into larger biomolecules has always been intriguing. Numerous studies have been devoted to characterize the fragment ions (and/or precursor) of this important parent molecule. Previous mass spectrometric and theoretical investigations unequivocally reported $C_3H_3N^+$ (m/z 53) and $HCCH^+$ (m/z 26) as the dominant fragment ions of Pym^+ cation. It was established that the parent ion eliminates a single HCN molecule to produce the first fragment, which subsequently disintegrates into $HCCH^+$ through the loss of another neutral HCN. Interestingly, there is a long-standing controversy concerning the structure of the heavier $C_3H_3N^+$ daughter ion.[1] Although the lighter ion was thermochemically identified as the acetylene cation ($C_2H_2^+$), there are no spectroscopic interrogations that confirm the structure of both fragment ions. In our work, we employ mass-selected gas-phase infrared photodissociation (IRPD) spectroscopy to disentangle this intricacy. The daughter ions successfully undergo cluster formation with inert gas tag(s) (Ar and N_2), which are finally photofragmented by IR photons. The corresponding IRPD spectrum of the mass-selected parent cluster is analyzed with the aid of the dispersion corrected density functional theory. Our investigation shows a dominant contribution of the kinetically favored *cis* and *trans* forms of the $HCCNCH^+$ isomer[2] and a moderate population of the most stable H_2CCCNH^+ monomer. Furthermore, the IR spectrum of the Ar-tagged $HCCH^+$ complex reproduces the π-bound $C_2H_2^+$-Ar dimer spectrum, which confirms this lighter fragment as the acetylene cation. We further report different ligand binding motifs for both the fragment ions and the parent Pym^+ in the 3 μm range.

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The ultrafast dynamics of polycyclic aromatic hydrocarbons upon ionization using XUV radiation at 30.3 nm

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The role of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium is an important topic in astrochemistry today. Disentangling the chemical processes involved in the interaction of PAHs with energy-rich radiation in such environments is an important step in this direction.

In this work, we present results from a pump-probe study of the ultrafast fragmentation of three medium sized PAHs: fluorene, phenanthrene and pyrene. These molecules were ionized using extreme ultraviolet (XUV) radiation at 30.3 nm provided by the free-electron laser (FEL) at Hamburg, FLASH. The subsequent dynamics in the femtosecond regime were probed using 810 nm near-infrared pulses temporally delayed relative to the pump FEL pulse. The time dependent yield of the relevant ion channels were tracked using time-of-flight mass spectrometry. The objective of these experiments was to determine the lifetimes of the excited cationic PAHs following XUV excitation and to formulate a better understanding of their preferred reaction pathways under such conditions. We have been able to qualitatively identify the fragmentation pathways of these PAHs upon photoionization and subsequent interaction with the probe laser.

The solid-state formation of complex organic molecules from dust fragment analogues (C_2H_2)

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Complex organic molecules (COMs) have been identified toward various star-forming regions from translucent cloud to the solar system. Their formation mechanisms are still under debate and have been the subject of numerous experimental and theoretical studies including non-energetic and energetic processing. [1,2] Besides sugar-relative species ($C_nH_{2n}O_n$), which have been intensively studied along with the surface chemistry scheme of CO-H_2CO-CH_3OH, the icy origin of acetaldehyde and its (de-)hydrogenated derivatives, which are commonly observed in molecular cloud before CO freezes out, remains unclear. In this work, we investigate possible solid-state reactions between simple hydrocarbons (e.g., C_2H_2), likely originated from the fragmentation of PAH^+ as well as hydrogenated carbonaceous-dust, and H/OH-radicals, generated via atomic addition or induced by energetic processing, under the H_2O-rich ice formation scenario. Ultra-high vacuum experiments were performed to study the surface chemistry observed during the C_2H_2+(O_2)+H co-deposition and the ion irradiation of C_2H_2+H_2O ice mixture. Fourier-transform infrared spectroscopy was applied to *in situ* monitor the initial and newly formed species. After that, a temperature-programmed desorption experiment combined with a quadrupole mass spectrometer (TPD-QMS) was used as a complementary analytical tool. The spectral assignments were further confirmed in isotope labeling experiments using $^{18}O_2$. The investigated chemistry on grain surface not only results in the (semi-)saturated hydrocarbons like C_2H_{2n}, but also lead to the COM formation, such as ketene, vinyl alcohol, acetaldehyde, and ethanol at low temperature (~10 K). It is concluded that the H/OH-radical addition reactions on C_2H_2 acting as molecular backbone provide an efficient pathway toward interstellar COMs and hold the potential of forming even more biologically relevant species like aldoses and polyols. *(*) chuang@mpia.de*

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Retrieval of laser frequency comb repetition rate and carrier envelope offset frequency from an interferogram

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We describe a method to compute the repetition rate and carrier envelope offset frequency of a laser frequency comb from an interferogram recorded with a commercial Fourier transform spectrograph. In the interferogram multiple strong interference patterns are observed. The distance between these patterns depends on the repetition rate [1]. These interference patterns are identical except for a phase shift between the interference signal and its envelope [2]. When cross correlating these interference patterns we can extract the relative phase and thereby the offset frequency. We apply our method to simulated and measured data, reaching a relative precision of 1.8E−8 for the repetition rate and 1.3E−2 for the offset frequency in the measurement. The errors in both measurements are highly correlated. These values may be used to calibrate the FTS as described in [3].

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Experimental study of isotope effect in reaction of $O^+(^4S)$ ions with H_2, HD and D_2

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The temperature dependence of reactions of ground-state $O^+(^4S)$ ions with H_2, HD and D_2 molecules was measured using 22-pole RF ion trap at temperatures from 15 up to 300 K [1]. For all three reactions the measured reaction rate coefficients are nearly constant in whole covered temperature range. In the covered temperature range the temperature dependencies of branching ratios $BR(OH^+)$ and $BR(OD^+)$ of production of OH^+ and OD^+ ions in reaction with HD were also measured showing nearly equal production of both ions, $BR(OH^+) \sim BR(OD^+) \sim 0.5$. Good agreement of the rate coefficients and the branching ratios with previous experimental data [2, 3, 4] and results of calculations [5, 6, 7] was obtained at 300 K, where these data are only available.

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Clusters of chiral PAHs — with and without H_2O

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Cosmic water ices containing polycyclic aromatic hydrocarbons (PAHs) sustain great interest as likely catalytic sites for chemical reactions driven by ultraviolet radiation in the interstellar medium. Prototypical clusters of small PAHs with a few water molecules are thus appealing case studies, as they can be considered simplified models to probe the initial steps of ice grain evolution and retrieve primary structural motifs. Studies performed on chiral substrates are, however, poorly explored. Here we discuss the first steps of self aggregation and micro-solvation of [4]helicene, the smallest PAH with a helical sense (Fig. 1). Based on laboratory observations using high resolution microwave spectroscopy at DESY, we discuss aggregation preferences in the binding of water to the chiral substrate.[1] Further investigations carried out using VUV radiation at SOLEIL reveal the formation of large clusters of [4]helicene. Preliminary theoretical modelling anticipates certain trends in the formation of homochiral and heterochiral clusters. We discuss these aggregation motifs and the relation between cluster size and ionisation potentials.

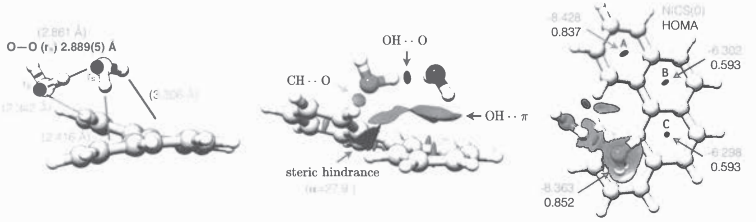

Fig. 1. The [4]helicene — $(H_20)_2$ cluster. [1]

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Structural, vibrational, and hydration properties of a protonated interstellar aromatic molecule: The case of benzonitrile

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Despite the widespread consensus on the ubiquity of polycyclic aromatic hydrocabons (PAHs) in the interstellar medium, any specific PAH is yet to be detected. The recent extraterrestrial discovery of benzonitrile (BN),[1] the first and only detected interstellar aromatic molecule, further consolidates a huge repository of larger aromatic species in this environment. These molecules often undergo various complex reactions, for example protonation, which are often triggered by the abundant H_3^+ ion, cosmic radiation, etc. Therefore, the detection of BN suggests the presence of its protonated form (H^+BN). In our work, we implement the messenger-tagging technique to produce various clusters of H^+BN with both protic (H_2O) and aprotic ligands (Ar and N_2), which are irradiated with infrared (IR) photons to record the IR spectra of the mass-selected parent clusters. The acquired spectra are further analyzed by the dispersion corrected density functional theory that establishes various binding motifs of the ligands and other intrinsic molecular parameters. From the π-bound H^+BN-Ar complex, in which the solvent barely influences the H^+BN properties, we estimate the characteristic NH stretch frequency of the monomer at 3555 ± 3 cm^{-1}.[2] In a protic environment, an intracluster proton migration takes place in the $H^+[BN\text{-}(H_2O)_n]$ clusters with $n\geq2$. Our investigation further shows the formation of a strong hydrogen-bonded network within the larger water clusters to solvate the additional proton whereas, in the aprotic environment (Ar and N_2), internal solvation of the positive charge dominates. We further notice a striking similarity between the IR spectra of $BN\text{-}H^+(H_2O)_{n=4\text{-}6}$ complexes and the untagged H^+W_{n+1} clusters, revealing the role of BN dopant in the bare H^+W_{n+1} environment.

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High-resoultion IR spectrum of TiO and its Isotopologues

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Molecules based on refractory elements such as titanium (Ti) are present around oxygen rich late type stars. Refractory elements form molecules at temperatures well above thousand Kelvin. As a result in the envelope of M- type stars, like the red supergiant star VY Canis Majoris, titanium monoxide (TiO) is one of the first molecules which is thought to be formed and recent investigations in the optical-[1] and sub-mm [2,3] wavelength region found TiO and its abundant isotopologues to be present in the atmosphere of late type stars. Due to the lack of laboratory data no high resolution IR observations of TiO are available. In view of high resolution instruments, e.g. EXES on board of SOFIA, laboratory data are of high demand.

We present first rotationally resolved infrared spectrum of titanium monoxide. TiO is produced by laser ablation of titanium seeded in N_2O/He buffer gas. In the adiabatic expansion of a supersonic jet the molecules cool down to rotational temperatures of 30 K. An ec-QCL was used, to probe the TiO molecules in the zone of silence of the supersonic jet. During the 10 µs time of flight through the detection region the ec-QCL is rapidly tuned in frequency. Spectral intervals of 0.03 cm^{-1} are averaged 600 times before stepping to the next frequency interval. Combining the individual intervals results in a rotationally resolved infrared spectrum of TiO and its isotopologues.

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Magnetically-Stimulated Diffusion of Rydberg Atoms in the Cosmic Environment

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A well-known property of all gaseous systems—ranging from cosmic plasmas to the laboratory installations for thermonuclear fusion—is that the external magnetic field suppresses diffusion of the gas in the transversal direction. However, the highly-excited Rydberg gases can exhibit just the opposite behavior—when the magnetic field stimulates rather than suppresses the process of diffusion—which is explained by a complex interplay between the dynamics of center-of-mass and electron degrees of freedom. This effect was predicted for the first time by Schmelcher and Cederbaum in 1992 [1, 2]. Unfortunately, their calculations referred only to the case of the so-called “linear” (strongly elongated) atoms, where the orbital quantum number l was much less than the principal quantum number n. Such atoms are usually produced by laser irradiation in the laboratory experiments, but they are not typical for the natural objects.

As distinct from the above-mentioned case, we calculated the coefficient of diffusion of the Rydberg atoms in the states with $l \approx n$, which are usually produced by the three-body recombination in plasmas [3]:

$$D \approx e\, a_0^5 m_i^{-2} c^{-3} B^3 n^{10},$$

where e is the elementary electric charge, m_i is the mass of the ion, a_0 is Bohr radius, and c is the speed of light. Despite a very small numerical factor in the right-hand side, this coefficient can be appreciable for very strong magnetic fields B and/or the atoms with large principal quantum numbers n.

It was originally suggested by Schmelcher and Cederbaum [1, 2] that the magnetically-stimulated diffusion should be important in the magnetospheres of neutron stars, possessing huge values of the magnetic field. Besides, it might be appreciable also in the regions of radio-recombination lines [4], where atoms with huge principal quantum numbers (up to 1000) are formed.

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Rate Coe-fficients for NH_3-He Collisions: First results from Pump-Probe Chirped-Pulse Experiments

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The kinetics of rotational inelastic NH_3-He collisions are studied using pump-probe experiments carried out with a K-band waveguide chirped pulse Fourier transform microwave spectrometer by observing NH_3 inversion doublets in the ground vibrational state. The population of one inversion doublet is altered by the pump pulse. Due to resonant collisions the resulting deviation from equilibrium is propagating to other states and interrogated by probe pulses as a function of the pump-probe delay time.

First results of this ongoing project will be presented including a comparison with previous experimental studies[1] as well as simulations based on rate coefficents derived from close coupling calculations[2].

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Extraterrestrial origin of life:
how the building blocks of life may form in space

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The origins of the most basic organic molecules required for life on earth (e,g, amino acids, nucleobases, phospholipids, etc.,), the so-called “building blocks of life”, have been the focus of significant reseach ever since the early experiments by Miller and Urey in the 1950s. Over the last 40 years, however, astronomical observations of a diverse and ubiquitous inventory of bio-organic molecules in most space environments have given rise to the hypothesis that life’s building blocks, once formed in space, may have provided the molecular seeds for life on earth via meteorite or cometary impacts. Given the fact that both ionizing radiation and matter exist throughout the universe, the existence of this panoply of bio/organic molecules in space suggests that life’s building blocks (e.g. aminoacids, nucleobases) can be synthesized via space-radiation processing of molecular ices in cold regions of the interstellar medium, or on solar system bodies. This radiation processing, or synthesis, can be studied in the laboratory, but to date, most efforts focus on stellar UV radiation, or high energy particles (stellar wind, cosmic rays, etc.). The latter produce abundant low energy electrons (LEEs) below 100 eV in matter, however the role of LEEs in the synthesis of life’s building blocks in space has, until recently, been rather assumed than studied. In this thesis, I describe an extended and detailed investigation in which bio-organic molecules, including amino acids, may be formed by LEE in simulated space environments: thin films of differing molecular composition (e.g., O_2, CH_4, CO_2, NH_3, and mixtures thereof) are condensed under ultra-high vacuum upon a metallic substrate at ~20 K, and exposed to low energy (0-100 eV) electron irradiation. Multiple in situ surface-analysis methods, namely electron stimulated desorption (ESD) of ions, X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption(TPD), have been employed to investigate the LEE-driven chemistry and to observe the formation of new complex chemical species. Among these we identify acetylene (C_2H_2), ethane (C_2H_6), propylene (C_3H_6), and ethanol (C_2H_5OH), as well as Glycine (NH_2CH_2COOH), the simplest building block of proteins, formed in CH_4:CO_2:NH_3 ices by LEEs down to 9.5eV; still unidentified are molecules containing C_2O_2, C_2O_3, N_2, and NO moieties, or CN and HCN subunits, the basic building blocks of Adenine. LEEs induce the production of new chemical species containing both C-O and C=O, as well as O-C=O, N-O, N=O, and multiple C-C bonds.

Near Edge X-Ray Absorption Fine Structure (NEXAFS) Spectroscopy of Phenanthrene in different charge and dehydrogenation states.

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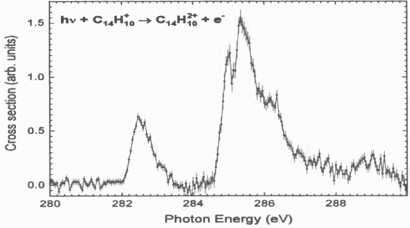
We focus on studying the structural changes induced by different charge and dehydrogenation states of Polycyclic Aromatic Hydrocarbons (PAHs). PAHs are thought to be an integral part of the interstellar medium and as such would undergo ionization and dehydrogenation from multiple radiation sources. Previous laboratory studies point to a connection between PAHs and fullerenes that are already detected in the interstellar medium. We are interested in studying PAHs after ionization and dehydrogenation to monitor their resulting structural changes and to further explore the connection to fullerenes. We applied the photon-ion merged beam technique using the Photon- Ion-spectrometer at PETRA III (PIPE) at the soft X-ray beamline P04. This beamline provides variable polarization soft X-ray radiation in the energy range of 250 eV to 3 keV enabling us to perform Carbon K-edge absorption spectroscopy which is sensitive to the structural changes. The PIPE end station is equipped with an analyzing magnet that allowed us to mass and charge select ions of interest, before interacting with photons generated from PETRA III. A double focusing dipole demerger magnet behind the interaction region allowed us to investigate particular fragmentation channels.In this work, we initially selected the following monocations and dications of phenanthrene: $C_{14}H_{10}^{+}$, $C_{14}H_{9}^{+}$, $C_{14}H_{8}^{+}$, $C_{14}H_{10}^{2+}$ and $C_{14}H_{8}^{2+}$.. After interacting with X-ray photons ranging from 280 eV to 320 eV, photoionization X-ray spectra were collected for the selected fragmentation channels. Below is an example of a recorded spectrum.



Measured cross sections for photoionization of $C_{14}H_{10}^{+}$ forming $C_{14}H_{10}^{2+}$ in the photon-energy range from 280 eV to 290eV.

Chirped Pulse mmWave Spectroscopy of Complex Molecules

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Our laboratory chirped pulse spectrometer operational between 75 and 110 GHz (coincident with ALMA Band 3) will be discussed here with special focus on its stability and sensitivity, as well as its prospects on absolute intensity calibration.

Preliminary results focus on pure rotational transitions of methalcyanide (CH_{3CN}) and pyridine (C_5H_5N) in the gasphase. These spectra are used to obtain mollecular and higher order distortional constants from rotational transitions from vibrational ground states as well as vibrational satellite of complex molecules. Especially high sensitivity is a focus of our research to be able to measure isotopic species of molecules of astrophysical interest. As the principle setup coincides in many aspects with our emission spectrometer (see Wehres et. al.), a combination of chirped pulse measurements and emission spectroscopy is discussed briefly.

Additionally we show and discuss current improvements and developments of our instrument and discuss further desired candidates on future research directions for the spectroscopy of the fingerprint-like rotational transitions of complex molecules.

Chirped-Pulse Microwave Spectroscopy of Complex Molecules

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The Cologne chirped-pulse microwave spectrometer is operational between 12 and 26.5 GHz and has been described before [1]. Here, the basic principle and the experimental setup will be presented. From the master thesis of B. Heyne noise measurements taken with the hot-cold method will be discussed. Furthermore, the sensitivity was determined by using a spectrum of OCS and its different isotopologs. Moreover, a closer examination of OCS at different temperatures will be shown and an intensity calibration will be performed. In addition, a spectrum of 2-cyanobutane recorded with a heatable nozzle will be presented.

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Methyl mercaptan and its most abundant isotopologs: global modelling of v_t = 0, 1, 2 torsion-rotation spectrum at millimeter and submillimeter wavelengths

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Methyl mercaptan (CH_3SH) is an important sulfur-bearing species in the interstellar medium, terrestrial environment, and potentially in planetary atmospheres. In recent line surveys towards Sgr B2(N) [1] using the Atacama Large Millimetre/sub-millimetre Array (ALMA) methyl mercaptan was found at levels that some of its isotopologs could be detected as well. The aim of our study was to provide accurate spectroscopic parameters for methyl mercaptan $^{12}CH_3{}^{32}SH$ and its most abundant minor isotopologs $CH_3{}^{34}SH$ and $^{13}CH_3SH$ to support radio astronomical observations at millimeter and submillimeter wavelengths. New records of the torsion-rotation spectrum of CH_3SH were obtained in the 49−510 GHz with natural isotopic abundance. Also we used the results of the earlier measurements in the 1.1−1.5 THz frequency range [2]. The successful analysis of the spectrum, which is complicated by the large-amplitude internal rotation of CH_3 group versus the SH frame, was performed up to the second excited torsional state, and the obtained data were modeled with the RAM36 program [3]. Predictions based on these fits were used to search for $CH_3{}^{34}SH$ and $^{13}CH_3SH$ with the Atacama Large Millimeter/submillimeter Array (ALMA) toward the hot molecular core Sgr B2(N2), but blends with emission lines of other species prevented their firm identification in this source. In the presentation the details of our spectroscopic study as well as the results of ISM search for $CH_3{}^{34}SH$ and $^{13}CH_3SH$ will be discussed.

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Building-up of a precision spectrometer using a REMPI detection scheme

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The molecular composition of diffuse interstellar matter is still an unsolved problem in astrophysics. For more than a hundred years, the carriers of the diffuse interstellar bands (DIBs) in the visible spectral range have been largely unknown. A first success was achieved in 2015 with the assignment of C_{60}^{+} as one of the carriers of some DIBs. [1] Despite this success, the majority of the bands remain unassigned due to the lack of laboratory data. Complex organic hydrocarbons such as polycyclic aromatic hydrocarbons, their ions, or radicals amongst others constitute potential carriers of the DIBs.

The use of a time-of-flight mass spectrometer in combination with a frequency-selective multiphoton ionization scheme (REMPI) facilitates the sensitive measurement of optical spectra of possible DIB carriers under controlled laboratory conditions. Molecular radicals and ions are produced in an electrical discharge, where organic precursor molecules are ionised or fractionated and form new, highly reactive and short-lived species. Using helium as a buffer gas, these are then diluted into a molecular beam and probed by a pulsed, tunable dye laser. In a planned extension, ro-vibrational transitions of the molecules can be specifically excited by the use of a frequency comb-stabilized infrared optical parametric oscillator system before they are ionized using the dye laser. In this presentation, the design and operation of the spectrometer are presented and first mass-selected molecular spectra are shown.

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Fullerene Oligomers and Polymers as Carriers of Unidentified IR Emission Bands

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Several unidentified infrared emission bands (UIBs) have been assigned to neutral C_{60} molecules present in circumstellar and interstellar environments. However, due to the similarity of the infrared (IR) spectra of C_{60} in the solid state and in the gas phase, as of yet there is no consensus on the aggregation state of C_{60}. We show that even strong covalent chemical bonding might have very little influence on the IR spectrum of C_{60}, and that therefore such chemically bonded C_{60} could be the carrier of the same UIBs.[1] It would best explain observations like the missing emission from C_{60} ions and a large variation of relative band intensities between different sources. We demonstrate that such a chemically bonded C_{60} can be produced by the co-condensation of C atoms together with C_{60} molecules, which leads to the formation of a three-dimensional C_{60} polymer film.[1,2] Such polymerized C_{60} molecules cannot easily desorb, while their spectral properties in the visible and IR spectral ranges are almost undisturbed by polymerization.

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Astrochemical studies at the Cryogenic Storage Ring

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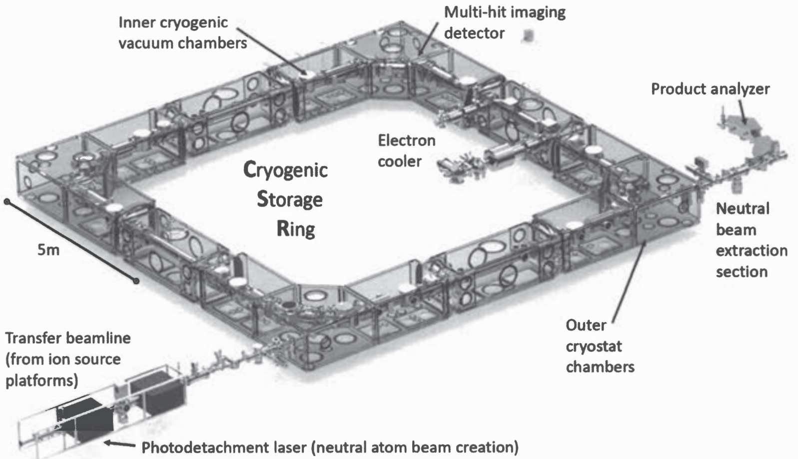
The new Cryogenic Storage Ring (CSR) at the Max Planck Institute for Nuclear Physics in Heidelberg is moving from the commissioning phase toward scientific operation. The CSR provides long storage times at extremely high vacuum and low temperatures for atomic and molecular ions of almost arbitrary mass [1]. The experimental vacuum chambers of the CSR can be cooled down to 5K, and it has been shown that within a few minutes of storage infrared-active molecular ions (e.g., CH^+ [2] and OH^- [3]) will cool to their lowest rotational states by spontaneous emission of radiation.

Equipped with an ion-neutral collision setup and a low-energy electron cooler, the CSR offers unique possibilities for astrochemical experiments under true interstellar conditions. We will present an overview of the capabilities of the CSR along with first experimental results on collisions of C atoms with H_3^+ and on the electron recombination of HeH^+ [4].



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Cold and Controlled Reactions of Ions and Molecules

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Reactions between ions and radical molecules play an important role in the chemistry that drives dynamics in the interstellar medium and during combustion of hydrocarbons. Unfortunately, experimental measurements of these reactions are very challenging, and thus very rare. We use tools borrowed from the cold atom community to measure ion-molecule reactions in a well-controlled environment. Here, we can study reactions between atoms and molecules in single quantum states at low temperatures. Our high sensitivity allows us to study reactions where the reaction rate can be as low as one reaction per minute. I will present the capabilities of this cold ion-molecule reaction apparatus and some example reactions[1,2] we have been able to study using this new system, including $C_2H_2^+$ with propyne and allene.

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Unravelling the formation of substituted polycyclic aromatic hydrocarbons in the interstellar medium by plasma sources

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Detected through the unidentified infrared bands (UIR), polycyclic aromatic hydrocarbons (PAHs) are thought to be omnipresent in the interstellar medium and to play a key role in its physics and chemistry. In the extreme energetic conditions of the interstellar medium (ISM), PAHs are expected to undergo ionisation, fragmentation and dehydrogenation processes when interacting with the interstellar energy rich radiation. Therefore, depending on the interstellar environment, PAHs can potentially exist in different charge and dehydrogenation states. They can also contribute to the creation of a wide range of molecules, from small molecules, like H_2 and acetylene, to more complex organic molecules, such as oxygen and nitrogen containing molecules.

The reactivity of these molecules under extreme energetic conditions can be studied in the laboratory by means of electrical discharge sources combined with molecular beam cooling. In plasma conditions these molecules are expected to dissociate and to recombine to form new species. In this respect, we have coupled an electrical discharge nozzle with mass-resolved IR-UV ion dip spectroscopy using the free electron laser FELIX (550-1800cm^{-1}) and chirped pulse broadband microwave spectroscopy, to give insight into the chemistry that can potentially take place when PAHs undergo the extreme energetic conditions of the ISM. The two techniques are complementary to each other. The combination of mass spectrometry with IR-UV spectroscopy exploits the advantage of probing and characterising the created species either via their mass as well as via their unique IR signature. Species that cannot be unambiguously characterised by IR-UV ion dip spectroscopy can be probed in depth via their microwave spectra, which are known to be fingerprints of the molecules.

In this work, we have investigated the products formed upon the discharge of PAHs with simple organic molecules that are prevalent in the ISM. We investigated the differences in PAHs such as sizes and degrees of aromaticity by choosing PAHs as naphthalene ($C_{10}H_8$), fluorene ($C_{13}H_{10}$), phenanthrene ($C_{14}H_{10}$), and pyrene ($C_{16}H_{10}$) to discharge with acetonitrile (CH_3CN), a nitrogen containing interstellar molecule. For all the investigated PAHs, addition of specific functional groups such as cyano (CN) methyl (CH_3) and ethynyl (CCH) groups as well as insertion of carbon atoms to form PAHs with additional and larger ring systems have been observed and their spectra in the mid-IR range have been characterised, thus providing us with relevant insight into the underlying processes. Proposed formation mechanisms are also presented.

Spectroscopic signature and optical constants of interstellar ice analogues

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Water is the major component of interstellar ice present in dense molecular clouds. The minor components, although, play an important role in influencing the chemical and physical properties of the ice. It is believed to influence the chemistry and energy balance of interstellar clouds. Although invisible in the IR spectroscopic range, the interaction of O_2 with the H_2O matrix environment perturbs the symmetry of the molecule which becomes visible in the mid-IR.

Also, we can directly measure optical constants of molecules using a THz time domain spectrometer and derive dust opacities in the millimeter and sub-millimeter part of the electromagnetic spectrum. Knowing the dust opacity allows us to model the dust continuum emission. Doing so, we want to answer the question: how do dust opacities change in thick icy mantles compared to those available in the literature?

We present a spectroscopic characterization of water-oxygen mixtures in various molecular ratios, to support the astronomical observations, investigating the effect of present CO and CO_2 on the O_2 band strength.

Additionally, we present direct measurements of optical properties for astrophysical ice analogues using coherent THz radiation. Measurements for CO will be complemented by measurements for H_2O, CO_2 and N_2.

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Considerations for and recent developments of the Cologne Database for Molecular Spectroscopy (CDMS)

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The Cologne Database for Molecular Spectroscopy was founded more than 20 years ago as a resource of rest frequencies for radio astronomers. It developed into a prime resource to identify molecular species observed in space. The rest frequencies are calculated by fitting experimental data, usually from laboratory spectroscopic studies, to established Hamiltonian models. The quality of the rest frequencies depends strongly on the critical evaluation of the Hamiltonian model and of the experimental data [1]. We will discuss the aspect of experimental data using the SH^+ example. The CDMS is also part of the Virtual Atomic and Molecular Data Centre, VAMDC [1].

Discussions of recent observational results, in part through participation in larger ALMA programs, have influenced the development of the CDMS content and have led to new laboratory spectroscopic investigations. We will present some examples.

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X-ray versus UV irradiation of H_2O:CO:NH_3 ice mixtures leading to complex organic molecules

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The formation of complex organic molecules (COMs) in the ice driven by X-rays and ultraviolet (UV) photons is presented. X-ray processing of ice mantles in circumstellar regions of young stars is expected to be important during the first 100 Myr. After this period, UV photons also contribute to this processing. Secondary UV photons are likely the main source of ice irradiation in interstellar clouds. For comparison of X-rays versus ultraviolet photon ice processing, infrared spectroscopy for the ice and mass spectrometry for the gas phase was employed.

Several COMs were identified in these experiments, some of astrobiological interest such as NH_2CH_2COOH (glycine), $HCONH_2$ (formamide), or CH_3CHO (acetaldehyde), similar to those detected during the Rosetta mission in comet 67P/Churyumov-Gerasimenko.

Quantum state-dependent reactive collisions of OH^- with ultracold Rubidium in a hybrid trap

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The study of ion-molecule reactions plays a vital role in cold chemistry, thus implying the need of well-controlled ion ensembles in a cold environment. The internal and external degrees of freedom of molecular ions, trapped in multipole radio frequency ion traps, can be cooled via collisions with neutral atoms [1]. Usually the coolant undergoes collisions with a thermal shield mounted on a cryostat attaining temperatures of about 4 K. This lower temperature limit can be overcome, using a laser-cooled buffer-gas localized at the center of the ion cloud [2].

In our hybrid atom-ion trap, the hydroxyl anions are stored in a 8-pole radio frequency wire trap and a dense cloud of ultracold buffer-gas (Rubidium) confined in a dark spontaneous-force optical trap (Dark-SPOT). The overlap of atoms and anions leads to elastic and inelastic collisions, cooling the external and internal degrees of freedom respectively. The ab initio calculations also predict reactive collisions, which can be used to probe the effective core potentials used in theoretical studies [3]. By varying the ratio of excited and ground state atoms quantum state dependent reactive collisions can be studied. In this contribution the latest results will be presented.

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Infrared Cavity Ringdown Spectroscopy of Molecules in Supersonic Jets

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The surprising chemical diversity of molecules in space can be seen in a wide variety of regions. Atoms in the vicinity of old dying stars combine to form molecules and serve as seeds for dust production (example: silicon carbides). The interstellar molecules are, unlike here on earth, often unsaturated compounds that are highly reactive or even of an ionic nature. These species, which are difficult to produce on earth, are valuable probes to determine the local physical conditions in space. The recent availability of high-resolution infrared (IR) instruments on telescopes such as EXES/SOFIA and TEXES/N-Gemini has created a demand for IR spectroscopic data. Our aim is to perform spectrally highly resolved and extremely sensitive measurements on astrophysically relevant molecules in the mid-infrared region, *i.e.* the typical fingerprint region of molecules, utilizing the highly sensitive cavity ringdown (CRD) method. Suitable light sources are powerful quantum cascade lasers (QCLs) above 4.5 µm, as well as OPOs (Optical parametric oscillators) for the wavelength range 2 - 4.7µm. To achieve a high precision the lasers are stabilized by a frequency comb. This cavity enhanced IR spectrometer is combined with various molecular sources producing supersonic jets. Available sources are heating sources (e.g. for hydrogen peroxide), as well as laser ablation and electrical discharge sources to generate transient molecules *in situ*. We started investigations on hydrogen peroxide and silicon carbides. The experimental setup as well as first results will be presented.

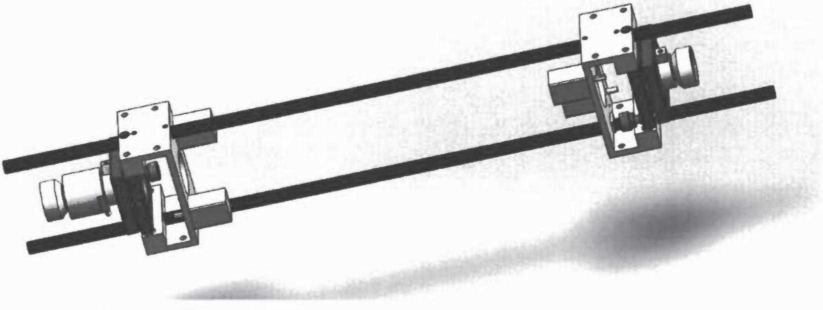

Figure 1: The CRD cavity of our CARMA (Comb Assisted iR Multipass Absorption) experimental setup.

Geometry and Optical Properties of Astrochemically Relevant Silicon Carbide Clusters

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Ejecta of carbon rich stars contribute significantly to interstellar dust. The emitted particles are generally hot and consist of single atoms or ions. With increasing distance to the star, this matter cools down and starts to condense, eventually forming first molecules like the previously observed SiC [1], Si_2C [2], SiC_2 [3], etc. Other observations show that larger silicon carbide grains may be present in the interstellar medium (ISM) [4]. Up to now, it is still unclear how these dust grains are created. It seems likely that they form from the small SiC molecules via condensation, but no intermediates have been detected so far. In this contribution we present the energetic, geometric, and optical properties of small silicon carbide clusters obtained via photodissociation spectroscopy, mass spectrometry, and quantum chemical calculations in order to allow for a better understanding of the stabilities and formation routes of interstellar dust particles in the envelopes of carbon-rich stars. We show the first optical spectrum of a silicon carbide cation and present hitherto unknown ground state geometries of some cationic silicon carbide clusters.

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Analysis of $N^+ + H_2 \rightarrow NH^+ + H$ reaction endothermicity by experimental study of isotope effects and the reverse reaction

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The reaction $N^+ + H_2 \rightarrow NH^+ + H$ has an activation energy of 19±3 meV for H_2 in thermal equilibrium (determined in the present work). However, it is still not clear, whether this activation energy is caused by the reaction endothermicity or by a barrier on the reaction path. The issue of $N^+ + H_2 \rightarrow NH^+ + H$ reaction endothermicity is a long-standing question for theoretical and experimental astrochemists [1,2] as well as for quantum chemists [3], who are still not able to determine the NH^+ binding energy in pure *ab-initio* calculations with sufficient accuracy. This contribution presents the thermal rate coefficients of reactions of N^+ with H_2, D_2, and HD measured in a cryogenic radiofrequency ion trap. We show that all these data are compatible with the hypothesis that the observed activation energies are due to reaction endothermicity. This is in accord with our measurements of the reverse reaction rate coefficients.

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Experimental study of diamond formation in astrophysical environments

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Diamond represents a major part of the carbonaceous cosmic dust. Yet, the formation route of cosmic diamond is still not understood. This motivates our experimental study of a route similar to a chemical vapor deposition (CVD) process, which would take place under conditions found in cosmic regions where diamond may be formed: the interstellar medium, the envelopes of young stars, those of evolved stars, and in protoplanetary and planetary environments.

The lifetime of carbon materials in hydrogen-rich, cosmic environments depends on its chemical stability. It is studied by exposing samples to atomic and molecular hydrogen, and to UV photons, while they are kept at temperatures ranging from 10 to 1400 K. The stability of a sample is characterized by its mass-loss rate as a function of these conditions. The samples consist of graphite, amorphous carbon, and diamond.

Taking into account the data on chemical stability, carbon atoms are deposited on substrates under the conditions most favorable to the formation of diamond by CVD. The solid condensates are characterized with Raman scattering spectroscopy, with IR, UV, and visible absorption spectroscopy, and with high-resolution transmission electron microscopy.

The results are intended for predicting the cosmic sites of efficient diamond formation.

Spectroscopic Study of the Protonated Amine $CH_3NH_3^+$

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Protonated molecules are important reaction partners in gas-phase chemistry. Thus, these ionic systems are of importance in the interstellar medium (ISM) for the formation of complex molecules. Protonated molecules such as H_3^+ have been detected in the ISM, with the suggestion that even more complex protonated species might exist.

At the same time, amines might play an important role in the -NH chemistry in the ISM. The already complex methylamine, CH_3NH_2, has been detected with strong abundances in the ISM. With its early formation within the ISM chemical network, it will be important for the formation of more complex molecules. Due to its large proton affinity - compared to H_3^+ - $CH_3NH_3^+$ should also be formed in the ISM. As $CH_3NH_3^+$ is a symmetric top, its spectroscopic spectrum is predicted to be rather simple, facilitating astronomical searches in the ISM.

We performed first laboratory spectroscopy on protonated methylamine in the mid-infrared using the FELion ion trap at the Free Electron Laser for Infrared eXperiments (FELIX) at Radboud University, Nijmegen. Infrared photodissociation of $CH_3NH_3^+$-Ne cluster was used to record the vibrational spectra of this molecule. Additionally, we observed the pure rotational spectrum for the first time using the cryogenic ion trap setup COLTrap in Cologne. For this prolate symmetric top molecule, 13 transitions between 80 GHz and 240 GHz are detected. In this poster we will present the observed spectra and derive its spectroscopic parameters. Furthermore, we will discuss possible implications for first astronomical searches of $CH_3NH_3^+$ in the ISM.

IR/NIR spectroscopy of astronomically relevant fullerene derivatives

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Since fullerenes do not possess considerable permanent electric dipole moment, their astronomical observations are performed in IR and NIR ranges, corresponding to vibrational and electronic transitions. We present new results on ionic and neutral hydrogenated fullerenes and azofullerenes, studied by He-tagging gas-phase and matrix isolation techniques. Endohedral $H_2@C_{60}^+$ has been investigated as well [1].

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Experimental Molecular Emission Spectroscopy: Adopting an ALMA-Type Cartridge Receiver

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New exciting discoveries and findings made by radio astronomy have been reported one after another these days. The frequency range in radio astronomy provides us important information of not only images such as a super massive black hole[1], protoplanetary disks[2,3], and galaxies in early universe[4], but also chemical compounds including gas molecules and dust grains[5]. Particularly, observed emission as well as absorption lines supply a great deal of details on physical properties, gas kinematics, and chemical compositions[6,7] which hold the key to understanding the origin of the chemical complexity to the formation and evolution of the solar system.

In general, highly accurate interpretation of observed spectra is implemented by comparison with theoretically calculated and/or experimentally measured absorption/extinction spectra. One of major problems in the ALMA era is that experimental data related to both organic and inorganic compounds in millimeter and submillimeter ranges are inadequate to identify each spectral line accurately[8,9]. Thereupon we have experimentally carried out the emission type molecular spectroscopy for astronomically relevant materials in the frequency range between 216 GHz and 260 GHz. Superconductor-Insulator-Superconductor (SIS) mixer for ~230 GHz band mounted on the ALMA-type cartridge receiver as a heterodyne apparatus (SUMIRE) is applied in this measurement. In here, we introduce our experimental broadband and high-resolution spectroscopic apparatus and a measured spectrum as well as future prospects. Newly obtainable experimental data have infinite possibilities for comprehending of a crucial role of atoms, molecules, and dust grains in astronomical environments.

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Emission spectroscopy using heterodyne receivers

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Two laboratory emission spectrometers between 70-110 GHz (coincident with ALMA Band 3) and 300-400 GHz (coincident with ALMA Band 7) have been described before[1,2] and will be discussed here with special focus on its stability and sensitivity, as well as its prospects on absolute intensity calibration[3].

Following-up on these recent advances towards heterodyne detection, we present preliminary results using the SOFIA (Stratospheric Observatory for IR Astronomy) upGREAT laboratory setup, operational around 2 THz, for the spectroscopy of complex molecules. First spectra focus on pure rotational transitions of vinyl cyanide (C_3H_3N). These spectra are used to estimate intensities of ro-vibrational transitions coming from low-lying vibrational bands of polycyclic aromatic hydrocarbons (PAHs). The results are used as feasibility study to exploit future research directions for the spectroscopy of the fingerprint-like ro-vibrational transitions of PAHs at around 2 THz.

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Reaction studies of astrophysically relevant anions

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After the radioastronomical discovery of the first interstellar anions, interest has grown in understanding the formation and destruction pathways of negative ions in the interstellar medium (ISM). Our 22-pole cryogenic ion trap is a useful tool to simulate interstellar conditions. The properties and chemistry of atomic hydrogen and its different charged forms are key to the evolution of the dilute ISM.

Our group has previously performed reaction rate studies on C_nH^- and C_n^- anions [1] with molecular hydrogen, but reactions with atomic hydrogen may also play a significant role. We have incorporated a hydrogen atom source into our system, and have begun investigating the reactions of CN^- with atomic hydrogen with the aim to measure reaction rate coefficients at cold temperatures.

Furthermore, the simplest anion, H^-, is expected to be present in the interstellar medium, but its detection is difficult as it possess only a single bound state. The most fundamental reaction of H^- is the proton transfer reaction with H_2, and occurs via tunneling through the reaction barrier at low temperatures [2,3]. Starting with D^-, we study the reaction $D^- + H_2 \rightarrow H^- + HD$.

We report on progress and the current status of these experiments.

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Probing RNA stability and formation in simulated prebiotic environments on the early Earth and in Space

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Complex organic molecules like nucleobases (Pearce and Pudritz, 2015), amino acids (Lai et al, 2019) and fatty acids (Cobb and Pudritz, 2014) were found in many meteorites. Recent studies of the comet 67P/Churyumov-Gerasimenko were able to identify the amino acid glycine in a comet for the first time (Altwegg et al., 2016). Comets and meteorites could be an important sources of prebiotic molecules for the early Earth. In our laboratories, we aim to uncover the role of these extraterrestrial materials in the synthesis and stability of RNA. The facilities at the CASICE laboratory will allow us to expose RNA and its building blocks to a wide range of conditions such as low temperatures (down to 10 K), different atmospheres and solvents as well as to UV irradiation. We use spectroscopic techniques to investigate the reaction of nucleobases and nucleotides in these different conditions, which simulate cometary bodies and environments plausible for the early Earth. The higher UV flux of the young sun could have influenced the selection for canonical nucleobases (Cataldo, 2018; Fornaro et al., 2013). To investigate this question we studied the photosensitivity of uracil, uridine, adenine, adenosine, cytidine and cytosine. The samples were irradiated with a UV source and Raman spectra were recorded to survey photolysis. Uracil and uridine showed the highest photosensitivity. Moreover, the nucleotide uridine showed a higher UV resistance compared to its corresponding nucleobase uracil, which suggests photoselection as a plausible contributor to the driving force towards a rise in chemical complexity.

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