

# AstroChemical Newsletter #72

November 2021

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## Abstracts

### Tunneling of hydrogen and deuterium atoms on interstellar ices (Ih and ASW)

Gunnar Nyman

Model calculations are performed to investigate the kinetic isotope effect of hydrogen and deuterium atom diffusion on hexagonal ice and amorphous solid water. Comparisons with experimental results by Kuwahata et al. (2015) at 10 K are made. The experimentally derived kinetic isotope effect on amorphous solid water is reproduced by transition state theory. The experimentally found kinetic isotope effect on hexagonal ice is much larger than on amorphous solid water and is not reproduced by transition state theory. Additional calculations using model potentials are made for the hexagonal ice, but the experimental kinetic isotope effect is not fully reproduced. A strong influence of temperature is observed in the calculations. The influence of tunnelling is discussed in detail and related to the experiments. The calculations fully support the claims by the Kuwahata et al. (2015) that on amorphous solid water the diffusion is predominantly by thermal hopping while on the polycrystalline ice tunnelling diffusion contributes significantly.

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### Molecules with ALMA at Planet-forming Scales (MAPS) XIII: HCO<sup>+</sup> and disk ionization structure

Y. Aikawa, G. Cataldi, Y. Yamato, K. Zhang, A. S. Booth, K. Furuya, S. M. Andrews, J. Bae, E.A. Bergin, J. B. Bergner, A.D. Bosman, L. I. Cleaves, I. Czekala, V. V. Guzman, J. Huang, J. D. Ilee, C. J. Law, R. Le Gal, R. A. Loomis, F. Menard, H. Nomura, K. I. Oberg, C. Qi, K. R. Schwarz, R. Teague, T. Tsukagoshi, C. Walsh, D. Wilner

We observed HCO<sup>+</sup> J=1-0 and H<sup>13</sup>CO<sup>+</sup> J=1-0 emission towards the five protoplanetary disks around IM Lup, GM Aur, AS 209, HD 163296, and MWC 480 as part of the MAPS project. HCO<sup>+</sup> is detected and mapped at 0.3 arcsec resolution in all five disks, while H<sup>13</sup>CO<sup>+</sup> is detected (SNR>6 sigma) towards GM Aur and HD 163296 and tentatively detected (SNR>3 sigma) towards the other disks by a matched filter analysis. Inside a radius of  $R \lesssim 100$  au, the HCO<sup>+</sup> column density is flat or shows a central dip. At outer radii ( $> \sim 100$  au), the HCO<sup>+</sup> column density decreases outwards, while the column density ratio of HCO<sup>+</sup>/CO is mostly in the range of  $\lesssim 1e-5$ - $1e-4$ . We derived the HCO<sup>+</sup> abundance in the warm CO-rich layer, where HCO<sup>+</sup> is expected to be the dominant molecular ion. At  $R > \sim 100$  au, the HCO<sup>+</sup> abundance is  $\sim 3e-11$  -  $3e-10$ , which is consistent with a template disk model with X-ray ionization. At the smaller radii, the abundance decreases inwards, which indicates that the ionization degree is lower in denser gas, especially inside the CO snow line, where the CO-rich layer is in the midplane. Comparison of template disk models with the column densities of HCO<sup>+</sup>, N<sub>2</sub>H<sup>+</sup>, and N<sub>2</sub>D<sup>+</sup> indicates that the midplane ionization rate is  $> \sim 1e-18$  s<sup>-1</sup> for the disks around IM Lup, AS 209, and HD 163296. We also find hints of an increased HCO<sup>+</sup> abundance around the location of dust continuum gaps in AS 209, HD 163296, and MWC 480.

This paper is part of the MAPS special issue of the Astrophysical Journal Supplement.

Full-text URL: <http://arxiv.org/abs/2109.06419>

### Molecules with ALMA at Planet-forming Scales (MAPS). X. Studying deuteration at high angular resolution toward protoplanetary disks

Gianni Cataldi, Yoshihide Yamato, Yuri Aikawa, Jennifer B. Bergner, Kenji Furuya, Viviana V. Guzman, Jane Huang, Ryan A. Loomis, Chunhua Qi, Sean M. Andrews, Edwin A. Bergin, Alice S. Booth, Arthur D. Bosman, L. I. Cleaves, Ian Czekala, John D. Ilee, Charles J. Law, Romane Le Gal, Yao Liu, Feng Long, Francois Menard, Hideko Nomura, Karin I. Oberg, Kamber R. Schwarz, Richard Teague, Takashi Tsukagoshi, Catherine Walsh, David J. Wilner, Ke Zhang

Deuterium fractionation is dependent on various physical and chemical parameters. Thus, the formation location and thermal history of material in the solar system is often studied by measuring its D/H ratio. This requires knowledge about the deuteration processes operating during the planet formation era. We aim to study these processes by radially resolving the DCN/HCN (at 0.3" resolution) and N<sub>2</sub>D<sup>+</sup>/N<sub>2</sub>H<sup>+</sup> (0.3-0.9") column density ratios toward the five protoplanetary disks observed by the Molecules with ALMA at Planet-forming scales (MAPS) Large Program. DCN is detected in all five sources, with one newly reported detection. N<sub>2</sub>D<sup>+</sup> is detected in four sources, two of which are newly reported detections. We derive column density profiles that allow us to study the spatial variation of the DCN/HCN and N<sub>2</sub>D<sup>+</sup>/N<sub>2</sub>H<sup>+</sup> ratios at high resolution. DCN/HCN varies considerably for different parts of the disks, ranging from 0.001 to 0.1. In particular, the inner disk regions generally show significantly lower HCN deuteration compared with the outer disk. In addition, our analysis

confirms that two deuterium fractionation channels are active, which can alter the D/H ratio within the pool of organic molecules.  $\text{N}_2\text{D}^+$  is found in the cold outer regions beyond  $\sim 50$  au, with  $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$  ranging between 0.01 and 1 across the disk sample. This is consistent with the theoretical expectation that  $\text{N}_2\text{H}^+$  deuteration proceeds via the low-temperature channel only. This paper is part of the MAPS special issue of the Astrophysical Journal Supplement.

Accepted for publication in the Astrophysical Journal Supplement.

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## A Revised Description of the Cosmic Ray-Induced Desorption of Interstellar Ices

O. Sipilä, K. Silsbee, P. Caselli

Non-thermal desorption of ices on interstellar grains is required to explain observations of molecules that are not synthesized efficiently in the gas phase in cold dense clouds. Perhaps the most important non-thermal desorption mechanism is one induced by cosmic rays (CRs), which, when passing through a grain, heat it transiently to a high temperature – the grain cools back to its original equilibrium temperature via the (partial) sublimation of the ice. Current cosmic-ray-induced desorption (CRD) models assume a fixed grain cooling time. In this work we present a revised description of CRD in which the desorption efficiency depends dynamically on the ice content. We apply the revised desorption scheme to two-phase and three-phase chemical models in physical conditions corresponding to starless and prestellar cores, and to molecular cloud envelopes. We find that inside starless and prestellar cores, introducing dynamic CRD can decrease gas-phase abundances by up to an order of magnitude in two-phase chemical models. In three-phase chemical models our model produces very similar results to the static cooling scheme – when only one monolayer of ice is considered active. Ice abundances are generally insensitive to variations in the grain cooling time. Further improved CRD models need to take into account additional effects in the transient heating of the grains, introduced for example by the adoption of a spectrum of CR energies.

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## Reducing the complexity of chemical networks via interpretable autoencoders

T. Grassi, F. Nauman, J. P. Ramsey, S. Bovino, G. Picogna, B. Ercolano

In many astrophysical applications, the cost of solving a chemical network represented by a system of ordinary differential equations (ODEs) grows significantly with the size of the network, and can often represent a significant computational bottleneck, particularly in coupled chemo-dynamical models. Although standard numerical techniques and complex solutions tailored to thermochemistry can somewhat reduce the cost, more recently, machine learning algorithms have begun to attack this challenge via data-driven dimensional reduction techniques. In this work, we present a new class of methods that take advantage of machine learning techniques to reduce complex data sets (autoencoders), the optimization of multi-parameter systems (standard backpropagation), and the robustness of well-established ODE solvers to explicitly incorporate time-dependence. This new method allows us to find a compressed and simplified version of a large chemical network in a semi-automated fashion that can be solved with a standard ODE solver, while also enabling interpretability of the compressed, latent network. As a proof of concept, we tested the method on an astrophysically-relevant chemical network with 29 species and 224 reactions, obtaining a reduced but representative network with only 5 species and 12 reactions, and a x65 speed-up.

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## Vibrational and Rotational Spectral Data for Possible Interstellar Detection of $\text{AlH}_3\text{OH}_2$ , $\text{SiH}_3\text{OH}$ , and $\text{SiH}_3\text{NH}_2$

A. G. Watrous, B. R. Westbrook, M. C. Davis, and R. C. Fortenberry

This work provides the first full set of vibrational and rotational spectral data needed to aid in the detection of  $\text{AlH}_3\text{OH}_2$ ,  $\text{SiH}_3\text{OH}$  (silanol), and  $\text{SiH}_3\text{NH}_2$  (silylamine) in astrophysical or simulated laboratory environments through the use of quantum chemical computations at the CCSD(T)-F12b level of theory employing quartic force fields for the three molecules of interest. Previous work has shown that  $\text{SiH}_3\text{OH}$  and  $\text{SiH}_3\text{NH}_2$  contain some of the strongest bonds of the most abundant elements in space.  $\text{AlH}_3\text{OH}_2$  also contains highly abundant atoms and represents an intermediate along the reaction pathway from  $\text{H}_2\text{O}$  and  $\text{AlH}_3$  to  $\text{AlH}_2\text{OH}$ . All three of these molecules are also polar with  $\text{AlH}_3\text{OH}_2$  having the largest dipole of 4.58 D and the other two having dipole moments in the 1.10–1.30 D range, large enough to allow for the detection of these molecules in space through rotational spectroscopy. The molecules also have substantial infrared intensities with many of the frequencies being over 90 km mol<sup>-1</sup> and falling within the currently uncertain 12–17  $\mu\text{m}$  region of observed infrared spectra. The most intense frequency for  $\text{AlH}_3\text{OH}_2$  is  $\nu_9$  that has an intensity of 412 km mol<sup>-1</sup> at 777.0 cm<sup>-1</sup> (12.87  $\mu\text{m}$ ).  $\text{SiH}_3\text{OH}$  has an intensity of 183 km mol<sup>-1</sup> at 1007.8 cm<sup>-1</sup> (9.92  $\mu\text{m}$ ) for  $\nu_5$ , and  $\text{SiH}_3\text{NH}_2$  has an intensity of 215 km mol<sup>-1</sup> at 1000.0 cm<sup>-1</sup> (10.00  $\mu\text{m}$ ) for  $\nu_7$ .

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## Fundamental Vibrational Frequencies and Spectroscopic Constants of Substituted Cyclopropenylidene (c-C3HX, X = F, Cl, CN)

B. R. Westbrook, D. J. Patel, J. D. Dallas, G. C. Swartzfager, T. J. Lee, and R. C. Fortenberry

The recent detection of ethynyl-functionalized cyclopropenylidene (c-C3HC2H) has initiated the search for other functional forms of cyclopropenylidene (c-C3H2) in space. There is existing gas-phase rotational spectroscopic data for cyano-cyclopropenylidene (c-C3HCN), but the present work provides the first anharmonic vibrational spectral data for that molecule, as well as the first full set of both rotational and vibrational spectroscopic data for fluoro- and chloro-cyclopropenyldenes (c-C3HF and c-C3HCl). All three molecules have fundamental vibrational frequencies with substantial infrared intensities. Namely, c-C3HCN has a moderately intense fundamental frequency at 1244.4 cm<sup>-1</sup>, while c-C3HF has two large intensity modes at 1765.4 and 1125.3 cm<sup>-1</sup> and c-C3HCl again has two large intensity modes at 1692.0 and 1062.5 cm<sup>-1</sup>. All of these frequencies are well within the spectral range covered by the high-resolution EXES instrument on NASA's Stratospheric Observatory for Infrared Astronomy (SOFIA). Further, all three molecules have dipole moments of around 3.0 D in line with c-C3H2, enabling them to be observed by pure rotational spectroscopy, as well. Thus, the rovibrational spectral data presented herein should assist with future laboratory studies of functionalized cyclopropenyldenes and may lead to their interstellar or circumstellar detection.

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## Diastereoselective Formation of trans-HC(O)SH Through Hydrogenation of OCS on Interstellar Dust Grains

G. Molpeceres, J. García de la Concepción, I. Jiménez-Serra.

With the presence of evermore complex S-bearing molecules being detected lately, studies on their chemical formation routes need to keep up the pace to rationalize observations, suggest new candidates for detection, and provide input for chemical evolution models. In this paper, we theoretically characterize the hydrogenation channels of OCS on top of amorphous solid water as an interstellar dust grain analog in molecular clouds. Our results show that the significant reaction outcome is trans-HC(O)SH, a recently detected prebiotic molecule toward G+0.693. The reaction is diastereoselective, explaining the seemingly absence of the cis isomer in the astronomical observations. We found that the reaction proceeds through a highly localized radical intermediate (cis-OCSH), which could be essential in the formation of other sulfur-bearing complex organic molecules due to its slow isomerization dynamics on top of amorphous solid water.

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## Differential Condensation of Methane Isotopologues Leading to Isotopic Enrichment under Non-equilibrium Gas-Surface Collision Conditions

Michelle R. Brann, Stephen P. Hansknecht, Xinyou Ma, and S. J. Sibener

We examine the initial differential sticking probability of CH<sub>4</sub> and CD<sub>4</sub> on CH<sub>4</sub> and CD<sub>4</sub> ices under nonequilibrium flow conditions using a combination of experimental methods and numerical simulations. The experimental methods include timeresolved in situ reflection-absorption infrared spectroscopy (RAIRS) for monitoring on-surface gaseous condensation and complementary King and Wells mass spectrometry techniques for monitoring sticking probabilities that provide confirmatory results via a second independent measurement method. Seeded supersonic beams are employed so that the entrained CH<sub>4</sub> and CD<sub>4</sub> have the same incident velocity but different kinetic energies and momenta. We found that as the incident velocity of CH<sub>4</sub> and CD<sub>4</sub> increases, the sticking probabilities for both molecules on a CH<sub>4</sub> condensed film decrease systematically, but that preferential sticking and condensation occur for CD<sub>4</sub>. These observations differ when condensed CD<sub>4</sub> is used as the target interface, indicating that the film's phonon and rovibrational densities of states, and collisional energy transfer cross sections, have a role in differential energy accommodation between isotopically substituted incident species. Lastly, we employed a mixed incident supersonic beam composed of both CH<sub>4</sub> and CD<sub>4</sub> in a 3:1 ratio and measured the condensate composition as well as the sticking probability. When doing so, we see the same effect in the condensed mixed film, supporting an isotopic enrichment of the heavier isotope. We propose that enhanced multi-phonon interactions and inelastic cross sections between the incident CD<sub>4</sub> projectile and the CH<sub>4</sub> film allow for more efficacious gas-surface energy transfer. VENUS code MD simulations show the same sticking probability differences between isotopologues as observed in the gas-surface scattering experiments. Ongoing analyses of these trajectories will provide additional insights into energy and momentum transfer between the incident species and the interface. These results offer a new route for isotope enrichment via preferential condensation of heavier isotopes and isotopologues during gas-surface collisions under specifically selected substrate, gas-mixture, and incident velocity conditions. They also yield valuable insights into gaseous condensation under non-equilibrium conditions such as occur in aircraft flight in low-temperature environments. Moreover, these results can help to explain the increased abundance of deuterium in solar system planets and can be incorporated into astrophysical models of interstellar icy dust grain surface processes

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## Probing the Chemical Complexity of Amines in the ISM: Detection of Vinylamine (C<sub>2</sub>H<sub>3</sub>NH<sub>2</sub>) and Tentative Detection of Ethylamine (C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>)

Shaoshan Zeng, Izaskun Jiménez-Serra, Víctor M. Rivilla, Jesús Martín-Pintado, Lucas F. Rodríguez-Almeida, Belén Tercero, Pablo de Vicente, Fernando Rico-Villas, Laura Colzi, Sergio Martín, and Miguel A. Requena-Torres

Amines, particularly primary amines (R-NH<sub>2</sub>), are closely related to the primordial synthesis of amino acids since they share the same structural backbone. However, only a limited number of amines has been identified in the interstellar medium, which prevents us from studying their chemistry as well as their relation to prebiotic species that could lead to the emergence of life. In this Letter, we report the first interstellar detection of vinylamine (C<sub>2</sub>H<sub>3</sub>NH<sub>2</sub>) and tentative detection of ethylamine (C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>) toward the Galactic center cloud G+0.693-0.027. The derived abundance with respect to H<sub>2</sub> is  $(3.3 \pm 0.4) \times 10^{-10}$  and  $(1.9 \pm 0.5) \times 10^{-10}$ , respectively. The inferred abundance ratios of C<sub>2</sub>H<sub>3</sub>NH<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> with respect to methylamine (CH<sub>3</sub>NH<sub>2</sub>) are  $\sim 0.02$  and  $\sim 0.008$ , respectively. The derived abundance of C<sub>2</sub>H<sub>3</sub>NH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, and several other NH<sub>2</sub>-bearing species are compared to those obtained toward high-mass and low-mass star-forming regions. Based on recent chemical and laboratory studies, possible chemical routes for the interstellar synthesis of C<sub>2</sub>H<sub>3</sub>NH<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> are discussed.

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## Imaging the water snowline around protostars with water and HCO<sup>+</sup> isotopologues

Merel L.R. van 't Hoff, Daniel Harsono, Martijn L. van Gelder, Tien-Hao Hsieh, John J. Tobin, Sigurd S. Jensen, Naomi Hirano, Jes K. Jorgensen, Edwin A. Bergin, and Ewine F. van Dishoeck

The water snowline location in protostellar envelopes provides crucial information about the thermal structure and the mass accretion process as it can inform about the occurrence of recent ( $< \sim 1,000$  yr) accretion bursts. In addition, the ability to image water emission makes these sources excellent laboratories to test indirect snowline tracers such as H<sub>13</sub>CO<sup>+</sup>. We study the water snowline in five protostellar envelopes in Perseus using a suite of molecular line observations taken with the Atacama Large Millimeter/submillimeter Array (ALMA) at  $\sim 0.2''$ - $0.7''$  (60-210 au) resolution. B1-c provides a textbook example of compact H<sub>2</sub>18O (3<sub>(1,3)</sub>-2<sub>(2,0)</sub>) and HDO (3<sub>(1,2)</sub>-2<sub>(2,1)</sub>) emission surrounded by a ring of H<sub>13</sub>CO<sup>+</sup> (J=2-1) and HC<sub>18</sub>O<sup>+</sup> (J=3-2). Compact HDO surrounded by H<sub>13</sub>CO<sup>+</sup> is also detected toward B1-bS. The optically thick main isotopologue HCO<sup>+</sup> is not suited to trace the snowline and HC<sub>18</sub>O<sup>+</sup> is a better tracer than H<sub>13</sub>CO<sup>+</sup> due to a lower contribution from the outer envelope. However, since a detailed analysis is needed to derive a snowline location from H<sub>13</sub>CO<sup>+</sup> or HC<sub>18</sub>O<sup>+</sup> emission, their true value as snowline tracer will lie in the application in sources where water cannot be readily detected. For protostellar envelopes, the most straightforward way to locate the water snowline is through observations of H<sub>2</sub>18O or HDO. Including all sub-arcsecond resolution water observations from the literature, we derive an average burst interval of  $\sim 10,000$  yr, but high-resolution water observations of a larger number of protostars is required to better constrain the burst frequency.

Accepted for publication in the Astrophysical Journal

Full-text URL: <https://arxiv.org/abs/2110.08286>

## Formation of complex organic molecules in hot molecular cores through nondiffusive grain-surface and ice-mantle chemistry

Robin T. Garrod, Mihwa Jin, Kayla A. Matis, Dylan Jones, Eric R. Willis, Eric Herbst

A new, more comprehensive model of gas-grain chemistry in hot molecular cores is presented, in which nondiffusive reaction processes on dust-grain surfaces and in ice mantles are implemented alongside traditional diffusive surface/bulk-ice chemistry. We build on our nondiffusive treatments used for chemistry in cold sources, adopting a standard collapse/warm-up physical model for hot cores. A number of other new chemical model inputs and treatments are also explored in depth, culminating in a final model that demonstrates excellent agreement with gas-phase observational abundances for many molecules, including some (e.g. methoxymethanol) that could not be reproduced by conventional diffusive mechanisms. Observed ratios of structural isomers methyl formate, glycolaldehyde and acetic acid are well reproduced by the models. The main temperature regimes are identified in which various complex organic molecules (COMs) are formed. Nondiffusive chemistry advances the production of many COMs to much earlier times and lower temperatures than in previous model implementations. Those species may form either as by-products of simple-ice production, or via early photochemistry within the ices while external UV photons can still penetrate. Cosmic ray-induced photochemistry is less important than in past models, although it affects some species strongly over long timescales. Another production regime occurs during the high-temperature desorption of solid water, whereby radicals trapped in the ice are released onto the grain/ice surface, where they rapidly react. Several recently-proposed gas-phase COM-production mechanisms are also introduced, but they rarely dominate. New surface/ice reactions involving CH and CH<sub>2</sub> are found to contribute substantially to the formation of certain COMs.

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# Announcements

## From Clouds to Planets II: The Astrochemical Link

In 2015, we gathered at the Harnack Haus in Berlin to discuss about star and planet formation and the crucial role played by Astrochemistry in our understanding of the various steps that transform an interstellar cloud in stellar systems like our own. It is now time to meet again and present the exciting results that have been achieved in recent years, thanks to ALMA, IRAM, JVLA, GBT, APEX, SOFIA and other facilities, as well as thanks to coordinated efforts in the laboratory and theory (in particular, quantum chemistry and chemical-dynamical models of evolving clouds and disks). This will be important to cast a fresh look into the future, which we already know is going to be bright, thanks to revolutionary telescopes coming up in the near future (such as JWST and ELT) and next decades (SKA and ngVLA).

During the conference, we will make a journey through space and time, starting from interstellar clouds and then moving to cloud filaments and dense cores on the verge of star formation, to protostars and their embedded disks, to planet-forming disks to exoplanet and finally landing in our Solar System, while delving into laboratory facilities and theoretical calculations and simulations. Each evening, before dinner, there will be a general talk on each topic of the conference (the “aperitive talk”), to allow all communities to understand better the “big picture” and to facilitate finding links across disciplines, which always provide fertile ground in our journey towards understanding our astrochemical origins.

Students and young researchers will be encouraged to attend and interact with all participants, to present their work and broaden their horizons. Some financial help will be available for them upon request.

The total number of participants is limited to less than or equal to 120.

SOC

Paola Caselli (Chair), Dmitry Semenov (co-Chair), Kathrin Altmegg, Til Birnstiel, Cecilia Ceccarelli, Christiane Helling, Izaskun Jimenez-Serra, Zhi-Yun Li, Nikku Madhusudhan, Alessandro Morbidelli, Ewine van Dishoeck, and Stephanie Walch.

Pre-registration open at <https://events.mpe.mpg.de/e/astrolink2>

## Thematic school LaboAstroMolec - registration opened

We are pleased to announce that the registration to the thematic school on « Laboratory Astrophysics : tracking the evolution of cosmic matter towards molecular complexity » is now opened.

First of all, please visit the following website and proceed to a pre-registration. <https://lab-astrophysic.sciencesconf.org>

The school will take place at “Les Houches School of Physics”, located in the Chamonix valley of the French Alps in March 13-18 2022. This winter school is a PCMI-supported initiative and is addressed to a very broad audience, extending well beyond its own frontiers. It includes the fields of astrochemistry and planetary sciences.

This school focuses on advanced experimental and theoretical approaches used to produce, analyze and investigate the properties and the evolution of extraterrestrial analogs in the laboratory, and dedicated to improve our understanding of the origin and evolution of complex molecular matter observed in space, from dense molecular clouds up to the formation of new stars, planetary bodies and comets. The program will present a wide range of complementary and advanced methods allowing the production, analysis and investigation of properties and evolution of extraterrestrial analogs, that were developed in recent years in close connection to the most relevant astronomical observations. Emphasis will be put on the degree of chemical and/or structural complexity which can be achieved in the gas and solid phases and at their interface under space conditions. The methods used to characterize the physics of silicates and carbonaceous dust, and to investigate the formation/destruction processes of ices will be detailed. Techniques used to analyze matter from cometary and asteroid origins will also be presented. During the school, interactive sessions with invited teachers will be organized and all participants are encouraged to present their own work during poster sessions.

The organizing committee : Jean-Hugues Fillion, Ludovic Biennier, Grégoire Danger and Aude Simon