QuantumGrain Workshop

Emerging Horizons in the Chemistry of the Universe

Barcelona, June 9th – 12th

Book of Abstracts

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 865657) for the project "Quantum Chemistry on Interstellar Grains" (QUANTUMGRAIN).

QUANTUMGRAIN
Quantum Chemistry on Interstellar Grains

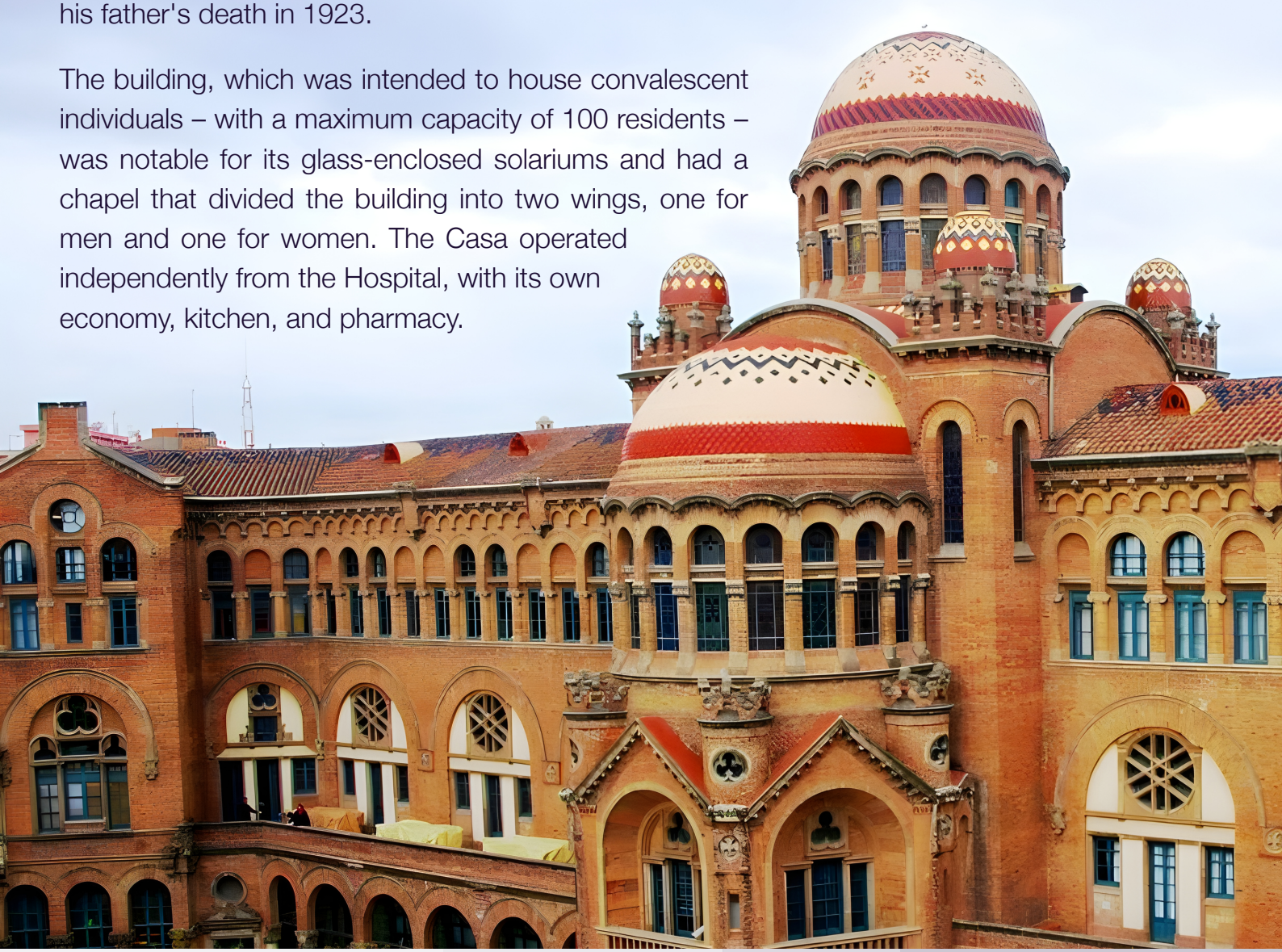
Venue

Casa de Convalescència

Casa de Convalescència, one of the last works of Catalan Modernism, is part of the complex of the Hospital de la Santa Creu i Sant Pau, designed at the end of the 19th century to address the lack of hospital facilities in Barcelona.

The growth of the city and advances in medicine had rendered the old hospital of Santa Creu, dating from 1401 and located in the Old Town, obsolete. The construction of the Casa was directed by Pere Domènech i Roura, who collaborated with his father, Lluís Domènech i Montaner, and took over the management of the construction works after his father's death in 1923.

The building, which was intended to house convalescent individuals – with a maximum capacity of 100 residents – was notable for its glass-enclosed solariums and had a chapel that divided the building into two wings, one for men and one for women. The Casa operated independently from the Hospital, with its own economy, kitchen, and pharmacy.



How to get there

Sant Antoni Maria Claret 171
08041 Barcelona

(Inside the Sant Pau Hospital complex)

By metro

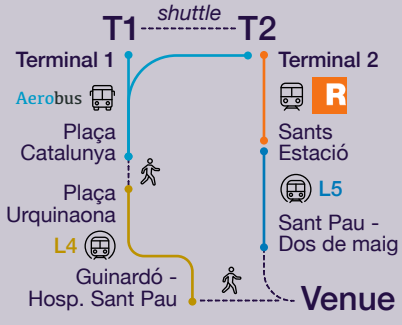
Yellow line (L4)
Stop: Guinardó – Hospital de Sant Pau

Blue line (L5)
Stop: Sant Pau – Dos de maig

By bus

Lines 15, 19, 20, 45, 47, 50, 51, 92 and 192.

From the airport



Relevant information

QuantumGrain Workshop

Emerging Horizons in the Chemistry of the Universe

Sunday, June 9th

13:00 Welcome & reception

15:00 Opening

S 1 — *Chair: Albert Rimola*

15:20 Cecilia Ceccarelli
16:00 Julia Santos
16:20 *Coffee break*

S 2 — *Albert Rimola*

16:45 Nadia Balucani
17:15 Chiara Mininni
17:35 Silvia Alessandrini

18:00 Complimentary social dinner

Monday, June 10th

S 3 — *Marta de Simone*

9:30 Giulia Perotti
10:00 Joan Enrique-Romero
10:20 Zeyuan Tang
10:40 Bhala Sivaraman
11:00 *Coffee break*

S 4 — *Marco Minissale*

11:30 Fabrice Duvernay
12:00 Eleonora Bianchi
12:20 Vincent Esposito
12:40 Partha Bera

13:00 Complimentary lunch

S 5 — *Germán Molpeceres*

15:00 Thanja Lamberts
15:30 Miguel Sanz-Novo
15:50 Alex Byrne
16:10 Stefan Vogt-Geisse
16:30 *Coffee break*

S 6 — *Victoria Cabedo*

17:00 Marco Minissale
17:20 Andrés Megías
17:40 Gabriella Di Genova

18:00 Poster session and complimentary dinner

Tuesday, June 11th

S 7 — *Eleonora Bianchi*

9:30 Stefan Bromley
10:00 Marta de Simone
10:20 Julie Vitorino
10:40 Hexu Ye
11:00 *Coffee break*

S 8 — *Rafael Martín-Doménech*

11:30 Izaskun Jiménez
12:00 Gunnar Nyman
12:20 Juan Carlos del Valle
12:40 Victoria Cabedo

13:00 Complimentary lunch

S 9 — *Joan Enrique-Romero*

15:00 Piero Ugliengo
15:30 Rafael Martín-Doménech
15:50 Samuel Del Fre
16:10 Anessa Ahmad
16:30 *Coffee break*

S 10 — *Silvia Alessandrini*

17:00 Elettra Piacentino
17:20 Lisa Giani
17:40 Marten Raaphorst

20:00 Complimentary banquet dinner

Wednesday, June 12th

S 11 — *Thanja Lamberts*

9:30 Cristina Puzzarini
10:00 Germán Molpeceres
10:20 Basile Husquinet
10:40 Joan Mariñoso
11:00 *Coffee break*

S 12 — *Albert Rimola*

11:30 Naoki Watanabe
12:00 Dario Campisi
12:20 Sándor Demes
12:40 Ni-En Sie

13:00 Closing ceremony, complimentary lunch

Important information

** Complimentary coffee breaks and meals will be served at the venue.*

*** Wednesday's banquet dinner will be held at the "La Pomarada" restaurant (Passeig de Gràcia, 78 Principal, 08008, Barcelona).*

Organising committee

Albert Rimola (chair)
Mònica Cervera
Eric Mates-Torres
Niccolò Bancone
Vittorio Bariosco
Alicja Bulik
Andreha Gelli
Leana Jubert
Harjasnoor Kakkar
Berta Martínez Bachs
Gerard Pareras
Jessica Perrero

Sponsors

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QUANTUMGRAIN Quantum Chemistry on Interstellar Grains

UAB Universitat Autònoma de Barcelona

Detailed program

Sunday, June 9th

S1 Chair: Albert Rimola

13:00 Welcome and reception

15:00 Opening

15:20 | Cecilia Ceccarelli (Université Grenoble Alpes)
I1. "*The Emergence of Molecular Complexity in Solar-like Planetary Systems*"

16:00 Julia Santos (Leiden Observatory)
C1. "*The origin and fate of interstellar sulfur-bearing molecules: a combined observational and laboratory work*"

16:20 – 16:45 *Coffee break*

S2 Chair: Albert Rimola

16:45 | Nadia Balucani (DCBB, Università degli Studi di Perugia)
I2. "*Crossed molecular beam studies of bimolecular reactions and their role in astrochemistry*"

17:15 Chiara Mininni (INAF-IAPS)
C2. "*Molecular vs. continuum emission: a comparison of the morphology in ALMAGAL clumps*"

17:35 Silvia Alessandrini (ROT&Comp Lab, University of Bologna)
C3. "*Formation of complex imines in the interstellar medium: new suggestions from gas-phase reaction mechanisms*"

18:00 **Complimentary dinner**

Monday, June 10th

S3 Chair: Marta de Simone

9:30 | Giulia Perotti (Max Planck Institute for Astronomy)
I3. "*A Sharper View: Astrochemistry in the JWST era*"

10:00 Joan Enrique-Romero (Leiden Institute of Chemistry)
C4. "*On the formation of HCN and HNC on interstellar ices*"

10:20 Zeyuan Tang (Center for Interstellar Catalysis, Aarhus University)
C5. "*Structure and IR spectroscopy of nanosilicate clusters from machine learning interatomic potential*"

10:40 Bhala Sivaraman (Physical Research Laboratory)
C6. "*Interstellar Quantum Dots – Analogues Synthesized in the Laboratory*"

11:00 – 11:30 *Coffee break*

S4 Chair: Marco Minissale

11:30 | Fabrice Duvernay (PIIM, Aix-Marseille Université)
I4. "*Solid Interstellar Radical Chemistry (SIRC): A new methodology to study radical reactivity in interstellar ice analogs*"

12:00 Eleonora Bianchi (Excellence Cluster ORIGINS)
C7. "*Astrochemistry reveals accretion shocks at the onset of planet formation*"

12:20 Vincent Esposito (NASA Ames Research Center)
C8. "*Anharmonic IR Absorption and Emission Spectra of Polycyclic Aromatic Hydrocarbons*"

12:40 Partha Bera (NASA Ames Research Center)
C9. "*Binding of Molecules, Radicals, and Ions with Small Water Clusters: Implications for Molecular Abundance on Grain Surfaces*"

Monday, June 10th (continued)

13:00 – 15:00 *Lunch*

S5 Chair: Germán Molpeceres

15:00 | Thanja Lamberts (Leiden Institute of Chemistry and Leiden Observatory)
I5. "*Towards understanding non-polar ices: treating CO and CO_2*"

15:30 Miguel Sanz-Novo (Centro de Astrobiología, CSIC-INTA)
C10. "*New discoveries in the G+0.693-0.027 molecular cloud: detection of HOCOOH, HNSO, $HOCS^+$ and glycolamide, the first interstellar glycine isomer*"

15:50 Alex Byrne (McGuire Group, MIT)
C11. "*Sensitivity Analysis of a Dark Molecular Cloud Chemical Model and Application to Aromatic Chemistry*"

16:10 Stefan Vogt-Geisse (Universidad de Concepción)
C12. "*Combining Grain-Ice Models for efficient computation of Accurate ab initio Binding Energies on Amorphous Solid Water: New results from the Binding Energy Evaluation Platform*"

16:30 – 17:00 *Coffee break*

S6 Chair: Victoria Cabedo

17:00 Marco Minissale (PIIM, Aix-Marseille Université)
C13. "*The quantum side of molecular desorption*"

17:20 Andrés Megías (Centro de Astrobiología, CSIC-INTA)
C14. "*Predicting the composition of astronomical ice mixtures with machine learning*"

17:40 Gabriella Di Genova (DCBB, Università degli Studi di Perugia)
C15. "*Sulfur reactivity on ice: a theoretical study*"

18:00 – 20:00 **Poster session + complimentary dinner**

Tuesday, June 11th

S7 Chair: Eleonora Bianchi

9:30 | Stefan Bromley (Nanoclusters and Nanostructured Materials Group, University of Barcelona)
I6. "*The Stardust Simulator: Towards a Bottom-up Understanding of Growth and Properties of Silicate Dust Grains*"

10:00 Marta De Simone (ESO European Southern Observatory)
C16. "*Exploring the molecular richness in early Solar-type protostars with a multi wavelength approach*"

10:20 Julie Vitorino (LERMA, CY Cergy Paris Université)
C17. "*Sulphur storage in cold molecular clouds: the case of the $NH4^+SH^-$ salt and its behavior on interstellar dust grains*"

10:40 Hexu Ye (University of Bologna)
C18. "*Gas-phase formation route for trans-HC(O)SH and its isomers under interstellar conditions: a state-of-the-art quantum-chemical study*"

11:00 – 11:30 *Coffee break*

S8 ⋮

11:30 | Izaskun Jiménez-Serra (Centro de Astrobiología, CSIC-INTA)
I7. "*Towards prebiotic chemistry in the interstellar medium*"

12:00 Gunnar Nyman (University of Gothenburg)
C19. "*Formation and growth of grains in our Universe*"

Tuesday, June 11th (continued)

Chair: Rafael Martín-Doménech

12:20 **Juan Carlos del Valle** (Institute for Theoretical Chemistry, University of Stuttgart)
C20. "*A look into the stereoselectivity in the formation of interstellar sugar precursors on amorphous solid water: from vinyl alcohol to (Z)-1,2-ethenediol*"

12:40 **Victoria Cabedo** (Heriot-Watt University)
C21. "*Metal catalysis in astrophysical environments*"

13:00 – 15:00 *Lunch*

S9 Chair: Joan Enrique-Romero

15:00 **Piero Ugliengo** (Department of Chemistry, University of Torino)
I8. "*Adsorption of S-bearing species at interstellar icy grain: an ab-inito approach on large model clusters*"

15:30 **Rafael Martín Doménech** (Centro de Astrobiología, CSIC-INTA)
C22. "*Ice origins of OCS*"

15:50 **Samuel Del Fre** (PhLAM, Université de Lille)
C23. "*Ab initio molecular dynamics study of vibrational energy redistribution in CO aggregates: towards a new understanding of the (photo)desorption mechanism*"

16:10 **Anessa Ahmad** (University of Leeds)
C24. "*Binding environments of precursors to complex organic molecules in protoplanetary disks: A computational study*"

16:30 – 17:00 *Coffee break*

S10 Chair: Silvia Alessandrini

17:00 **Elettra L. Piacentino** (Öberg Astrochemistry Lab, Center for Astrophysics, Harvard University)
C25. "*Reactions of P, S, and C atoms and oxides on water ice clusters*"

17:20 **Lisa Giani** (Institut de Planétologie et d'Astrophysique de Grenoble)
C26. "*Gas-phase formation of methyl cyanide (CH_3CN) and cyanodiacetylene (HC_5N) in the ISM: theoretical calculations and astrochemical modeling*"

17:40 **Marten Raaphorst** (Leiden Institute of Chemistry, Leiden University)
C27. "*Hydrogenation network of cyanoacetylene under cold conditions*"

20:00 **Banquet dinner**

Wednesday, June 12th

S11 Chair: Thanja Lamberts

9:30 **Cristina Puzzarini** (ROT&Comp Lab, University of Bologna)
I9. "*Astrochemistry @ROT&Comp Lab: Unveiling exotic chemistry and molecules in the interstellar medium*"

10:00 **Germán Molpeceres** (Instituto de Física Fundamental, CSIC)
C28. "*Shedding light on the mystery of NH_2OH in cold interstellar environments*"

10:20 **Basile Husquinet** (Max Planck Institute for Extraterrestrial Physics & CY-LERMA, Cergy-Paris University)
C29. "*Structure of the 3 μm IR absorption band for thin layers of ASW*"

10:40 **Joan Mariñoso** (Nanoclusters and Nanostructured Materials Group, University of Barcelona)
C30. "*Dependence of the 10-micron feature on nanosilicate size*"

11:00 – 11:30 *Coffee break*

S12 Chair: Albert Rimola

11:30 Naoki Watanabe (Institute of Low Temperature Science, Hokkaido University)
I10. "*Behavior of Carbon atoms on Ice at Low Temperatures*"

12:00 Dario Campisi (Kästner Group, University of Stuttgart)
C31. "*Tunneling Toward Interstellar PAHs: O and H's Quantum Leap*"

12:20 Sándor Demes (Institut de Physique de Rennes, Université de Rennes)
C32. "*Accurate collisional excitation data for non-LTE modelling of large carbon cycles in cold ISM clouds*"

12:40 Ni-En Sie (Institute of Low Temperature Science, Hokkaido University)
C33. "*The detection of radical adsorbates on ice with the PSD-REMPI method*"

13:00 **Closing ceremony and lunch**

Poster session

Monday at 18:00

Jacob Allitt	**P1.** Astrocatalysis: In Operando Studies of Catalysis of Space-abundant Transition Metals
Niccolò Bancone	**P2.** Computational investigation over the adsorption and reactivity of HCN on cosmic silicates models
Vittorio Bariosco	**P3.** Unveiling Cosmic Ice Grains: Investigating Sulfur-Bearing Species Through Calculated Binding Energies, Frequency Distributions, and Diffusion Barriers
Alicja Bulik	**P4.** Insights into Interstellar Ice Mantles: A Computational Approach to Predicting Infrared Spectral Features and Binding Energies
Andreha Gelli	**P5.** Exploring interstellar dust grains growth in molecular clouds: ab initio study of SiO reactivity
Leana Jubert	**P6.** Energy dissipation in H_2 formation on dust grain surfaces
Harjasnoor Kakkar	**P7.** Formation of CO_2 on Interstellar Water Ice: A Computational Approach
Ginny Karir	**P8.** Phenylethynyl Radical ($C_6H_5C{\equiv}C\cdot$), its Cation and Thermal Decomposition in the Gas-Phase
Barbara Keresztes	**P9.** Examination of the Astrochemically Relevant Ices Containing CH_3OH and CH_3NH_2
Alexandros Kyriazis	**P10.** Computational Investigation of Reactions between Magnesium Silicate Clusters and Methylidyne Radical
Berta Martínez Bachs	**P11.** Insights on the Energy Dissipation Process Released by the Formation of Formamide on Interstellar Water Ice Surfaces
Eric Mates-Torres	**P12.** Computational Approach for the High-throughput Screening of Molecular Cosmic Interactions
Gerard Pareras	**P13.** Mechanistic insights on Methanol formation via Fe^0 and Fe^{II} silica supported single atom catalysis in interstellar medium conditions. The concept of Astrocatalysis in the early Solar System
Jessica Perrero	**P14.** Non-Energetic Ethanol Formation via "Radical + Ice Component" in Interstellar Cold Cores
Jan Postulka	**P15.** Hydroxyl Radicals on Water Surface: Modeling Dynamics and Recombination
Namrata Rani	**P16.** Computational Quantum Quest Towards the Depleted Sulfur in the ISM
Alejandro Rivero	**P17.** High-Dimensional Atomistic Neural Network Potential to study the vibrational energy redistribution in CO aggregates
Anita Schneiker	**P18.** Experimental and theoretical investigation of astrophysically relevant low-temperature reactions of lactones and amino acids
Reace Willis	**P19.** Coupling theory and experimental data to revisit old reactions and their implications for the modelling of TMC-1
Tobe Vorsselmans	**P20.** Binding energies of small interstellar molecules on neutral and charged amorphous solid water surfaces
Andreu A. de Donato	**P21.** Hydroxylated Silicon Oxide Cluster Cations: Structure, Infrared Spectroscopy, and Astronomical Relevance

Oral presentation abstracts

I1

The Emergence of Molecular Complexity in Solar-like Planetary Systems

Cecilia Ceccarelli[1]

[1] *Univ. Grenoble Alpes, CNRS, IPAG, 38000 Grenoble, France*

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Our is the only planet known to have developed a particularly complex chemistry which led to life. Whatever the origin of life, exogenous or endogenous, numerous evidence suggests that molecular complexity had already begun and developed when the Solar System was an embryo inside a cold molecular cloud. In this presentation, I will review the major advances in our comprehension of chemistry during those ancient eons, based on what we observe in the solar-like planetary systems forming in the Sun's vicinity today and our ability to understand them. I will also give an overview of the many challenges that remain to be overcome.

C1

The origin and fate of interstellar sulfur-bearing molecules: a combined observational and laboratory work

Julia C. Santos,[1,2] Ko-Ju Chuang,[1] Harold Linnartz,[1] Ewine F. van Dishoeck[2]

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[2] *Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands*

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The observable sulfur content in dense interstellar clouds and protostellar environments corresponds to only a small fraction of the expected cosmic value, with the bulk of its reservoir remaining currently unknown. One hypothesis is that the missing sulfur is locked away in or beneath the icy mantles that shroud interstellar dust grains, challenging its observation. This conspicuous characteristic unique to sulfur-bearing species makes them prominent puzzle pieces in understanding the evolution of volatile and refractory components throughout the different stages of star formation. Sulfur dioxide (SO_2) and carbonyl sulfide (OCS) are particularly relevant since both are major carriers of gaseous sulfur and are the only sulfurated molecules detected in interstellar ices to date. Hydrogen sulfide (H_2S) is another riveting case, whose efficient predicted formation on interstellar dust grains contrasts with its observationally constrained upper limits. In this presentation, I will showcase laboratory experiments on interstellar ice analogues that allow us to explore potential formation and destruction routes for sulfurated species and offer particularly promising new pathways to OCS in interstellar ices, as well as direct quantification of H_2S destruction mechanisms. I will also present recent results on ALMA observations of gaseous SO_2 and OCS towards massive sources in comparison to ice counterparts obtained with infrared observatories—including JWST. Such comparisons provide powerful information on the chemical and physical environments of these molecules. Combined, our experimental and observational results contribute to elucidating the still elusive origin and fate of sulfur-bearing molecules in star-forming regions

I2

Crossed molecular beam studies of bimolecular reactions and their role in astrochemistry

Nadia Balucani[1,2]

[1] *DCBB, Università degli Studi di Perugia, Perugia, Italy*
[2] *INAF Osservatorio Astronomico di Arcetri*

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The low-pressure conditions of the interstellar medium are among the most difficult aspects to reproduce in laboratory experiments as they usually exceed the best vacuum we can achieve in terrestrial laboratory by far. Yet, it is crucial to observe the results of single binary reactive collisions since the presence of termolecular collisions or fast subsequent collisions can stabilize, also partly, the reactive intermediate(s) thus altering the reaction course. The crossed molecular beam technique allows us to investigate bimolecular reactions under single collision conditions, thus avoiding the effects of secondary collisions or wall collisions (termolecular collisions are impossible in that kind of setup).

In this contribution, some recent results obtained by using the Perugia crossed molecular beam machine with mass spectrometric detection and related to reactions of interest in the chemistry of the interstellar medium or other extraterrestrial environments will be illustrated.

C2

Molecular vs continuum emission: a comparison of the morphology in ALMAGAL clumps

Chiara Mininni,[1] Sergio Molinari,[1] Juan Soler,[1] Milena Benedettini,[1] Alessandro Coletta,[1,2] Alessio Traficante,[1] Davide Elia,[1] Eugenio Schisano,[1] Stefania Pezzuto,[1] Alice Nucara,[1] and the ALMAGAL team

[1] *INAF – IAPS, via Fosso del Cavaliere, 100, I-00133 Roma, Italy*
[2] *Dip. di Fisica, Università di Roma La Sapienza, P.zzle Aldo Moro 2, I-00185 Roma, Italy*

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The analysis of the line emission at millimetric wavelengths is a powerful tool for studying the kinematic and thermal conditions of the gas in star-forming regions. However, the question of how well different species trace the emission of dust in the continuum at various scales has been addressed in the literature either by comparing the region of emission of the different lines with the region emitting in the continuum or by using intensity correlators, such as Pearson's coefficient. In this work, we present an innovative approach to this problem based on the analysis of the correlation between the morphology of the moment-0 maps of lines from eight of the most common molecular species observed in high-mass star-forming (H_2CO, CH_3OH, DCN, HCCCN, CH_3CN, CH_3OCHO, SiO, and SO) regions and the continuum emission from dust at 1.4 mm on an unprecedented statistically robust sample. The observations are part of the ALMAGAL program, which has observed more than 1000 candidate high-mass starforming clumps selected from the Herschel Infrared Galactic Plane Survey (Hi-GAL) catalogue [1,2] with the ALMA interferometer at 1.4 mm. Observed clumps cover different evolutionary stages and fragmentation properties, and have masses above 500 $M_\odot$. The morphological analysis is based on the astroHOG package [3], using the method of the histogram of oriented gradients (HOG). The HOG method uses the intensity gradient orientation to characterise the similarities between two images and evaluates whether the relative gradients in the two images are preferentially parallel (i.e. the distribution of the angles between the direction of the two gradients peaks around 0°), implying that the morphology of the two images is similar. Across the subsample of more than 900. We run the comparison with astroHOG over the continuum diffuse emission and over a masked portion of the continuum emission that corresponds only to the densest regions. We found that the analysed species can be divided into two groups. CH_3CN, DCN, HCCCN, and CH_3OCHO show a good correlation, while for H2 CO, CH_3OH, SO, and SiO, the emission mostly does not follow the morphology of the dense part of the continuum, nor of the diffuse emission. Analysing the ALMAGAL data with the astroHOG method and Pearson's coefficient, the most widespread tool used for comparing the emission of different tracers in the literature, the former gives more accurate and reliable results.

References

[1] Elia et al. 2017, MNRAS, 47, 1
[2] Elia et al. 2021, MNRAS, 504, 2
[3] Soler et al. 2019, A&A, 622, A166

C3

Formation of complex imines in the interstellar medium: new suggestions from gas-phase reaction mechanisms

Silvia Alessandrini,[1] Hexu Ye,[1] Cristina Puzzarini[1]

[1] *Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via Francesco Selmi 2, Bologna I-40126, Italy*

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Cyanomethanime (CH_2NCN and HNCHCN) and propargylamine (HNCHCCH) have both been observed in the interstellar medium (ISM) [1-4] and their presence was explained thanks to efficient gas-phase formation routes involving methanimine (CH_2NH) and the CN or the CCH radicals, respectively [5,6]. Their mechanisms are very similar to that between CH_2NH and the OH radical that leads to the formation of formamide [7]. These processes point out the role of CH_2NH as precursor of interstellar complex organic molecules (iCOMs) and seem to suggest that a general gas-phase reaction mechanism (GRM) can be invoked [8]. Assuming this, we investigated a large set of reactions between methanimine and a small radical, already observed in the ISM, namely HCO, HCS, SH, NO, NS, SiN, CP, and C_3N [9].

First, for each radical, the exothermicity of the reaction was investigated (with the products straightforwardly derived from the GRM), also including H-abstraction. In the second step, for the exothermic reactions, the reactive potential energy surfaces (PESs) were explored to address: (i) the presence of non-submerged energy barriers with respect to the reactants and (ii) the approach between them. All these steps employed a composite scheme based on coupled-cluster techniques on double-hybrid density functional geometries. The PESs were used in kinetic calculations to determine the rate coefficients of all relevant reaction channels. This unveiled the formation of new complex imines that are potential candidates for astronomical observations and thus require to be studied experimentally. This result and other considerations will be discussed to highlight the importance of the GRM.

References

[1] Zaleski, D. P., Seifert, N. A., Steber, A. L. et al. ApJL 2013, 65, L10.
[2] Rivilla, V. M., Martín-Pintado, J., Jiménez-Serra, I. et al. MNRAS 2019, 483, L114-L119.
[3] Andrés, D. S., Rivilla, V. M., Colzi, L et al, *arXiv preprint doi : 10.48550/arXiv.2404.03334*
[4] Bizzocchi, L., Prudenzano, D., Rivilla, V. M. et. al. A&A 2020, 640, A98.
[5] Vazart, F., Latouche, C., Skouteris, D. et al. ApJ 2015 810, 111.
[6] Lupi, J., Puzzarini, C., Barone, V. ApJL 2020, 903, L35.
[7] Vazart, F., Calderini, D., Puzzarini, C. et al. JCTC 2016, 12, 5385-5397.
[8] Puzzarini, C. 2022 FSPAS. *8*, 811342.

I3

A Sharper View: Astrochemistry in the JWST era

Giulia Perotti[1] and the Ice Age, JOYS, and MINDS teams

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Over the past two years, the James Webb Space Telescope (JWST) has been surveying a large number of molecular clouds, protostars and planet-forming disks with exquisite precision, providing the community with new insights into the physical and chemical structures of these objects. In this occasion, I will give an overview of recent findings from Cycle 1 JWST ERS and GTO programs Ice Age, JOYS, and MINDS. Compared to previous infrared facilities, JWST offers unprecedented sensitivity, spatial resolution (R=3400-1600), and spectral coverage (0.6-28 μm). These observations reveal a diverse chemistry in the ices of dense clouds and protostars [1,2], as well as in the gas of inner disk regions (< 10 au) [3,4]. We find chemical pathways leading to complex ices in clouds and protostellar envelopes, while the distribution of CO ice in protoplanetary disks indicates that it is trapped in the CO_2 ice matrix on the dust grains [5,6]. These findings add a level of complexity in our understanding of how exoplanetary atmospheres relate to their formation histories.

References

[1] McClure et al. *Nature Astronomy* 2023, 7, 431-443
[2] Rocha et al. *A&A* 2024, 683, A124
[3] Henning et al. *PASP* 2024, in press
[4] Perotti et al. *Nature* 2023, 620, 516-520
[5] Strum et al. *A&A* 2023, 679, A138
[6] Bergner et al. *ApJ* 2024, submitted

C4

On the formation of HCN and HNC on interstellar ices

Joan Enrique-Romero,[1] Thanja Lamberts[1,2]

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HCN and HNC play a crucial role in the development of more complex C- and N-bearing molecules in space (e.g., [1—5]). In addition to this, they are routinely used to trace the physical structure of nebulae and star forming regions as they are great dense-gas and temperature tracers. The formation of HCN and HNC in the interstellar medium may occur on the surfaces of interstellar icy dust particles through the hydrogenation of CN radicals [6]. These processes are usually assumed to asymmetrically form HCN in excess, completely overlooking HNC.

The composition of these icy surfaces is dominated by either water or CO, depending on the environmental conditions [7]. However, it's noteworthy that the CN radical can form hemibonded complexes with water, introducing intricacy to its surface chemical evolution [8]. Additionally, CN may give rise to NCCO radicals via a reaction with CO, characterized by a low energy barrier [8].

In this work we use density functional theory benchmarked with highly accurate post-HF methods to explore (i) the interaction between CN radicals and water and CO ices and (ii) the capacity of adsorbed CN radicals to form HCN and HNC as well as other species because of the different binding modes of CN on each ice surface. Finally, we discuss the importance of these findings in the current astrochemical context.

References

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C5

Structure and IR spectroscopy of nanosilicate clusters from machine learning interatomic potential

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Nanosilicates are likely to be abundant in the interstellar medium (ISM) and might be directly detected by the James Webb Space Telescope (JWST) [1]. The interpretation of JWST observations depends on IR spectroscopic data from laboratory measurements and/or quantum chemical calculations. Herein, we generate structure models of nanosilicates with the state-of-the-art global optimization structure search [2] and provide theoretical IR spectra with anharmonic and temperature effects considered. Machine learning interatomic potentials are used to accelerated calculations, allowing the long-time simulation of large-size nanosilicates at the hybrid density functional theory (DFT) accuracy [3]. We expect those simulated data are helpful for aiding the interpretation of the upcoming JWST observations and for understanding the properties of silicate dust grains in the ISM.

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C6

Interstellar Quantum Dots – Analogues Synthesized in the Laboratory

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Graphene and quantum dots, are to-date, elusive constituents of the ISM dust that are harder to detect. In addition, our understanding of the synthesis of graphene and quantum dots in PAH rich astrochemical icy dust is limited.

We subjected the benzonitrile ice formed at 4 K to vacuum ultraviolet (9 eV) radiation. After irradiation, the ice was warmed to room temperature, which left a brownish-black residue on the KBr substrate. The IR and VUV spectrum of the residue is observed to have characteristic aromatic signature. The residue is then transferred to a quantifoil grid for High-Resolution Transmission Electron Microscope (HR- TEM) imaging. HR-TEM micrographs revealed the presence of graphene in the residue (Fig – 1). This result suggests that N-graphene could be present in PAH rich ISM dust and also in the benzene and nitrogen-rich icy clouds of Titan. In addition, the residue was observed to contain a large number of ***graphene quantum dots*** [1].

From our recent laboratory experiments, simulating the ISM shock conditions we found the presence of ***mineral quantum dots*** which may contribute to the emission features in the ISM.

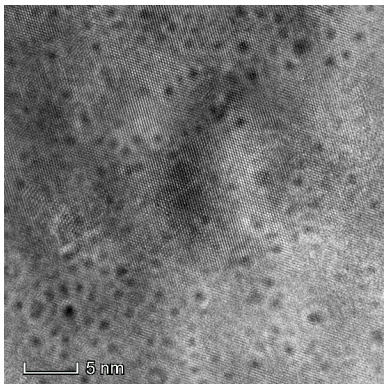

Figure 1: Quantum dots (black circular patches) beneath a layer of graphene.

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I4

Solid Interstellar Radical Chemistry (SIRC): A new methodology to study radical reactivity in interstellar ice analogs

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The interstellar medium (ISM) is composed of 99% gas and 1% dust, by mass. In dense molecular clouds, where matter is concentrated, the temperature is about 10 K, leading to the condensation of atoms and molecules on solid grains forming interstellar ices. These molecules are constantly bombarded by energetic photons (UV, X) and particles (H^+, e^-, heavy ions) coming from the surrounding stars. The energy input is sufficient to break chemical bonds and form radical species whose reactivity can lead to more complex molecules [1]. The study of the formation of these molecules is of special interest because interstellar ices represent an efficient chemical reactor and the products are incorporated in the asteroids, comets and planets of forming stellar systems. To better understand the chemistry of the ISM, we have simulated these processes in the laboratory using a physical chemistry experiment, that allows the generation of ice analogs on a cold finger (11 K) and under vacuum (10^{-9} mbar). We use a hydrogen plasma lamp to mimic the UV radiation (Lyman-α: 121.6 nm) of a nearby star and initiate free radical reactivity processes within the sample. Nevertheless, the radical intermediates formed in the interstellar ice analogues are difficult to detect by classical analytical techniques such as infrared spectroscopy or mass spectrometry. It is therefore impossible to conclude on the reaction pathways taking place in our samples. This is why the central objective of this project is to develop new methodologies allowing the characterization of radicals as well as the control of their reactivity in ice analogs [2]. Our main results show that the use of cryogenic noble gas matrix isolation technique and electron paramagnetic resonance spectroscopy for sample analysis are extremely promising tools to draw accurate reaction schemes. Using this new methodology, about ten radicals and many relevant products for the ISM chemistry such as glycolaldehyde, methyl formate, sugars and carboxylic acids have been characterized from methanol photolysis allowing to better constrain formation mechanisms [2].

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C7

Astrochemistry reveals accretion shocks at the onset of planet formation

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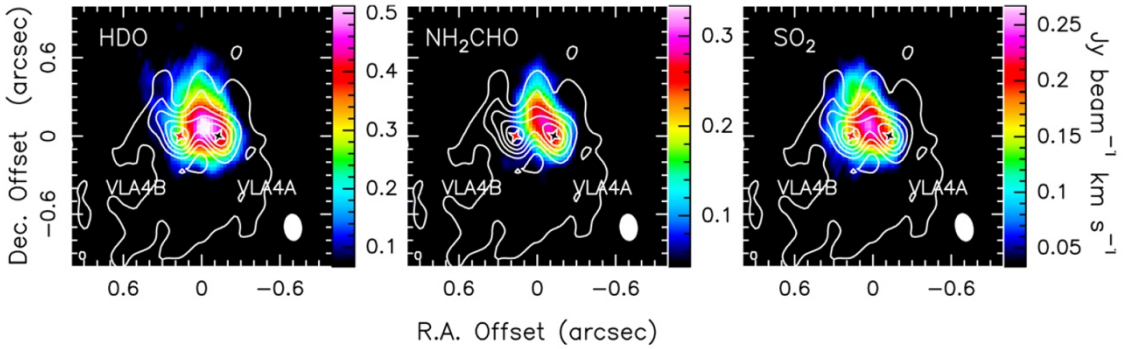
I will present observations of the binary system SVS13-A conducted using the Atacama Large Millimeter/submillimeter Array (ALMA) telescope. The high-angular resolution (~40 au) enables the mapping of two circumstellar disks around each protostar and accretion streamers on the protostellar disks. We observed several emission lines from sulfur dioxide (SO_2), deuterated water (HDO), and interstellar complex organic molecules such as methanol (CH_3OH), acetaldehyde (CH_3CHO), formamide (NH_2CHO), and dimethyl ether ($CH3OCH_3$) [1,2]. The distinct spatial distributions of these different molecular tracers suggest chemical segregation between the two disks forming within the same cloud, with only ~90 au of separation. We interpret this chemical differentiation as the result of the combined effect of dust opacity and different molecular binding energies [1]. Furthermore, a kinematic analysis suggests that these molecules are not simply produced by thermal sublimation but instead by an accretion shock at the interface between the accretion streamer and the disk [2]. This work highlights the dual significance of molecular desorption and binding energy distribution data as essential components and additional tools for interpreting astronomical observations in the planet-forming regions of young disks.



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C8

Anharmonic IR Absorption and Emission Spectra of Polycyclic Aromatic Hydrocarbons

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Gas-phase polycyclic aromatic hydrocarbons (PAHs) are ubiquitous throughout the universe, and their emission dominates the near- and mid-infrared (IR) spectrum of various astronomical sources such as molecular clouds, protoplanetary disks, and galaxies. This emission is used as a tracer for the temperature, density, and radiative characteristics of the local chemical and physical environment. These data are then utilized as input for astrochemical and astrophysical models that are integral to understanding the lifecycle (or evolutionary) dynamics of these sources. Focusing on astrochemistry, PAH molecules provide a rich source of accessible carbon while PAH clustering and stacking provide precursors of carbonaceous dust grains that participate in the subsequent growth of pebbles, boulders, and ultimately planets. Carbon based dust also acts as the medium on which interstellar ices composed of H_2O and CO_2, among other molecules, accumulate. Chemistry within these ices produces new molecules, seeding the chemical complexity that is found in geological features on Earth. In order to provide a foundation for the analysis of new high-fidelity JWST data, computational tools have been developed at NASA Ames to produce fully anharmonic IR absorption and cascade emission spectra of PAHs. The computational spectra are validated and benchmarked with new and existing laboratory measurements. This work sets the stage for future implementation of the code as a tool for populating the NASA Ames PAH IR Spectroscopic Database (PAHdb) with anharmonic spectra of vast numbers of PAHs for use in the interpretation of astronomical PAH data from missions such as JWST, Spitzer, ISO, and RST.

C9

Binding of Molecules, Radicals, and Ions with Small Water Clusters: Implications for Molecular Abundance on Grain Surfaces

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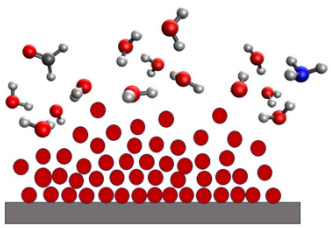
Accurate binding energies of molecules to water clusters are relevant to understanding intermolecular interactions and various chemical applications. They enter models of interstellar chemical processes, as binding to icy grains influences surface reactions, and thus affects calculated gas-phase abundances. Unfortunately, many astrochemical molecules (especially radicals and ions) are incompletely characterized in these models. To address this, we report computational searches for optimal structures and benchmark binding and condensation energies for sets of neutral, radical, cationic, and anionic molecules of astrochemical relevance with clusters of water molecules. These calculations utilized reliable density functionals for geometry optimization and coupled cluster single point calculations with large basis sets. Four energetic binding motifs (weak, intermediate, strong, or covalently bonded) were observed depending on the chemical nature of the guest molecule. Neutral closed and open shell molecules with strong dipoles and a greater potential for hydrogen bonding are more tightly bound to water clusters compared to non-polar ones. For closed-shell cationic and anionic species, barrier-less reactions with water clusters occur, which reveals radical-free routes to molecular processing on amorphous ice surfaces. I will discuss how these improved binding energies for key reactions led to improved outcomes of observed molecules in the gas-grain protoplanetary disk simulations. Some hydrocarbons are bright in disks and its emission shows ring like structures that coincide with the edge of the emission from dust. New ALMA data indicate that these emissions originate from regions close to the disk midplane. Our improved binding energies such as for hydroxyl and their incorporation into gas-grain models produce hydrocarbons much closer to the star and in greater abundance in the midplane of disks in protoplanetary disk simulations which aligns with the observations.



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I5

Towards understanding non-polar ices: treating CO and CO_2

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In cold, dense interstellar regions, atoms and molecules adsorb, diffuse, and react on the surfaces of dust grains, after which they can evaporate back into the gas phase. This leads to the build-up of molecular icy mantles of up to 100 monolayers thick. The interplay between the different surfaces processes determines which molecules are formed, where, and whether or not they are astronomically observable, either in the solid or gas phase.

A major component of interstellar ices is H_2O and in the last decennia many efforts have been made towards understanding reactivity as a whole and/or surface processes individually on amorphous solid water surfaces. However, two other molecules are crucial components of interstellar ices as well: CO and CO_2.

In this talk I will highlight novel endeavors in the treatment of non-polar interstellar ice analogs with a particular focus on the dispersion-based interaction and possible pitfalls when it comes to standard optimization strategies. Furthermore, I will discuss the differences between acetaldehyde formation on water and carbon monoxide clusters [1,2], how to calculate the binding energy of CO on pure (large) CO clusters [3], what happens to vibrational energy when CO molecules are excited [4], and calculating infrared spectra for CO_2:H_2O mixtures [5], thereby setting the stage for future reactivity studies.

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C10

New discoveries in the G+0.693-0.027 molecular cloud: detection of HOCOOH, HNSO, $HOCS^+$ and glycolamide, the first interstellar glycine isomer

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In recent years, there has been a notable increase in new interstellar discoveries within the field of astrochemistry. In particular, the Galactic center molecular cloud G+0.6930.027 (hereafter G+0.693) is recognized among the most relevant "astronomical mines" based on the detection of nearly 20 new interstellar molecules. Herein, we will present four of the latest discoveries, based on the excellent sensitivity of an ultradeep spectral survey carried out with the Yebes 40 m and IRAM 30 m telescopes toward G+0.693.

Firstly, we report the detection of the cis-trans conformer of carbonic acid (HOCOOH), the first interstellar molecule containing three oxygen atoms and the third carboxylic acid detected in the interstellar medium (ISM) to date [1]. Despite limitations in available laboratory data, we were able to detect several clear and unblended spectroscopic features directly in the radio astronomical data using the spectral survey as a “conventional” laboratory spectrum. We derived a molecular abundance with respect to H_2 of 4.7×10^{-11}. Afterward, we present the discovery in space of HNSO, the first species detected in the ISM containing, simultaneously, N, S and O [2]. We identified numerous K_a = 0, 1 and 2 transitions belonging to HNSO ranging J_{up} = 2 to J_{up} = 10, including several completely unblended features. We derive a fractional abundance relative to H_2 of $\sim6\times10^{-10}$, which is about ~37 and ~4.8 times less abundant than SO and SO_2, respectively. Although there are still many unknowns in the interstellar chemistry of NSO compounds, HNSO appears as a promising link between N-, S- and O- interstellar chemistry. We also report the detection of O-protonated carbonyl sulfide ($HOCS^+$) through the observation of a nearly complete progression of K_a = 0 transitions ranging from J_{lo} = 2 to J_{lo} = 13 [3]. We obtained a fractional abundance relative to H_2 of $\sim7\times10^{-11}$. We also compared the O/S ratio across different interstellar environments and G+0.693 stands as the source with the lowest O/S ratio, suggesting that S is not significantly depleted within this cloud due to the action of large-scale shocks. Finally, we report the discovery of the first interstellar glycine isomer, glycolamide [4]. We derived a molecular abundance with respect to H_2 of 5.5×10^{-11}. We searched for other $C_2H_5O_2N$ isomers, including the higher-energy anti conformer of glycolamide and two conformers of glycine (the simplest amino acid), which were not detected in the current data.

All in all, the discovery of these new species in the ISM sheds light on the actual levels of interstellar chemical complexity and will also provide an opportunity to conduct further harmonized observational, theoretical, and laboratory endeavors.

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C11

Sensitivity Analysis of a Dark Molecular Cloud Chemical Model and Application to Aromatic Chemistry

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Kinetic models are increasingly relied upon to explain the chemical origins of detected complex organic molecules (COMs) but require rate coefficients for many gas-phase reactions. However, only a small portion of reactions have been examined under conditions relevant to ISM (i.e. T = 10 K) due to the challenging and time-consuming nature of these studies. This necessitates estimations based on chemical intuition or extrapolation that introduce significant uncertainty, the effects of which are not often quantified [1] [2]. Sensitivity analysis techniques have been proven to be capable of identifying key reactions in complex chemical networks, including those used for dark cloud modeling [3]. We will present the results of two complementary sensitivity analyses of gas-phase rate coefficients on a modern dark cloud network using the 3-phase NAUTILUS code [4]. A focus will be placed on the recently-detected, polycyclic aromatic hydrocarbon (PAH) cyanonaphthalene ($C_{10}H_7CN$) as it is consistently underproduced by models. We find that both methods identify similar important reactions despite using different definitions of sensitivity. Notably, reactions involving hydrogenation, oxidation, and carbon-chain growth have large impacts on many species in the network. In terms of cyanonaphthalene, formation of the phenyl cation ($C_6H_5^+$) as the first six-membered ring and formation of phenyl radical (C_6H_5) as a key precursor to naphthalene are found to be the major limiting steps. Recommended pathways for future study will be discussed, such as alternate routes to formation of naphthalene and hydrogenation of C_3H_n hydrocarbons.

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C12

Combining Grain-Ice Models for efficient computation of Accurate ab initio Binding Energies on Amorphous Solid Water: New results from the Binding Energy Evaluation Platform

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In this work, we introduce the BEEP-1 dataset, encompassing accurate mean binding energy values and standard deviations for 160 interstellar molecules bound to amorphous solid water. The molecules included are sourced from the Gas-grain network benchmark established by Semnov et al. [1]. The dataset categorizes molecules into four groups based on their predominant binding mechanisms: dispersion forces or electrostatic interactions, further distinguished between radicals and closed-shell molecules. Our methodology involved analyzing small water clusters, ranging from 2 to 5 molecules, to sample for different binding sites. Benchmark computations were performed using the CCSD(T)/CBS//CCSD(T)-F12/cc-pVDZ reference level of theory on selected sites. For binding site optimization and binding energy calculations, we employed the most accurate DFT model chemistry available. We further present a model that maps the binding energy values from our enhanced model surface [2] to those derived from the small water cluster analysis. This approach allows us to scale the mean binding energy values and calculate their standard deviations accurately.

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C13

The quantum side of molecular desorption

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It is well known that dust grains, due to their catalytic role, strongly influence the chemical composition of molecular clouds in the interstellar medium. Astronomical observations show that many molecular species formed on interstellar grains populate the gas phase. This is possible thanks to various mechanisms, such as photodesorption or electroninduced desorption, coupling gas and dust. Recently, many experimental studies have been performed to understand and characterize such mechanisms.

This talk will focus on the experimental study of two of these processes: thermal and chemical desorption. We will present experimental results used to derive the desorption properties of many astrophysically relevant molecules (e.g. COMs) and atoms (e.g. N and O atoms) adsorbed on amorphous solid water ice, graphite or silicates.

We critically evaluate the desorption parameters (the binding energies, Eb, and the preexponential factor, ν) commonly used in astrochemistry. In addition, we show that a nontrivial determination of the pre-exponential factor ν using transition state theory (TST) can affect the value of the binding energy [1-4].

We also discuss the role of chemical desorption, which links the solid and gas phases without the intervention of external agents such as photons, electrons, or other energetic particles [6-8]. This process allows the rapid return of molecules formed on dust surfaces to the gas phase. We have derived an analytical expression to quantify the chemical desorption process on different substrates such as oxidized graphite and amorphous silicate. This expression, which depends on the equipartition of the energy of the newly formed products and the binding energy of the products, reproduces well the experimental results on bare surfaces. On icy surfaces, however, the chemical desorption process is strongly reduced and cannot be well quantified by our experimental results.

We will conclude the talk with some possible insights into the quantum side of molecular desorption.

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C14

Predicting the composition of astronomical ice mixtures with machine learning

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Current observations carried out by James Webb Space Telescope (JWST) allow to observe the absorption features of icy mantles that cover interstellar dust grains, which are mainly composed of H2 O, CO, CO_2, and other minor species. Thanks to its sensitivity and spectral resolution, JWST has the potential to observe ice signatures towards hundreds of sources in different stages along the star formation process. However, identifying the spectral features of the different species and quantifying the composition of the ice is not trivial, and requires a detailed spectroscopic analysis.

We present a software called AICE (Automatic Ice Composition Estimator) based on artificial neural networks that, given the infrared absorption spectrum of the ice (2.5–10 μm), predicts its fractional composition in terms of H_2O, CO, CO_2 and CH_3OH. In order to train the model, we have used hundreds of laboratory experiments of ice mixtures, mainly coming from the Leiden Ice Database (LIDA), after proper baseline subtraction and normalization. Once trained, the model takes less than 1 second to execute and predict the ice composition, showing a typical error of ~3–4 % in the species fraction.

We also tested our model with two JWST ice spectra reported toward highly-extinguished background stars from the 'IceAge' project [1], showing a good agreement with previous estimations of the ice composition [1,2]. We propose that this machine learning approach will allow to systematically analyze plenty of different ice spectra and derive statistics, due to its fast execution and simplicity to use. Besides, this model can be enhanced and re-trained with more laboratory data, improving its accuracy and enlarging the list of targeted species to others like CH_4, NH_3 or even more complex species.

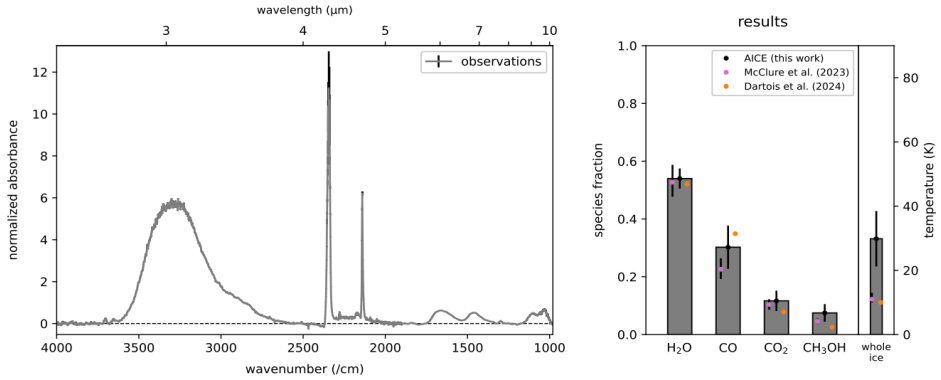

Figure 1: Left: Observed ice spectrum of NIR38 by JWST [1]. Right: Predictions by this work and others [1,2].

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C15

Sulfur reactivity on ice: a theoretical study

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Astrochemistry is a multidisciplinary subject that allows us to investigate the formation and destruction routes of molecules found in extraterrestrial environments, such as planets and moons, comets or the interstellar medium (ISM) [1].

Many sulfur species (H_2S, OCS, SO, S_2, SO_2 and CS_2) have been identified in the coma of the comet 67P/Churyumov-Gerasimenko [2] and some have been proposed as the main carriers of S, such as H_2S and OCS, condensed in the icy mantles of interstellar dust grains.

In this contribution, we present a theoretical investigation of the reactions involving atomic sulfur, in its first electronically excited state ^1D, with water ice.

S(^1D) is produced by UV-induced photodissociation of precursor molecules, such as OCS [3] and CS_2 [4], which are relatively abundant in extraterrestrial environments.

As soon as S(^1D) is formed on the ice surface, it will be able to react with water. According to our calculations, the reaction proceeds either by S(^1D) addition to one of the lone pairs of O or via insertion into one of the two O-H bonds. Two different intermediates can be formed: H_2OS and HOSH.

We computed the PES of the reaction S(^1D) + H_2O in gas phase and subsequently compared the results with the same reaction taking place on an 18-H_2O cluster ice surface model. The energetic profile of the same reaction on ice proves how water molecules act as catalysts by actively participating in the H transfer process (which is the one responsible, for example, of the conversion of H2 OS to HSOH), lowering the energy barriers compared to the analogous gas phase steps.

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I6

The Stardust Simulator: Towards a Bottom-up Understanding of Growth and Properties of Silicate Dust Grains

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Silicates are ubiquitously found as small dust particles throughout the universe. However, how these refractory grains are born and grow in the dying embers of evolved stars is an unresolved problem at the heart of astrochemistry. The high circumstellar temperatures (~1000 K) at which silicate dust is first observed to form requires the availability of highly efficient nucleation routes. The subsequent growth and properties of dust grains is also likely molded by the structure and chemistry of these initial seed species. Here, I give an overview of our efforts to tackle these issues by means of bottom-up computational chemical modelling as applied to nanosilicate grains, which are likely to be a hugely abundant dust species:

1) Following the initial reactions involved in the formation of circumstellar nucleation seeds [1,2],

2) Finding the most stable structures of nanosilicate grains [3],

3) Predicting the observable properties of populations of nanosized silicate grains [4,5]

Finally, I highlight our development of a “Stardust Simulator” code [5] which enables us to follow the detailed temperature-dependent dynamics of silicate grain growth from a few 10s of atoms to 1000s of atoms. The code allows us to analyse how numerous astronomically relevant properties of growing dust grains depend on temperature and chemical composition of the nucleating environment. I will highlight how these latter factors affect: grain morphology, density, surface roughness, dipole moment, crystallinity/amorphicity, segregation, and infrared spectra.

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C16

Exploring the molecular richness in early Solar-type protostars with a multi wavelength approach

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Solar type protostars represent the early stages of the formation of a planetary system and, thanks to recent evidences, also the stage where planet formation may already start. Characterising the chemical composition of young protostars is then crucial to retrieve the chemical content that forming planets may inherit.

From a chemical point of view the protostars can be characterized by a central hot (> 100 K), dense (> 10^7 cm^{-3}) and compact (< 100 au) region, called hot corino, where the ice mantles sublimate and the gas is enriched in the so-called interstellar Organic Molecules (iCOMs, i.e., saturated C-bearing species with more than six atoms). However, not every protostar has a hot corino region (less than 40 are known so far), and very few of them have been spatially resolved so their structure revealed. On the other hand, young protostars are characterized by molecular outflows where the chemistry is dominated by the sputtering and shattering of dust grains, triggering a new chemistry. The gas is then enriched in simple species, such as SiO, H_2CO, but lately also some iCOMs have been detected in molecular outflows. Therefore, they turned out to be perfect astrochemical laboratory where to study the iCOMs formation. In this context, two main questions remain open:

• What is the chemical composition and physical structure of planet forming regions?

• How are complex organic molecules synthesised in the hostile interstellar medium?

I will briefly show some latest results obtained in the context of the IRAM/NOEMASOLIS and ALMA&VLA - FAUST Large Program for the archetypical hot corino NGC 1333 IRAS 4A2 and its outflows. Indeed, we could explore the formation pathway of some iCOMs, and investigate the hot corino nature and structure in the inner 300 au. In particular, I'll show how crucial is the complementarity between cm and mm observations to explore the chemical complexity of protostars, and between observations and up-to-date astrochemical modelling in retrieving the history of these objects and information on the iCOMs formation path.

C17

Sulphur storage in cold molecular clouds: the case of the $NH_4^+SH^-$ salt and its behavior on interstellar dust grains

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In comets and in the cold phase of the interstellar medium (ISM), ammonium salts are considered to be important molecular species due to their properties. Indeed, the interactions between the cation and anion involved in the salt bond are strong enough to allow both species to remain on dust grains in the form of salt, far beyond their respective desorption temperatures as pure species ([1]). In the case of sulphur, the H_2S/OCS ratio observed in protostars could be explained by the presence of ammonium hydrosulfide ($NH_4^+SH^-$) salts ([2]).

Laboratory data about NH_4SH characteristics in ISM cold relevant conditions are rather scarce, as they usually focus on Jupiter's atmosphere ([3]). We propose to consolidate the laboratory data regarding the formation, signatures, characteristics, desorption, and behavior of $NH_4^+SH^-$ on interstellar dust grains. Temperature Programmed Desorption experiments and Fourier Transform InfraRed spectroscopy were performed at high and low temperatures, on a gold surface, with and without a water ice matrix. In addition, the salt was hydrogenated to mimic the ISM conditions.

The salt was found to form *in situ* at 10K, from a mixture of ammonia (NH_3) and hydrogen sulfide (H_2S). The NH_4^+ infrared feature (1485 cm^{-1}) is the most prominent at 80K. As pure species, under our experimental conditions, H_2S and NH_3 desorb respectively at 76K and 90K, whereas they are released into the gas phase at 153K when in the form of salt. The presence of water delays their desorption until that of the last water molecules, but does not affect the desorption kinetics. During hydrogenation, the salt is decoupled and no new product was detected.

Additionally, as a comparative study, salts have been introduced into the Nautilus gas-grain model in its three-phase form ([4]). Results show a good correlation with the observations of IRAS 16293-2422B ([2]), in contrast to when salts are not included in the model.

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C18

Gas-phase formation route for *trans*-HC(O)SH and its isomers under interstellar conditions: a state-of-the-art quantum-chemical study

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Sulfur is one of the ten most abundant elements in space and is ubiquitous in the interstellar medium (ISM). However, even if the number of detected S-bearing molecules has been increasing, their number and complexity are still limited [1]. Among them, the most complex are thiopropynal (HC(S)CCH), cyanothioformaldehyde (HC(S)CN) and *trans*-isomer of monothioformic acid (*t*-HC(O)SH) [2,3]. To provide new insights into the interstellar chemistry of sulfur chemistry, we aim at explaining their presence using gas-phase mechanisms, which also allow us to suggest new candidates for astronomical observations.

In my talk, I will discuss the formation pathways for the isomers of the CH_2SO family [4], which *t*-HC(O)SH belongs to. In particular, five different gas-phase reactions have been considered, which involve small molecular species already detected in the ISM such as SH, OH, H_2CS, H_2CO, H_2S, H_2O, HCS/HSC, and HCO [4]. For each reaction, the reactive potential energy surface (PES) has been determined using a double-hybrid density functional combined with a partially augmented triple-zeta basis set. Among the reactions considered, only that between H_2CS and OH can occur in the ISM because it is the only one being exothermic and presenting only submerged energy barriers. Therefore, for the H_2CS + OH reaction the energetics has been improved by exploiting a quantum-chemical composite scheme rooted in the coupled-cluster theory [5]. It has been found that this reaction leads to the formation of the observed *t*-HC(O)SH, with a H atom as co-product. Interestingly, kinetic calculations performed on top of this reactive PES suggest that *t*-HC(O)SH is efficiently formed, even if the most kinetically favored product is *t*-HC(S)OH. As a consequence, our study not only provides a suitable formation pathway for *t*-HC(O)SH, but it also suggests that *t*-HC(S)OH is a good candidate for astronomical observations [4]. Since these latter require an accurate experimental characterization of its rotational spectrum, in our work, accurate estimates of ground-state rotational constants have also been provided [4].

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Towards prebiotic chemistry in the interstellar medium

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In the past decade, Astrochemistry has witnessed an impressive increase in the number of detections of new molecular species in space. The majority of these detections are related to complex organic molecules, defined as carbon-based compounds with more than five atoms in their molecular structure. Interestingly, some of these complex organics are of prebiotic interest such as amino acetonitrile, a possible precursor of glycine. In the past few years, we have obtained ultra-sensitive, broadband spectral surveys toward one molecular cloud in the Galactic Center, G+0.693, known to be one of the richest chemical repositories in the Milky Way. Our spectral surveys carried out with the IRAM 30m and Yebes 40m telescopes have yielded the detection of 23 new molecular species, which include precursors of ribonucleotides, nucleobases, amino acids, sugars, proto-proteins and proto-lipids as found in theories of the origin of life (see e.g. [1],[2],[3],[4]). In this talk, I will present these recent findings and I will analyze how chemical complexity builds up in the interstellar medium, not only in the extreme environment of the Galactic Center but also during the initial and quiescent conditions of Solar-system formation.

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C19

Formation and growth of grains in our Universe

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First, I will discuss from first principles how seeds for dust grains form around AGB stars and Supernovae. We use a bottom-up-approach [1], i.e. we start from atoms, forming small molecules, which then continue to grow. To do this we optimize millions of molecular structures to find the most stable clusters of up to around 50 atoms. Preliminary optimization is done with a simple analytic Coulomb-Buckingham pair potential, which is followed by density functional theory calculations on selected structures. Chemical thermodynamics is one factor in grain formation. Another is kinetics, that is, how fast will the condensation process happen. To find this out we use transition state and RRKM theory.

I will also discuss how a grain can grow from small to large through sticking. Here the focus will be on nanometer sized grains and the addition of single atoms and diatomic molecules, one at a time. This addition is studied using molecular dynamics to compute sticking coefficients. For this purpose, we employ the modified reactive force field (ReaxFF) [4] built into the Amsterdam Modeling Suite (AMS) [2,3,5]. Combining the sticking coefficients with collision frequencies we can make a rough estimate of the growth rate of a grain, which has a rather weak dependence on temperature. We can also estimate a desorption rate, which has an exponential dependence on temperature. Consequently, we can find a temperature below which sticking adds more to the grain than what desorption removes. Neglecting other processes this tells us whether the grain grows or not for given densities and temperature.

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C20

A look into the stereoselectivity in the formation of interstellar sugar precursors on amorphous solid water: from vinyl alcohol to (Z)-1,2-ethenediol

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The origin of life in our planet is one of the holy grails of chemistry [1]. Regions between stars are hypothesized to have furnished prebiotic molecules to Earth, which can further develop into life-bearing compounds. The RNA-world hypothesis proposes that early life on Earth was based on the versatility of RNA molecules to both hold information and act as catalysts [2]. Glyceraldehyde, a key precursor in the RNA-world chemical scheme, is proposed to be formed from (Z)-1,2-ethenediol, a molecule that was recently detected towards the G+0.693-0.027 molecular cloud located in the galactic center [3].

In this work we computationally simulate the formation of (Z)-1,2-ethenediol from vinyl alcohol in a two-step synthesis involving an OH addition and a H abstraction reaction. We show how the different adsorption modes on the amorphous water ice surfaces affect the stereoselectivity of the reactions, leading to a mixture of (E)-1,2-ethenediol or 1,1ethenediol. H addition reactions were also considered yielding 1,1 and 1,2-ethanediol.

Two cluster models of amorphous solid water were considered. The first consisting of 18 H_2O molecules featuring dangling-hydrogen (dH) and oxygen (dO) and the latter one consisting of 33 H_2O molecules featuring a cavity as well [4]. Binding energies of all products from the OH addition reaction as well as for the subsequent H abstraction and addition have been calculated at MPWB1K/def2-TZVP level with Grimme's D3BJ dispersion correction [5]. The same level was used for modelling the OH radical addition to vinyl alcohol whereas H-additions and H-abstractions of the second reaction step are modelled using a reduced basis set and a broken symmetry formalism.

This work provides a comprehensive analysis of the formation of key prebiotic species in the RNA world scheme regarding the relationship between the adsorption of the species on amorphous solid water (ASW) and the stereoselectivity of the products.

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C21

Metal catalysis in astrophysical environments

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Models describing the formation of interstellar complex molecules (iCOMs) on dust grain surfaces generally assume that reactions occur on the ice phase covering the silicate cores, and tend to minimise the chemical role played by the dust grains themselves. When grains are not covered in ice, interactions between the solid and the gas phase are also important. Indeed, dust grains are also rich in metallic components, such as Fe and Ni, which are well known on Earth to act as catalysts for the formation of organic compounds, such as the Fischer-Tropsch synthesis (FT) to produce hydrocarbons, the Haber-Bosch (HB) for the synthesis of ammonia, and the cyclation of small hydrocarbons in Diels-Alder (DA) type reactions and further formation of aromatics and nanostructures. They also contain FeS phases, such as troilite or pyrrothite, which are also known to be reactive and could be important to the incorporation of S in complex iCOMs. Different works have already pointed to the importance of bare grain chemistry and in particular, of the catalytic activity of metallic inclusions [1, 2, 3, 4] and their potential role in the chemical evolution of different astrophysical environments.

In this talk, we will discuss the results of our experiments on the reactivity of chondritic meteorites under relevant protoplanetary conditions, towards the above mentioned syntheses [5, Cabedo et al. 2024, *submttd.*). Moreover, we will introduce and present the initial results of our new project on astrocatalysis, where we are investigating the catalytic processes that could occur in different astrophysical environments for different metallic compositions of the dust grains. Understanding all the chemistry occurring in dust grains is important to completely interpret all the observational data and have a better model of the evolution of iCOMs in different stages of star and planetary formation. All in a new era of telescope observations that allow to characterise better the composition of dust grains and their ices, as well as exoplanetary atmospheres and other environments inaccessible before nowadays.

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Adsorption of S-bearing species at interstellar icy grain: an ab-inito approach on large model clusters

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Binding energies (BEs) are key to understanding molecular evolution in dense clouds, influencing if a species is adsorbed to grain surfaces or stays in the gas phase. Typically presented as single values, BEs vary due to icy grains' amorphous nature, exhibiting diverse BE sites. Numerous grain models have been proposed in the literature yet lacking thorough physical and systematic descriptions. The recent release of ACO-FROST [1] introduces an automated process for simulating realistic icy grains, enabling the creation of amorphous ice models up to 1,000 atoms and a variety of adsorption sites leading to a final BE distribution. Its generality also supports congruent BE distribution sets for various adsorbates.

In the present contribution, the aforementioned procedure was applied to compute BE distribution of relevant S-bearing species, i.e., H_2S, OCS, CH_3SH. S-species were selected in order to contribute to a long-standing issue in the field: the Sulphur depletion problem.[2] BEs were computed within the ONIOM(B97-3c:GFN2) scheme and further refined at DLPNO-CCSD(T)//ONIOM level inclusive of CBS extrapolation. We will also discuss why the previous reported BE values are overestimated with respect to our new BE distribution [3]. Harmonic frequency spectrum for each OCS adsorption case was calculated, resulting in a final spectrum from all spectra convolution showing excellent agreement with the JWST spectrum [4], showcasing the model's reliability for BE and vibrational spectra. Furthermore, diffusion barriers ($\Delta E^{\ddagger}$) are often estimated as a BE fraction ($\Delta E^{\ddagger} = f \cdot BE$) [5], where f is an arbitrary fraction. Such assumptions critically affect reaction rates, exponentially dependent on $\Delta E^{\ddagger}$ [6]. Utilizing the resulting multiple surface minima for H_2S, we showed the criticality of the adopted literature f values, by computing *ab-initio* diffusion barriers of H_2S for all possible pathways on the surface, offering a never-before-reported diffusion barrier distribution in the literature.

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C22

Ice origins of OCS

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The fate of sulfur once it is incorporated into the interior of dense interstellar clouds is uncertain. Most of the sulfur in the dense interstellar medium (ISM) is expected to be locked in the solid phase, either on ice mantles or in (semi-)refractory form [1]. However, only OCS and SO_2 have been detected in interstellar ices [2-4], with reported abundances representing less than 5% of the cosmic sulfur abundance. As a result, the chemistry of sulfur in the dense ISM is currently unconstrained.

Even though OCS and SO_2 do not seem to represent the main S-reservoir in the dense ISM, understanding how this initial reservoir of sulfur in interstellar ices is built is of vital importance to constrain the sulfur chemistry in the ISM. In the case of OCS, direct accretion from the gas phase is ruled out due to its low gas-phase abundance [2], so *in situ* ice formation is usually invoked. Possible solid-state formation pathways proposed in the literature include sulfurization of CO (CO+S) and oxidation of CS (CS+O) [2].
The formation of OCS in interstellar ices has been studied in the laboratory under astrophysically relevant conditions. In particular, the sulfurization of CO has been explored in experiments with ice samples containing CO or CO_2 and a S source (such as SO_2 or H_2S) [5], while the oxidation of CS have been studied with ice samples composed of CS_2 and a O source [6]. However, previous works have not addressed the relative contribution of these two formation pathways to the formation of OCS in interstellar ices, or their dependence with the ice temperature.

In this talk I will present recent laboratory experiments studying the formation of OCS upon 2 keV electron irradiation of ice samples that contained CO or CO_2 (as a source of CO and O atoms) and CS_2 (as a source of CS and S atoms) at temperatures between 7 and 50 K. The isotopic labeling of the C in the CO and CO_2 molecules allowed us to distinguish the OCS molecules formed through the CO+S and the CS+O pathways. A preliminary analysis of the experimental results has revealed that the CS+O pathway dominates the formation of OCS molecules in CO_2:CS_2 ice samples at any temperature, and also in CO:CS_2 ices at T > 25 K.

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C23

Ab initio molecular dynamics study of vibrational energy redistribution in CO aggregates: towards a new understanding of the (photo)desorption mechanism

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The UV-induced desorption of molecules at the ice surface, which may explain the high abundance of gas phase molecules in the coldest environments of the ISM, has been extensively studied for CO, the second most abundant species in the ISM. Experimental and theoretical investigations have revealed that in pure CO ices, UV photodesorption may predominantly follow an indirect "Desorption Induced by Electronic Transition" (DIET) mechanism [1-3]. However, understanding the underlying molecular mechanisms, especially the nature of the energy transfers involved in indirect desorption pathways, has been a topic of ongoing scientific discussion. In this astrochemical context, we introduce an innovative study utilizing *ab initio* molecular dynamics (AIMD) simulations based on Density Functional Theory (DFT) to investigate an indirect desorption mechanism in CO ice [4]. Here, a highly vibrationally excited CO molecule (v=40) within 50 CO molecules aggregates initially created, optimized, and then thermalized at 15K, triggers the indirect desorption of surface molecules. This scenario represents the last part of the DIET mechanism, wherein the electronic energy due to the initial VUV excitation of one molecule is redistributed into a high vibrational state of its electronic ground state, and then transferred to neighboring molecules, potentially leading to desorption. Our study meticulously analyzes the redistribution of vibrational energy into translational, rotational, and other vibrational modes within the aggregate post-excitation, as well as the desorption mechanism. Our theoretical insights reveal that the desorption process starts with a sequence of energy transfers initiated by a collision between molecules, culminating in the desorption of vibrationally cold CO molecules. In addition, the theoretical energy distributions—vibrational, rotational and kinetic—of the desorbed molecules, are in perfect agreement with the experimental ones, which supports the pivotal role of vibrational relaxation in the desorption process.

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C24

Binding environments of precursors to complex organic molecules in protoplanetary disks: A computational Study

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Stars and their surrounding planetary systems form within dense molecular clouds. During the gravitational collapse of these clouds, dust and gas flows through a collapsing envelope, feeding a so-called protoplanetary disk, providing the material required to form a new planetary system.[1]

The cold midplane of protoplanetary disks is seeded with ices that originally formed on dust grains at the low densities (10^3 – 10^4 cm^{-3}) and temperatures (10 K) in the parent molecular cloud.[2] Infrared ices subsequently react with atomic hydrogen to form larger and more complex species such as H_2CO and CH_3OH, the processing of which via heat and/or radiation can further enhance the chemical complexity of interstellar ices.[3]

The presence of complex organic molecules (in the form of gas-phase methanol) in protoplanetary disks have finally been revealed around young stars in observations with ALMA (the Atacama Large Millimeter/submillimeter Array);[4] methanol is found to be rotationally cold and likely arising from non-thermal desorption from the cold icy reservoir in the disk midplane. The confirmation of methanol in protoplanetary disks has revealed the presence of a complex organic ice reservoir in disk midplanes for the first time. This reservoir may be processed to form molecules of higher complexity, the rates of which depend on the binding energies and binding environments of key radicals under the conditions in disk midplanes.[5] We have modelled amorphous solid water and methanol ices, as well as mixed water-methanol ices at several temperatures; 10K, 20K, 50K, and 70K, yielding a range a range of interstellar ices, from which we have extracted amorphous clusters. In this research talk, we explain the motivation behind this work, and show the results of some simulations of the binding of methanol, water and their associated radicals with our interstellar ice clusters. This research has been carried out using molecular dynamics simulations performed using the GROMACS software package, DFT calculations were performed using the Gaussian16 software package and binding energies were computed using the binding energy evaluation platform (BEEP)[6] at the mPWB1K-D3BJ def2-TZPV level of theory.[7]

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C25

Reactions of P, S, and C atoms and oxides on water ice clusters

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The availability of phosphorous (P) in space and its distribution between gas and solid phase carriers is not currently well constrained. P is essential for the formation of complex biotic molecules [1] and, on Earth has an abundance with respect to hydrogen is P/H ~ 10^{-3} [2]. The cosmic abundance of phosphorous is significantly lower with a value of about P/H ~ 2.57 ×10^{-7} [3]. Only a few detections of gas-phase phosphorous are currently available. In the form of PO and PN, phosphorous has been detected in star-forming regions [4,5] and around evolved stars. In all cases the P abundance is lower than the cosmic value averaging around P/H of about 10^{-10}–10^{-9} [5,6]. Solar system studies evidenced that solar P abundance is reflected in CI chondrites [7], and that phosphorous oxides might be good candidates as P carriers in meteorites and comets [8,9,10]. A recent computational study [11] has found that (H)PO_x (x=2,3) molecules possess low-volatility (binding energies > than 8000 K calculated with a 3 H_2O water cluster) and that in some cases are able to react with the water ice cluster to form PO_4. We computationally explore the barrierless reactivity of P atoms and oxides (P, PO, PO_2, PO_3) on a water ice cluster constituted of 16 water molecules, we run electronic structure calculations at the B3LYP/AUG-cc-pVDZ level of theory using Gaussian 16 [12]. We further extend or study to sulfur (S) and carbon (C) atoms and oxides and we use the C species, for which computational and laboratory studies are available, to benchmark our results. For each scenario we sample 3 reaction sites on the water cluster and in reactive cases we extend the study to characterize possible reaction pathway beyond the initial barrierless reactivity. We find that atomic and trioxide C reacts with the water cluster while S only reacts with water cluster in the atomic form. Phosphorous however is shown to have accessible pathways of reaction that from atomic P can lead to the formation of PO_4 moieties creating evidence for a track connecting volatile phosphorous to a possible low-volatility phosphorous reservoir.

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C26

Gas-phase formation of methyl cyanide (CH_3CN) and cyanodiacetylene (HC_5N) in the ISM: theoretical calculations and astrochemical modeling

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A large number of gas-phase prebiotic molecules have been observed in several extraterrestrial environments, such as interstellar clouds, comets and planetary atmospheres. Among them, nitriles—that is, organic molecules containing a -C≡N functional group—are believed to play a central role in prebiotic chemistry for the synthesis of amino acids and nucleobases [1,2]. We focused on two of the most often detected nitriles in the interstellar medium (ISM): methyl cyanide (CH_3CN) and cyanodiacetylene (HC_5N). Despite the large interest in these two molecules, the chemical processes leading to their formations are still debated and most of them have never been characterized in laboratory experiments or through theoretical calculations. Therefore, we performed an exhaustive revision of the processes reported in the literature and we carried out new quantum mechanics (QM) calculations to obtain accurate values of the rate constants at low temperatures (10-300 K) for the most important reactions. For methyl cyanide we performed QM calculation for eight reactions, and we found that half of the reactions in the astrochemical databases were incorrectly reported. For cyanodiacetylene, the second most abundant cyanopolyyne in the ISM, we found that three reactions were not updated with laboratory data present in the literature, and we performed new QM calculations for the reactions never investigated before.

We finally present new chemical networks of reactions forming interstellar methyl cyanide and cyanodiacetylene in the gas-phase and we discuss the implications of these results on the modeling of some relevant astronomical objects. We found an agreement between the model predictions and the observed abundances in cold (~10 K) and warm objects (~100 K). Moreover, we propose an explanation to the observed correlation between methyl cyanide and methanol in hot corinos, which is due to a chemical link in the gas-phase via the CH_3^+ ion.

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C27

Hydrogenation network of cyanoacetylene under cold conditions

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Cyanoacetylene (HC_3N) is a nitrogen-bearing carbon chain that is ubiquitous in the ISM. Once it is formed in the gas phase, it is thought to freeze out on the icy grain mantles in dense molecular clouds. Atop the ice it could react with a number of available chemical species, but little is known about the surface reactivity of HC_3N, in part because of experimental difficulties. In this work we present a computational investigation of the hydrogenation of HC_3N under interstellar conditions. We have performed DFT and CCSD(T)-F12 calculations to obtain the energy profiles of various hydrogenation pathways. Based on activation and reaction energies of the gas phase reactions, we found two likely reaction pathways. The first pathway leads to the formation of vinyl cyanide (C_2H_3CN) and ethyl cyanide (C_2H_5CN), which have both been detected in the ISM. The second pathway leads to the fully saturated species propylamine (C_3H_9N). Additionally, we present some first results on the interaction of HC_3N with H_2O ice clusters. The next step is to obtain the energy profiles for the HC_3N hydrogenation on an H_2O ice cluster, and to investigate the kinetics of the reactions. This will indicate whether HC_3N can hydrogenate to form saturated species on ice grains in the ISM.

Astrochemistry @ROT&Comp Lab: Unveiling exotic chemistry and molecules in the interstellar medium

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The starting point for the development of any astrochemical model is the knowledge of the molecular census of the astrophysical object under consideration, together with the corresponding molecular abundances. In this scenario, rotational spectroscopy plays a crucial role because most of the molecular species have been detected by radioastronomy owing to their rotational signatures [1,2]. To meet the required accuracy, these need to be characterized by laboratory studies [2-4], which are increasingly assisted by quantum-chemical calculations [2-4], also for the derivation of molecular abundances [5]. The subsequent step is to understand how the detected molecules were formed and how they can further react. In this respect, accurate computational approaches play a fundamental role [6-8].

In this presentation, by means of a few selected examples taken from the work done at the ROT&Comp Lab, I will address: (*i*) the interplay of experiment and theory in the field of rotational spectroscopy in support of astronomical observations; (*ii*) the exploitation of state-of-the-art computational approaches to derive non-LTE molecular abundances and formation pathways able to explain molecular detections.

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C28

Shedding light on the mystery of NH_2OH in cold interstellar environments

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Hydroxylamine (NH_2OH) is one of the interstellar molecules with the highest prebiotic potential. Containing an amino (R-NH_2) and an alcohol group (R-OH), NH_2OH has been proposed to take an active role in the synthesis of nucleotides and aminoacids [1,2]. Despite its relative chemical simplicity, NH_2OH, has only been recently detected in the interstellar medium, and in abundances lower than the ones predicted by chemical models [3, 4]. The mismatch between observations and models can be attributed to destruction mechanisms operating in the surface and mantle of cosmic grains, where this molecule is synthesized [e.g. 5]. Working under this assumption, in this contribution I will cover the following mechanisms:

1) Processing by H atoms [6].

2) Interaction with cosmic ray analogues.

With respect to 1), and using quantum chemical calculations and astrochemical models in tandem we were able to account for a reduction of two orders of magnitude in the predicted abundance of NH_2OH at 10 K, due to the balance between hydrogen abstraction ($HNO + H \rightarrow NO + H_2$) and addition ($HNO + H \rightarrow H_2NO$). At slightly higher temperatures, hydroxylamine abundance is greatly diminished thanks to reaction with heavy atoms (O, N) along its formation sequence.

For 2), we have experimentally studied the interaction of cosmic ray analogues (5 keV e^- and 15 keV H^+) on pure and mixed NH_2OH ices. The destruction cross sections derived from our experiments reveal that NH_2OH is one of the most easily destroyed molecules after interaction with cosmic rays. Moreover, the destruction of NH_2OH fastens when is diluted in a H_2O or H_2O/CO mixture. However, we also observe that the destruction of NH_2OH in realistic ice mixtures produces rich organic and prebiotic chemistry, reinforcing the view of this molecule as a key intermediate in the synthesis of prebiotic precursors.

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C29

Structure of the 3 μm IR absorption band for thin layers of ASW

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Context. Amorphous solid water (ASW) is the most abundant ice in the universe, ubiquitous in the interstellar medium [1]. In molecular clouds, ASW forms a mantle over dust grains, providing a chemical substrate where more complex molecules can form. With the high sensitivity and wavelength range of the James Webb Space Telescope (JWST), it is possible to characterize the morphology of ASW ice on interstellar dust grains.

Aims. We aim to measure in the laboratory the evolution of the infrared band at 3 μm of thin ASW films produced using different deposition methods under conditions mimicking those in pre-stellar cores.

Methods. Using the Fourier Transform Reflection Absorption InfraRed Spectroscopy (FT-RAIRS) instrument on the VENUS set-up based in LERMA laboratory at CY Cergy-Paris University [2], we have measured the spectral differences between ASW grown at 10K with three different methods of deposition: background deposition (saturated pressure), beam deposition (normal to the surface) and formed deposition (codeposition of O_2 and H to produce H_2O). The baselines are cleaned of set-up defects, mainly due to the gradual accumulation of crystalline water ice on the detector.

Results. We find a similar shape for the 3 μm features of water ices deposited by the beam and formed on the surface. These are more compact ASW compared to the water deposited by the background, which presents a wider spectral feature in the blue and red wings. For all three deposition methods, the evolution of the ASW ice band shape as a function of thickness is homothetic for very thin ice.

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C30

Dependence of the 10-micron feature on nanosilicate size

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Silicates are ubiquitous both terrestrial and throughout the universe, where they are often present as small particles. These particles are subject to high-energy processes in the interstellar medium (ISM) causing them to break down into many ultrasmall silicate fragments. This likely leads to the formation of a huge population of small nanosilicates in the ISM [1]. These nanosilicates are likely to play an important role in astrochemistry like for example in providing surface sites for astrochemical chemical reactions [2,3].

Infrared (IR) spectroscopy is an ideal tool for the identification and quantification of the structure and composition of interstellar dust. Astronomical observations show two main silicate features in the near and mid-IR region. One appears ~10 microns (assigned to Si-O stretching vibrational modes) and the other ~18 microns (assigned to O-Si-O bending vibrational modes).

These signals are characteristic of amorphous bulk silicates, with features at 11 microns being typically used to assign the degree of crystallinity of interstellar silicates. However, no observational IR signals have been yet assigned to small nanosilicate grains. Small nanosilicate grains have non-bulk like structures and distinct IR features [4].

Herein we first build an extensive nanosilicate population by means of global optimization searches and obtain their IR spectra using accurate Density Functional Theory (DFT) within the harmonic oscillator approximation. The resulting IR spectrum of the nanosilicate population is then compared to ones of crystalline and amorphous bulk silicate grains focusing on the 10-micron region of the spectrum.

Finally, we also analyze the growth of the silicate grains, and its effect on the 10-micron signal, by simulating the dynamics of nucleation process of silicates grains. To do so, we use an in-house developed code which uses classical interatomic potentials to run molecular dynamics simulations, in combination with classical forcefields which are accurate to obtain the IR spectra of silicate grains.

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I10

Behavior of Carbon atoms on Ice at Low Temperatures

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When the temperature of ice dust is elevated in star-forming regions, heavier species start to move and trigger another type of reactions, especially radical reactions, other than hydrogenation on the surface. Many kinds of complex organic molecules (COMs) in addition to methanol and their precursors are expected to be efficiently produced by reactions among heavy species. In particular, radical reactions are key for chemical evolution towards the COMs formation, as simulated in chemical models. However, because of experimental difficulty in directly detecting radicals on the ice surface, the detailed behavior of each radical is still unknown. For the sensitive detection of H atoms on ice, we previously developed a combination of photostimulated desorption (PSD) and resonance-enhanced multiphoton ionization (REMPI) methods, also known as the PSD-REMPI method. Recently, using the PSD-REMPI method, we were successful in monitoring the trace amount of small radicals on the ice surface at various temperatures [1, 2]. Our experiments provide information for the surface diffusion and subsequent reactions of radicals on ice under the interstellar relevant conditions.

The relative abundance of carbon (C) atoms to CO molecules in molecular clouds is in the range 5–15% [3], suggesting that C atoms may collide with ice dust and adsorb on them. Chemical reactions involving C atoms on the surface of dust are essential in the formation of complex organic molecules (COMs) because their skeletal evolution (for example, C–C bond formation) is expected to occur via C-atom insertion. According to quantum chemical calculations [4, 5], C atoms are often considered to immediately chemisorb to ice or even chemically converted to hydroxycarbene (HCOH) as an intermediate to formaldehyde (H_2CO). However, the behaviors of C atoms on ice were not investigated experimentally [2]. Using the PSD-REMPI method, we demonstrated experimentally that there are three destinations for C atoms landing on ice: chemisorption, immediate H_2CO formation, and physisorption leading to diffusive surface reactions. We also determined the activation energy for the surface diffusion of C atoms on ice to be ~88 meV.

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C31

Tunneling Toward Interstellar PAHs: O and H's Quantum Leap

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Polycyclic aromatic hydrocarbons (PAHs) are widely observed in space and are components of interstellar dust. PAHs account for ~20% of the carbon (C) in space. Understanding the mechanism to unlock C from PAHs is important to shed light on the formation of complex organic molecules (COMs), which play a crucial role in regulating the physics and chemistry of our universe and aiding in the origin of life [1]. While COM formation often begins with CO activation via hydrogenation, PAH breakdown could offer an alternative pathway. PAHs often host radicals such as oxygen (O) and hydrogen (H), which weaken their aromatic bonds. While superhydrogenation of PAHs is wellstudied [2], their interaction with atomic O as a possible route for their fragmentation remains underexplored [3].

Using density functional theory (DFT) and instanton theory [4], we predicted intermediate formations resulting from the reaction of O with naphthalene (Figure 1) and computed accurate tunneling rates. Similar to PAH hydrogenation, DFT suggests a sequence of O attachment. Once atomic oxygen reacts with the first C atom of naphthalene, intersystem crossing occurs from the triplet to the singlet spin state. O initially bridges Cs in naphthalene, catalyzing the barrier-less breakdown of a C-C bond, thus forming a heterocyclic ring. Subsequent oxygenation breaks down the PAH structure. Computed instanton rates reveal that tunneling is dominant at temperatures below 50K, with both O and C atoms tunneling through the potential barrier, aiding in the opening of the aromatic ring. Once one of the PAH rings is opened, the attack of two H leads to the fragmentation of the PAH, forming formaldehyde or, depending on H location, opening the second aromatic ring forming an aliphatic chain. These findings may clarify the role of PAHs in the formation of COMs, potentially linking them to the organic inventory formation in star-forming regions [1].

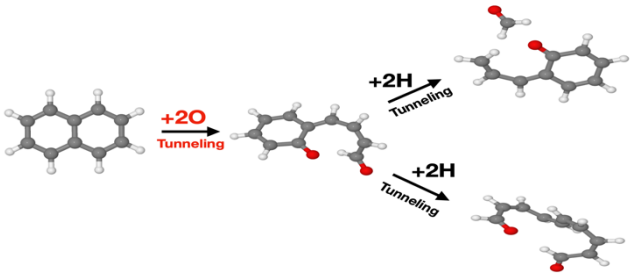

Figure 1: Oxygenation (in red) and hydrogenation (in black) tunneling of naphthalene aiding in fragmentation.

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C32

Accurate collisional excitation data for non-LTE modelling of large carbon cycles in cold ISM clouds

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Recent astronomical surveys have revealed an entirely new, complex molecular picture of the interstellar medium (ISM) through the detection of cyclic and aromatic carbon species. Following the first detection of benzonitrile [1], other large cycles have been detected in cold ISM clouds, such as cyclopentadiene (C_5H_6) [2]. In order to correctly interpret these observations, a complex, non-LTE analysis is often needed. This requires the proper knowledge of state-to-state collisional rate coefficients, since molecular excitations are mainly driven by collisions in such environments. We report the first collisional data for a large cyclic species – cyclopentadiene – calculated from the most accurate coupled channel (CC) quantum theory. Until now, such data were published only for benzonitrile and benzene, calculated from approximate scattering theories, e.g. by the coupled states (CS) model. We show on the example of C_5H_6, that the CC rate coefficients deviate from those of the CS ones usually by a factor up to 2 at low temperatures, which can have a significant impact on radiative transfer models.

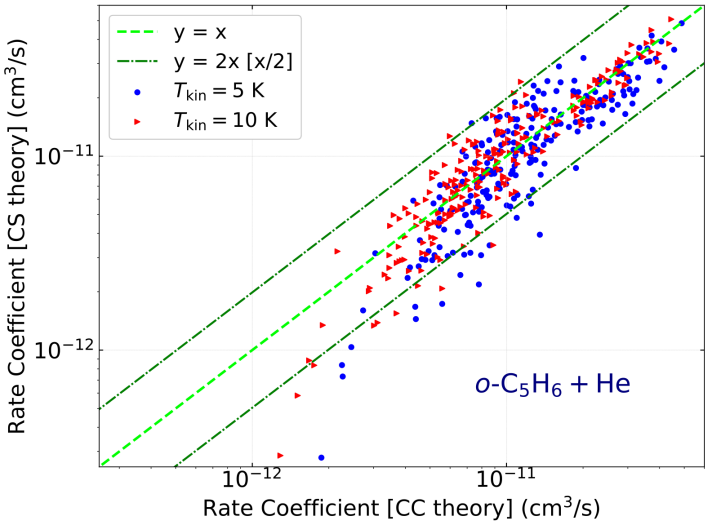

Figure 1: Comparison of the state-to-state collisional rate coefficients for the collision of ortho-C5 H 6 with He, calculated from the CC and CS theories.

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C33

The detection of radical adsorbates on ice with the PSD-REMPI method

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Recently our group developed a novel PSD-REMPI method, a combination of photostimulated desorption and resonance-enhanced multiphoton ionization, for detecting the radicals and atoms on the ice surface. This method has successfully detected the C atoms and OH radicals, and the activation diffusion barriers were also determined [1－3]. In this work, we aim to understand the behavior of the sulfur (S) atom on the icy grain surface, since it is one of the most important elements of terrestrial life, and it has been a popular research topic due to the “missing sulfur” issue in molecular clouds (MCs). Although several hypotheses were proposed to explain the fate of missing sulfur, none of them could satisfy the conditions.

It is suggested that S atoms on the ice surfaces would become H_2S by hydrogenation, contributing to the main sulfur budget. However, the astronomically detected H_2S is not as much as expected. Hence, we wonder if some fractions of S atoms can remain intact on the icy mantles without being hydrogenated, while these embedded S atoms are not detectable, leading to the origin of S depletion in MCs. To understand the behavior of S atom on the ice, we use H_2S on ice as a source of S atom since there is no conventional S atomic source. By irradiating the 193 nm laser to the ice sample, the H_2S would be dissociated into HS and furthermore S atom above 20 K where hydrogen cannot stay on the ice surface. In addition, H_2O cannot be dissociated by photons at this wavelength. By measuring the S intensity at different temperatures, we may be able to determine the activation barrier of S atom on ice surface, hope to shed light on the sulfur chemistry in MCs, and provide the value for astrochemical modeling. I will report the present status of experiments.

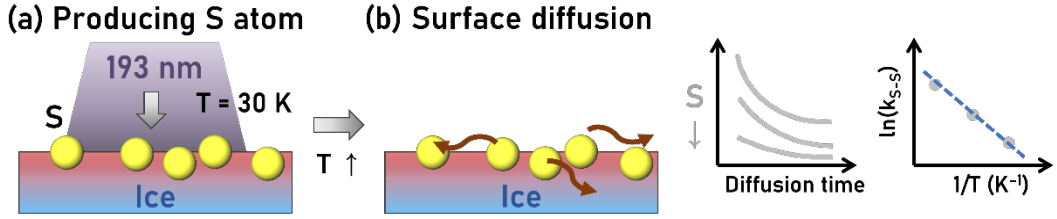

Figure 1: The schematic diagram of the experimental process.

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Poster presentation abstracts

P1

Astrocatalysis: *In Operando* Studies of Catalysis of Space-abundant Transition Metals

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In space, the cold stellar plasma of carbon rich AGB Red Giant stars is known nucleate nanocarbon formation [1]. In the laboratory, catalytic chemical vapour deposition can produce multiwalled carbon nanotubes from a variety of gaseous precursors, predominantly on silica supported iron and nickel catalysts [2]. The abundance of these metals in space therefore necessitates exploration of their catalytic potential in the formation of complex organic molecules (COMs), polycyclic aromatic hydrocarbons (PAH's) and carbon nanomaterials across various astrophysical environments.

The chemical complexity of COMs and PAHs must arise from the most abundant gas-phase molecules in the universe - H_2 and CO. This invokes the idea that simple chemical processes such as Fischer-Tropsch (FT), Haber-Bosch type reactions have a leading role to play in the synthetic route to such compounds. Here, the simplest molecules in the universe are converted into hydrocarbons, often catalysed by transition metal (TM) elements such as Fe, Ni, Co and Ru.

The catalytic effect of iron nanoparticles has already been partially explored on both the surface of reduced olivine [3] and in the dust of chondritic meteorites [4]. In both such investigations, it was found that iron nanoparticles catalyse the formation of complex hydrocarbons through Fischer-Tropsch type CO + H_2 chemistry.

Moreover, the leading hypothesis for the formation of COMs in space relies on these simple processes occurring on the surface of dust grains [5]. Space-weathering and sputtering of these abundant silicate grains is known to nucleate nanoclusters (NC) suitable for catalysis [6], whilst deposition of gas-phase atoms along the surface of the grains can yield suitable single atom (SA) catalytic systems [7].

The EPSRC funded project titled 'Astrocatalysis: In Operando Studies of Catalysis and Photocatalysis of Space-abundant Transition Metals' aims to explore this catalysis integrating experimental surface science studies of nanocarbon formation on both small molecular species and on large metallic clusters. To investigate the effect of astrocatalysis on the formation such molecules, we present an outline of our experimental procedure for the creation and characterisation of Fe_{13} NC on silica grain mimics, through laboratory techniques such AFM, XPS, RAIRS and TPD alongside some preliminary results on acetylene and ethylene (potential FT products) adsorption and polymerisation on Fe SA silica surfaces, by means of quantum chemical calculations.

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P2

Computational investigation over the adsorption and reactivity of HCN on cosmic silicates models

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Hydrogen cyanide (HCN) has been receiving an increasing attention as a possible precursor of life since when J. Oró synthesized adenine from a solution of HCN and ammonia.[1] Since HCN molecules are widespread in the interstellar medium and the products of its polymerization (including purines) have been detected on meteoritic fragments,[2] the scientific community is now investigating the possible pathways for the oligomerization of HCN in cosmic environments to form molecules of prebiotic interest. In this sense, the gas phase oligomerization of HCN is hindered by high energetic barriers which cannot be overcome at the conditions of a molecular cloud.[3] In the condensed phase, instead, more promising results were obtained, thanks to a more feasible acid-base chemistry.[4] For these reasons, the surfaces of interstellar dust grains, as well as other materials such as carbonaceous chondrites and cometary nuclei, may play a fundamental role in this type of chemistry. Moreover, it has been recently demonstrated that the surfaces of silicates, among the primary components of dust grains cores, are able to catalyze the polymerization of HCN to adenine.[5] In this work we characterized the adsorption and the reactivity of HCN molecules on periodic surface models of crystalline Mg_2SiO_4 (forsterite) by mean of density functional theory methods. We observed different types of HCN-forsterite interactions, involving both molecular and dissociative adsorptions and confirming that the ionic nature of forsterite plays a fundamental role in triggering the polymerization of HCN. By finely comparing the computed IR frequencies of our complexes with the experimental ones, we could identify which kind of HCN-forsterite interactions mostly contribute to laboratory observations of this system. Lastly, we are now computing reaction energies and activation barriers for the oligomerization of adsorbed HCN to its tetramer diaminomaleonitrile (DAMN), a fundamental intermediate in the prebiotic synthesis of adenine.

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P3

Unveiling Cosmic Ice Grains: Investigating Sulfur-Bearing Species Through Calculated Binding Energies, Frequency Distributions, and Diffusion Barriers

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Binding energies (BEs) are crucial parameters to understand the evolution of molecular species in dense clouds, determining whether a species is frozen onto the grain surfaces or free in the gas phase. Nowadays, BEs are usually provided as single point values. However, the predominant amorphousness of icy grains gives rise to a distribution of BE sites and values. Moreover, diffusion barrier (ΔE) are usually approximated as a fraction of the BE, i.e. $\Delta E = f * BE$ [1]. Nevertheless, these assumptions can severely influence the reaction rates due to their exponential dependence on the ΔE [2].

Until now, several grain models have appeared in literature, but they lack a comprehensive physical and systematical description. Recently, ACO-FROST, an automatic procedure to simulate realistic icy grains has been released [2]. This code allows us to build up models of amorphous ice up to 1,000 atoms and to simulate a large variety of BE sites.

In the present contribution, the aforementioned procedure was applied to compute BE distribution of high relevant S-bearing species, i.e., H_2S, OCS, CH_3SH. S-species were selected in order to contribute to a long-standing issue in the field: the Sulphur depletion problem.[3] BEs were computed at DFT level (B97-3c) and then refined with one of the highest levels of theory available (DLPNO- CCSD(T)). The previous reported BE values are overestimated with respect to our new BE distribution [4]. Besides, frequency distribution was calculated for OCS molecule and compared to the James Webb Space Telescope (JWST) observations [5]. The computed distribution outstandingly reproduces JWST data indicating the robustness of the model studied and thus defining a novel computational tool to predict icy species vibrational features. By leveraging the presence of multiple minima on the surface, we have the capability to establish connections enabling the computation of diffusion barriers for every conceivable diffusion pathway within the surface structure, yielding a distribution of diffusion barrier, which was never reported before in literature.

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P4

Insights into Interstellar Ice Mantles: A Computational Approach to Predicting Infrared Spectral Features and Binding Energies

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In the coldest, densest regions of the interstellar medium (ISM), dust grains are covered by thick ice mantles consisting mainly of water.[1] About 300 different molecular species have been detected in the gas phase of the ISM by means of radio and microwave observational measurements. [2] However, only a handful were identified in interstellar ices through infrared (IR) spectroscopy, e.g., CO, CO_2, NH_3, CH_4, OCS and CH_3OH. [2], [3] Observations of ices require a background-illuminating source for absorption, constraining the available lines of sight for investigation. Temperature, ice structure and contamination with other species can pose further challenges when experimental approach is taken to compare observational data. In the era of IR observations provided by the James Webb Space Telescope (JWST), it is vital to provide reference spectral data confirming JWST's assigned features. [3] In this contribution, presented results are based on quantum chemical computations on the adsorption complexes formed between the aforementioned species and water-dominated ice mantles, alongside their binding energies and simulated vibrational IR spectral features. An amorphous water ice model was considered to imitate the interstellar ices and the density functional theory (DFT) was employed to predict the molecule/ice adsorption complexes and carry out the frequency calculations and the simulate the IR spectral features. The results will be discussed and compared in the context of the recent findings from JWST. [3]

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P5

Exploring interstellar dust grains growth in molecular clouds: ab initio study of SiO reactivity

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Some studies suggested that silicon monoxide (SiO) found in the interstellar medium (ISM) could play a significant role in the formation of silicate dust grains.[1] Indeed, these grains are primarily composed of silicates, with orthosilicic acid, $Si(OH)_4$, being their precursor molecule. Employing ab initio calculations, we investigated the behavior of SiO, focusing on its reactivity with water molecules constituting the ice mantles covering interstellar dust grains in dense molecular clouds.[2]

By representing the ice mantle using two cluster models comprising 18 and 33 water molecules and employing the DFT method (ωB97X-D3) combined with the def2-TZVP basis set, we explored various reaction pathways aiming to form $Si(OH)_2$ and, subsequently, $Si(OH)_4$.

Our findings reveal that water ice serves not only as a reagent supplier and reactant concentrator but also as a catalytic agent.[3] The formation of $Si(OH)_2$ emerges as a crucial step in orthosilicic acid formation, characterized by a barrierless character facilitated by the reaction with a water molecule from the ice. We also identified the pathway $Si(OH)_2+O \rightarrow OSi(OH)_2+H_2O \rightarrow Si(OH)_4$ as the most favorable reaction channel, among those investigated, for $Si(OH)_4$ formation, owing to its barrier-free nature.

This study sheds light on SiO-water interactions, providing insights into $Si(OH)_4$ formation. It suggests that orthosilicic acid can form through the addition of H_2O, O, and H to SiO, implying that grains may form and grow even in dark, cold interstellar regions, beyond those where material is expelled by stars such as AGB and supernova remnants.[4,5] Additionally, the results of this work contribute to advancing our understanding of the chemical processes occurring on interstellar ice surfaces, particularly through reactions involving Si-containing species.

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P6

Energy Dissipation in H_2 Formation on Dust Grain Surfaces

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Molecular hydrogen (H_2) is the most abundant species within the Interstellar Medium (ISM), primarily originating through surface processes on dust grains [1]. Dust grains serve as solid-state supports for chemical reactions across diverse ISM environments, including both dense and diffuse interstellar clouds. In dense clouds, characterized by cold temperatures and high densities, dust grains are covered by icy mantles, predominantly of water. In contrast, diffuse clouds exhibit warmer temperatures and lower densities, with bare grains primarily composed of silicates or carbonaceous materials [2]. Dust grains can act as third bodies by dissipating the energy released by surface reactions [3][4][5]. However, our understanding of this energy dissipation process remains incomplete. In this study, we employ ab initio molecular dynamics (AIMD) simulations to investigate the energy dissipation associated with H_2 formation reactions. Our aim is to analyze how energy is partitioned between the newly formed H_2 and the grain, with a focus on determining the feasibility of chemical desorption (CD) under these conditions. Three different surface-type models were employed: i) amorphous water, resembling icy mantles covering dust grains in dense clouds, ii) silicate surfaces, and iii) graphene, both mimicking the bare grains found in diffuse clouds. Preliminary results indicate that, in certain cases, a fraction of the reaction energy is retained by the newly formed H_2, which is sufficient to induce CD of H_2 in these instances.

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P7

Formation of CO_2 on Interstellar Water Ice: A Computational Approach

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Solid CO_2 was first detected in the interstellar medium (ISM) in 1989, and since then, has been observed in varied physical environments ranging from quiescent regions of dark clouds to massive protostars.[1] Despite being one of the most abundant species in the ISM and a significant component of ice mantles covering dust grains, the formation route of CO_2 is still under speculation.[2] The low abundance of CO_2 in the gas phase indicates that it is formed exclusively on the solid ice surface. Moreover, there has been no clear, efficient process that can account for the majority of CO_2 formation[3]. In this work, we investigate some well-known radical-neutral reaction pathways on pure water ice clusters: CO with O, CO with OH, and HCHO with O. Quantum chemical calculations have been carried out for the preliminary benchmarking study using multiple DFT functionals on model gas-phase reactions, to ascertain a method that accurately describes the reaction properties. With the selected functional, potential energy surfaces of the reactions are obtained on an ice model i.e. a water cluster composed of 18 molecules. First insights will be presented based on the computational investigation of the reaction mechanisms to determine if they are energetically feasible. Additionally, the astrophysical implications of the results will be discussed in combination with the observations from experiments and astrochemical models of these widely studied reactions.

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P8

Phenylethynyl Radical ($C_6H_5C{\equiv}C{\cdot}$), its Cation and Thermal Decomposition in the Gas-Phase

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In this work, we report the gas-phase generation of the extremely reactive phenylethynyl radical (C_6H_5-CC•) and its reaction with acetylene, using mass spectrometry (MS) and photoion threshold photoelectron spectroscopy (TPES). Flash vacuum pyrolysis (FVP) of the precursors phenylethynyl iodide C_6H_5CC–I and phenylethynyl bromide C_6H_5CC–Br seeded in He were used to generate the highly reactive phenylethynyl radical (C_6H_5-CC•).The elusive radical (m/z 101) and its cation were characterized, along with the H-abstraction product, phenylacetylene C_6H_5CC–H (m/z 102), which was formed in high yields. Pyrolysis at higher temperatures resulted in formation of m/z 100 (C_8H_4) by loss of hydrogen atom from phenylethynyl radical. The potential energy surface of C_8H_4 was explored to identify the thermally formed isomers. The fitting of Frank-Condon simulations of all possible isomers with the experimental TPE spectra confirms the presence of substituted benzynes as well as open chain polyynes.

P9

Examination of the Astrochemically Relevant Ices Containing CH_3OH and CH_3NH_2

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Interstellar grains are crucial components of the interstellar medium (ISM). These grains can host an ice mantle on their surfaces, allowing the condensation of the gas-phase species. When reactions occur within this ice mantle, triggered by cosmic rays or UV irradiation, the reaction products can return to the gas phase, leading to changes in the composition of the gaseous phase of the ISM. Therefore, modeling the astrophysical ices and understanding the reactions influencing their composition are essential for gaining insight into the chemistry of the ISM.

An important intermediate molecule in the Stecker's synthesis is aminomethanol (NH_2CH_2OH), as it can lead to the formation of an important amino acid, glycine. Given its role in the pathway to glycine formation, investigating its formation from molecules detected in the ISM has astrochemical significance. Two significant astrochemical species are methanol (CH_3OH) and methylamine (CH_3NH_2). [1, 2, 3] These two molecules serve as potential precursors for the interstellar formation of NH_2CH_2OH, rendering their laboratory examination crucial for astrochemical studies.

Ices of pure CH_3OH, pure CH_3NH_2, and CH_3OH:CH_3NH_2 ice were examined using the VIZSLA experimental setup. [4] These samples were deposited onto a cold substrate at 3.2 K. Subsequently, the effects of cosmic rays and UV irradiation were simulated through 5 keV electron bombardment using a tunable electron gun. The chemical transformation of the ice was monitored using infrared (IR) spectroscopy. Following the electron irradiation, temperature-programmed desorption (TPD) was performed in all cases, heating the samples from 3.2 K to 300 K at a rate of 1 K/min. For each sample, two distinct experiments were performed: in the first case, molecules desorbing during TPD were trapped and analyzed using a quadrupole mass spectrometer (QMS), while in the second set of experiments, species in the gas phase were recondensed onto a second substrate, which was cooled down to 14 K. During the redeposition process, matrix isolation technique was employed, trapping the sample species in an argon matrix. This method, along with the redeposition, helped the identification of reaction products, enhancing spectral resolution.

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P10

Computational Investigation of Reactions between Magnesium Silicate Clusters and Methylidyne Radical

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In this study, the energetics of reactions involving magnesium silicate clusters $(MgSiO3)_n$ and methylidyne ($CH^{\bullet}$) were investigated computationally using density functional theory (DFT) based calculations. All calculations were carried out employing the PBE0 hybrid functional [1] and a light-tier numerical atom-centered orbital basis set within the Fritz Haber Institute Ab Initio Molecular Simulations package (FHI-AIMS). [2] Methylidyne ($CH^{\bullet}$) is one of the first identified molecules in space. It is one of the most abundant species in space [3] and exists both in neutral and in cationic form. [4] We calculated the Gibbs free energy for reactions of the form:

$$(MgSiO_3)_n + CH^{\bullet} \rightarrow (MgCO_3)(MgSiO_3)_{n-1} + SiH^{\bullet} \qquad n = 1\text{-}4$$

The aim is to check the stability of substituting a Si atom with a C atom in previously predicted $(MgSiO_3)_n$ structures (n = 1-4). [5] The lowest energy geometries of the $(MgCO_3)(MgSiO_3)_{n-1}$, species were predicted by the GOFEE approach, which trains a surrogate machine learning energy model with single point calculations at the same level of theory. [6] The energetics were investigated both for neutral–neutral reactions and neutral-ion reactions, with the latter being more characteristic of the ionizing conditions in interstellar environments. [7]

The results show that ion-molecule reactions are thermodynamically more favorable to occur and the distribution of the charge to the smaller species in both reactants and products increases the thermodynamic favorability. Specifically, reactions that involved CH^{+} exhibited significantly higher favorability. Moreover, as the predicted $(MgCO_3)(MgSiO_3)_{n-1}$ clusters increase in size, the stability of the cationic form decreases. Finally, theoretical infrared spectra of the resulting structures were also computed, for comparing with possible future observational data obtained from the James Webb Space Telescope (JWST).

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P11

Insights on the Energy Dissipation Process Released by the Formation of Formamide on Interstellar Water Ice Surfaces

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Ice mantles covering dust particles serves as a solid-state support for chemical reactions in the Interstellar Medium (ISM). Such water ice surfaces can act as third bodies by absorbing the energy released by surface reactions.[1] Indeed, the ability of ice mantles to absorb such energy is a crucial factor that will determine whether the newly formed species on their surface will remain adsorbed on the ice mantle or will be desorbed and ejected into the gas-phase, as is commonly assumed by astrochemical models.[1]–[4] In this contribution, we analyze the third-body role of water ice mantles for the radical-radical coupling between NH_2 and HCO, leading to the formation of formamide. This reaction presents a low energy barrier and is highly exothermic.[5] We have characterized its potential energy surface on an amorphous water ice model using static quantum chemical methods. Additionally, ab initio molecular dynamics simulations have been conducted to elucidate how the energy release by the reaction is dissipated within the amorphous water ice model. Our results indicate that the reaction energy is effectively and quickly transfer to the water ice underlying the absorbing ability of water ice surfaces. Therefore, the energy remaining on the newly formed formamide is not large enough to cause its ejection into the gas-phase and instead formamide will remain absorbed on the water ice mantle.

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P12

Computational Approach for the High-Throughput Screening of Molecular Cosmic Interactions

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Interstellar grains and cometary and meteoritic seeds have undoubtedly been found to be key for the formation of interstellar simple and complex organic molecules (iCOMs). To this date, 241 molecular species have been identified in our galaxy and beyond. Many studies have focused on identifying the effect that the interstellar bodies play on the formation process of these molecules; however, computational studies have mainly focused on the role of the icy surfaces that usually surround them, for they consider these ice shells as impenetrable layers where primordial molecules adsorb, diffuse and eventually react.

In our study, however, the vast diversity of materials present in the currently analysed stellar objects and the predicted presence of liquid water and exposed mineral surfaces in the latter stages of planetary formation led us to assess how the solid surface of interstellar, cometary and meteoritic grains interact with the molecular species in the interstellar medium. While the former are usually composed of silicates and pyroxenes of different compositions, *ca*. 275 different minerals have been found to constitute the latter two. In order to thoroughly study this variety of surface compositions and interacting molecular species, we propose a novel and unexplored approach to automatically investigate, by computational means, how most molecules in the observed universe interact with the known surface compositions. This thorough analysis will lay down the path to rationalise the abundance of certain molecular species in dense molecular clouds, as well as provide a foundation for the investigation of how very complex molecular species, such as amino acids and nucleobases, are formed in the latter stages of stellar formation.

P13

Mechanistic insights on Methanol formation via Fe0 and FeII silica supported single atom catalysis in interstellar medium conditions. The concept of Astrocatalysis in the early Solar System

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The detection of complex organic molecules (COMs) in interstellar regions that will eventually evolve into Solar-like planetary systems established a direct connection between organic chemistry in the interstellar medium (ISM) and within our solar system. This observation has shifted the understanding of chemical evolution leading to the formation of prebiotic molecules, bolstering the hypothesis that the origins of terrestrial life may have extraterrestrial components. Despite receiving considerable attention, the pathways for the formation and breakdown of iCOMs remain subjects of intense debate. Initially, it was thought that all observed molecules in such regions were formed through gas-phase chemistry. However, gas-phase chemistry under extreme conditions, characterized by low densities and temperatures, presents significant challenges. Interstellar grains play a crucial role in facilitating the formation of molecules that cannot occur in the gaseous phase. These grains are believed to enhance interactions among reactive species, promoting reactions on their surfaces, and moderating the excess energy of highly exothermic reactions. [1,2,3,4,5,6] Yet, their potential as chemical catalysts, providing pathways with low activation energies to expedite reaction rates, remains relatively unexplored. Nonetheless, various materials exhibiting catalytic properties are present in interstellar environments, including refractory grains containing abundant transition metals. [7] In this study, we offer novel insights into the mechanisms underlying the synthesis of short-chain alcohols and alkenes via the Fischer-Tropsch process under astrophysical conditions. We employ single-atom and nano-cluster iron (Fe)-containing silica surfaces as heterogeneous catalysts in an interstellar context. Our methodology involves quantum chemical calculations considering extended periodic surfaces to identify stationary points and transition states, ultimately constructing reaction potential energy surfaces. Additionally, we conduct binding energy and kinetic calculations based on the Rice–Ramsperger–Kassel–Marcus (RRKM) scheme to evaluate the catalytic efficacy of these grains and situate these reaction processes within the framework of astrochemistry. The discovery of astrocatalysis introduces an entirely new spectrum of synthetic pathways, catalyzing chemical evolution in space.[9]

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P14

Non-Energetic Ethanol Formation via “Radical + Ice Component” in Interstellar Cold Cores

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Ethanol (CH_3CH_2OH) is a relatively common molecule in the interstellar medium (ISM), found both in star-forming regions and in more evolved environments. Recent studies suggest that it could be a parent molecule of several so-called interstellar complex organic molecules (iCOMs), that are the building blocks of the molecules responsible for the origin of life and are thought to be inherited through the different stages of the evolution of a planetary system [1]. The formation route of iCOMs in cold ISM regions, where only gas-phase species and dust grains made of silicates and carbonaceous material covered in water-dominated ice mantles are present [2,3], remains under debate. We investigated the formation of CH_3CH_2OH on the surface of the icy mantles coating dust grains in the ISM with quantum chemical simulations. The “radical + ice component” scheme was tested as an alternative mechanism for the synthesis of ethanol on an 18 water molecules cluster, beyond the usual radical–radical coupling [4,5]. Results indicate that CH_3CH_2OH can potentially be formed by the proposed reaction mechanism. The reaction of CCH with H_2O on the water ice clusters can be barrierless, leading to the formation of vinyl alcohol precursors (H_2CCOH and CHCHOH). Subsequent hydrogenation of vinyl alcohol yielding ethanol is the only step presenting a low activation energy barrier. The establishment of a hemibond interaction between the two reactants is the pivotal interaction determining the positive outcome of the “radical + ice component” scheme [6].

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P15

Hydroxyl Radicals on Water Surface: Modeling Dynamics and Recombination

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Radical chemical reactions on cosmic dust grains play an important role in the formation of many chemical species. However, simulations of radical reactions on surfaces face many obstacles due to the need for long timescales and high-accuracy *ab initio* methods. To overcome the limitations of current methods, we propose the use of neural network potentials trained on QM/QM data that combine multi-reference and DFT calculations. To mimic the conditions of cosmic dust grains, simulations of two hydroxyl radicals on a surface of water cluster were performed. The simulations described a diffusion of hydroxyl radicals on the surface. Furthermore, they revealed the recombination of the two radicals, which leads to the formation of hydrogen peroxide—an important intermediate for the production of other species such as molecular oxygen. These results suggest that our approach is suitable for simulation of diffusion and radical surface reactions.

P16

Computational Quantum Quest Towards the Depleted Sulfur in the ISM

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Rapid strides in interstellar molecular census brings along a diverse chemical reaction network in the interstellar medium (ISM). More than 40% of the interstellar molecules are complex organic molecules (COM's). Despite significant advances in studying interstellar chemistry and detection of numerous COM's, the sulfur chemistry is still less understood particularly in the cold dense molecular clouds [1]. Sulfur being one of the six element of biological significance is of prime interest to astrochemical and astrobiological community in linking the extraterrestrial origin of life. Further, there exists a discrepancy between the amount of sulfur in its elemental and molecular forms and can be explained by the discovery of more sulfur-containing organic molecules corresponding to the interstellar oxygen chemistry [2]. However, to assist in expanding the sulfur census, the chemical insights into the mechanisms for the synthesis of sulfur molecules are quite rare under the astrophysical conditions. Towards this, the non-catalytic synthesis of thioacetaldehyde, sulfur analogue of the acetaldehyde, is studied in the gas-phase followed by synthesis on the ice-mantle surfaces using computational quantum-chemical methods. The Binding Energy Evaluation Platform (BEEP) is used to obtain the sampling sites of the reactants over the ice surface and hence the suitable reaction site to explore the surface chemical processes [3]. The results put forward a new chemical network for thioacetaldehyde under the exotic conditions of ISM, supporting the notion of the unknown reservoirs of sulfur in the complex organic molecules.

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P17

High-Dimensional Atomistic Neural Network Potential to study the vibrational energy redistribution in CO aggregates.

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In the challenging environment of the coldest regions of the interstellar medium (ISM), where temperatures hover around 10 K, understanding molecular processes on ice mantles is critical for astrochemical models. Continuing our previous study [1] using Ab Initio Molecular Dynamics (AIMD), where we explored the role of vibrational relaxation in inducing desorption in CO ice, this research extends our work through the integration of machine learning. We present the development of an Atomistic Neural Network Potential Energy Surface (ANN-PES) utilizing detailed DFT data from our prior AIMD simulations. This work details the steps taken to construct and validate the ANN-PES, emphasizing the integration from DFT-based methods with machine learning-enhanced framework. Preliminary results from molecular dynamics simulations using the obtained ANN-PES demonstrate its effectiveness in reproducing and predicting the dynamics of molecular desorption from CO aggregates, achieving lower computational costs and providing better statistical insights into the energy transfer processes observed experimentally. This continuation not only validates our earlier findings but also paves the way for more comprehensive simulations of astrochemical phenomena, offering significant improvements in predictive accuracy and computational efficiency.

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P18

Experimental and theoretical investigation of astrophysically relevant low-temperature reactions of lactones and amino acids

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The Astrophysically relevant low-temperature reactions of lactones, including γ-valerolactone (O=c-(COCH(CH_3)CH_2CH_2)) and γ-butirolactone (O=c-(COC$H_2CH_2CH_2$)), as well as amino acids, were investigated using theoretical and experimental methods.

Previous studies [1], [2] have demonstrated that γ-valerolactone and γ-butirolactone can undergo H-atom-abstraction reactions at both high and room temperatures. We investigated these reactions at low temperatures, relevant to molecular clouds. Our experimental results, conducted in a para-H_2 matrix, suggest that some reactions can also occur at low temperatures. Currently, the analysis of spectra and computations is underway, promising a more precise understanding of the resultant products. However, taking cues from prior studies and our own computational analyses, it appears that the H-atom-abstraction reaction from the γ C atom is the most probable scenario for both lactones.

Regarding amino acids, we investigated the formation of serine ($NH_2CH(CH_2OH)COOH$) from α-glycyl ($NH_2C{\cdot}HCOOH$) and hydroxymethyl ($\cdot CH_2OH$) radicals. The choice of this reaction path stems from evidence demonstrating the formation of the α-glycyl radical from glycine under conditions pertinent to the Interstellar Medium (ISM). [3] Additionally, the α C atom, where the reactive center of this radical resides, coincides with the location of the side chains of natural amino acids. Therefore, it was logical to hypothesize that larger amino acids might be produced through this radical mechanism within dark molecular clouds. However, experiments did not evidence the formation of serine. With the help of quantum chemical computations, we found a possible explanation for these unsuccessful experiments. According to this study, other feasible reactions between the radicals, such as H-atom transfer, can reduce the efficiency of amino acid formation.

Furthermore, we explored the formation of additional amino acids from the α-glycyl radical through reactions with radicals corresponding to the side chains of various amino acids on a theoretical basis. These theoretical investigations suggest that amino acids such as alanine ($NH_2CH(CH_3)COOH$) may be more readily generated through this type of reaction pathway, owing to the minimized occurrence of side reactions.

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P19

Coupling theory and experimental data to revisit old reactions and their implications for the modelling of TMC-1

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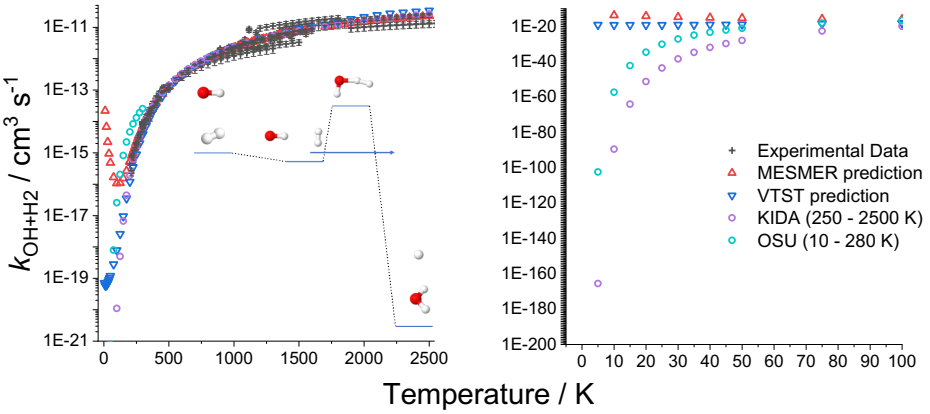
Many reactions have been studied experimentally at ambient and elevated temperatures and pressure, far fewer have been studied down to low temperatures (< 50 K). As such, rate coefficients for many reactions are extrapolated by many hundreds of Kelvins to temperatures relevant to the interstellar medium (ISM). This can cause the dramatic under prediction of the rate coefficient for these reactions at 5-10 K, if turnaround behaviour, as is seen for OH and methanol, occurs [1]. Theory can be used to improve the prediction of low-temperature kinetics when experiments to determine the rate coefficient have not or cannot be carried out. As H_2 is the most abundant molecule in the ISM, the reaction between H_2 and radicals could be an important control on their concentrations in cold molecular clouds. This work re-evaluates the rate coefficients for the reactions of OH, NH_2, CN and C_2H with H_2 in the 3-phase gas grain astrochemical model NAUTILUS [2].



New high-level ab-initio surfaces (PESs) were calculated at the CCSD(T)/CBS//B2PLYP-D3/aug-cc-pVTZ level. The temperature dependences of the reactions were then calculated using variational transition state theory in the KiSThelP program [3] and using RRKM theory in the energy grained master equation solver (MESMER) [4], where the PESs were fitted to experimental data from the NIST Kinetics database. The resulting bimolecular rate coefficients predicted at 10 K differed by up to 75 orders of magnitude from those derived using the UMIST (2022) and KIDA (2012) databases [5,6]; for example, the reaction of OH with H_2 shown in the figure above differed by 6×10^{75} at 10K.

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P20

Binding energies of small interstellar molecules on neutral and charged amorphous solid water surfaces

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The interstellar medium (ISM) is all but empty. To date, more than 300 molecules have already been discovered thanks to various forms of spectroscopy [1]. To explain the existence of such molecules in the ISM, gas-surface interactions between small molecules and dust particles must be considered. Considerable effort has already been made by the astrochemical community to study these dust grains [2,3]. These carbonaceous or silicon-based grains are surrounded by a layer of amorphous solid water (ASW) and are infused with different molecules, as shown in figure 1. In general, surface processes such as adsorption, diffusion, desorption, and chemical reactions can all be linked to the binding energy of molecules to the surface [4].

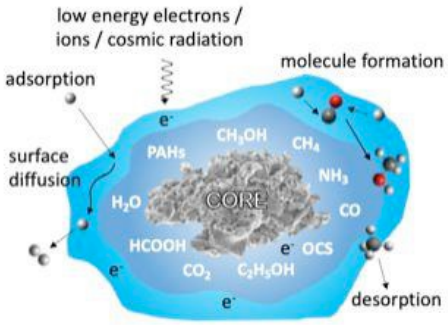

Figure 1: Schematic representation of dust grains in the ISM, along with typical surface processes.

Cosmic radiation and free electrons may induce a charge on the dust particles, and the binding energies can be affected by this charge [5]. In this research, we calculate the binding energies of CO, CH_4, and NH_3, on a neutral and charged ASW surface using DFT calculations. We conclude that the binding energy of CO and NH_3 is a direct function of their interaction with the negative surface charge, whereas the binding energy of CH_4 remains unaffected by the surface charge.

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P21

Hydroxylated Silicon Oxide Cluster Cations: Structure, Infrared Spectroscopy, and Astronomical Relevance

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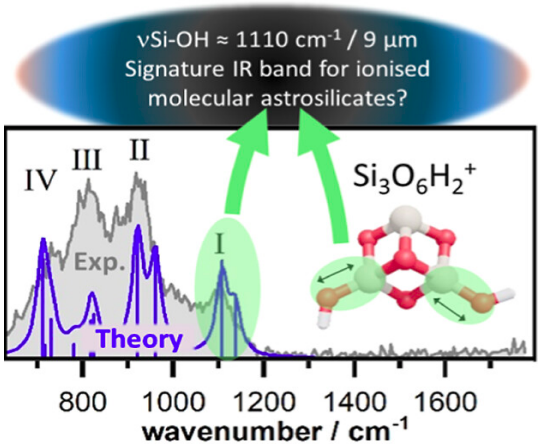
We use computational chemical modelling to elucidate the structure and vibrational spectra of $Si_xO_yH_2^+$ (x = 2–4) hydroxylated silicon oxide clusters prepared in cluster beam experiments [1]. Specifically, we compare experimental infrared (IR) multiple photon dissociation spectroscopy with IR spectra calculated by density functional theory calculations to infer the likely cluster isomers and the nature of the IR modes.

In an astronomical context, we discuss the potential relevance of $Si_xO_yH_z^+$ clusters as potential seeds for dust nucleation and catalysts for carbon-based chemistry in diffuse or translucent interstellar clouds, where all the necessary conditions for producing these species can be found.

In the produced clusters, the frequency of the isolated silanol Si–OH stretching vibrational mode is considerably blue-shifted compared to that in hydroxylated bulk silica and small inorganic compounds. This mode has a characteristic frequency range between 1200 cm^{-1} (8.3 μm) and 1090 cm^{-1} (9.2 μm) and is associated with the anomalously small Si–OH bond lengths in these ionised species. In IR observations such high frequency Si–O stretching modes are usually associated with a pure bulk silica component of silicate cosmic dust. The presence of $Si_xO_yH_2^+$ clusters in low silica astrophysical environments could thus potentially be detected via their signature Si–O band using the James Webb space telescope.



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