Workshop on Interstellar Matter 2025

Book of Abstracts

12-14 November 2025

Institute of Low Temperature Science,

Hokkaido University, JAPAN

PROGRAM

1st day: 12th, Wed

8:15– Registration

9:00–9:05 Opening remarks: Naoki Watanabe

Morning Session 1 (Observation)

9:05–9:45 **1.** Miguel Sanz-Novo (CSIC-INTA, Spain) **Invited**
"A molecular treasure trove in the Galactic Center: New discoveries toward the G+0.693-0.027 shocked molecular cloud"

9:45–10:05 **2.** Takashi Shimonishi (Niigata University, Japan)
"Exploring molecular complexity in the low-metallicity ISM"

10:05–10:25 **3.** Andrés Megías (Centro de Astrobiología (CAB), Spain)
"Predicting the composition of astronomical ices with machine learning"

10:25–10:45 Coffee Break

Morning Session 2 (Experiment)

10:45–11:25 **4.** Isabelle Kleiner (LISA/CNRS, France) **Invited**
"Spectroscopy of astrophysical molecules with large amplitude motions"

11:25–12:05 **5.** Ian Sims (Université de Rennes, France) **Invited**
"Low temperature gas-phase studies of collisional excitation, reactivity and cluster formation for astrophysical applications"

12:05–12:25 **6.** Nami Sakai (RIKEN, Japan)
"Laboratory spectroscopy of $^{13}CH_2DOH$ and its astronomical significance for tracing the formation of iCOMs"

12:25–14:00 Lunch

Afternoon Session 1 (Theory)

14:00–14:40 **7.** Tatsuhiro Murakami (Tokyo Metropolitan University, Japan) **Invited**
"Molecular dynamics simulations of interstellar chemical reactions"

14:40–15:00 **8.** Maria Mallo (IFF-CSIC, Spain)
"Ion-molecule routes towards cycles in TMC-1"

15:00–15:20 **9.** Paul Pirlot Jankowiak (RIKEN, Japan)
"Collisional excitation of H_2CO deuterated isotopologues by molecular hydrogen"

15:20–15:40 Coffee Break

Afternoon Session 2 (Model)

15:20–16:00 **10.** Valentine Wakelam (CNRS, France) **Invited**
"Astrochemical model: The good, the bad, and the ugly"

16:00–16:20 **11.** Yuto Komichi (The University of Tokyo, Japan)
"Study on chemical evolution during molecular cloud formation based on 3-dimensional MHD simulations"

16:20–16:40 **12.** Maria Murga (Institute of Astronomy of Russian Academy of Sciences, Russia)
"Catalytic pathways to polycyclic aromatic hydrocarbons in AGB stellar envelopes"

16:40–18:20 Poster Session (100 min)

2nd day: 13th, Thu

Morning Session 1 (Model & Observation)

9:00–9:20 **13.** Ryota Ichimura (NAOJ/SOKENDAI, Japan)
"Isotopomer-specific carbon isotope ratio of complex organic molecules in star-forming cores"

9:20–9:40 **14.** Judit Ferrer Asensio (RIKEN, Japan)
"c-C_3H_2 deuteration towards pre-stellar and starless cores in the Perseus molecular cloud"

9:40–10:20 **15.** Asunción Fuente (CSIC-INTA, Spain) **Invited**
"The trail of sulphur: from molecular clouds to life (SUL4LIFE)"

10:20–10:40 Coffee Break

Morning Session 2 (Theory)

10:40–11:00 **16.** Joan Enrique Romero (Leiden Institute of Chemistry, The Netherlands)
"Surface chemistry of CN radicals on interstellar ices: A route to molecular complexity"

11:00–11:20 **17.** Germán Molpeceres (IFF-CSIC, Spain)
"Theoretical studies of interstellar isomerism: Formic acid and beyond"

11:20–11:40 **18.** Eric Mates-Torres (Universitat Autònoma de Barcelona, Spain)
"Theoretical investigation of low-energy glycine formation and spectral masking in star-forming regions"

11:40–12:00 **19.** Berta Martíbez Bachs (Universitat Autonoma de Barcelona, Spain)
"Exploring nondiffusive pathways to acetaldehyde formation in interstellar ices: Insights from computational studies"

12:00–14:00 Lunch

Afternoon Session 1 (Experiment)

14:00–14:20 **20.** Gleb Fedoseev (Xinjiang Astronomical Observatory, China)
"Surface hydrogenation of interstellar polyynes: Bridging the gap between observations of unsaturated carbon chains in TMC-1 and linear alkanes in comet 67P"

14:20–15:00 **21.** Ni-En Sie (Hokkaido University, Japan) **Invited**
"The first detection of sulfur atom behavior on the silicate surface"

15:00–15:20 Coffee Break

Afternoon Session 2 (Experiment)

15:20–15:40 **22.** Franciele Kruczkiewicz (Leiden University, The Netharlands)
"Chemical complexity driven by H_2 and carbon atoms: formation of sulfur-bearing molecules H_2CS and CH_3SH"

15:40–16:00 **23.** Yi-Hsuan Chiu (National Central University, Taiwan)
"X-ray irradiation of H_2S-containing interstellar ice analogues"

16:00–17:40 Poster Session (100 min)

18:30– Banquet (@FMI)

3rd day: 14th, Fri

Morning Session 1 (Experiment)

9:00–9:20 **24.** Yasuhiro Oba (Hokkaido University, Japan)
"Nucleobases in Bennu, Ryugu, and carbonaceous meteorites"

9:20–9:40 **25.** Ludovic Biennier (Institut de Physique de Rennes, France)
"Laboratory investigation of shock-induced processing of cosmic carbon dust analogues"

9:40–10:20 **26.** Ralf I. Kaiser (University of Hawaii, U.S.A) **Invited**
"Astrochemistry - the final frontier"

10:20–10:40 Coffee Break

Morning Session 2 (Experiment)

10:40–11:20 **27.** Ilsa Cooke (University of British Columbia, Canada) **Invited**
"Cosmic-ray bombardment of icy troilite (FeS)"

11:20–11:40 **28.** Shiori Inada (The University of Tokyo, Japan)
"Mass spectrometric analysis of sublimation products from silicate dust"

11:40–12:00 Concluding Remarks

12:00–14:00 Lunch

14:00– Free Discussion and Lab Tour

Posters

Session 1: 12th,16:40–18:20
Session 2: 13th,16:00–17:40

1. Haruto Ishii (Toho University, Japan)
"Millimeter-wave spectroscopy of hydantoin in its vibrationally excited states"

2. Takahiro Oyama (RIKEN, Japan)
"Fourier-transform microwave spectroscopy of the fluorovinyl radical"

3. Mizuki Miyazaki (Shibaura Institute of Technology, Japan)
"Enrichment and Spectroscopy of CH_3OD as a Step Toward the First Characterization of CH_2DOD"

4. Kazuki Matsushita (Toho University, Japan)
"Microwave spectroscopy of Aminoacetonitrile"

5. Tomoki Ino (University of Toyama, Japan)
"Rotational spectroscopy of deuterated ethanol (CH_3CD_2OH) for astronomical detection"

6. Hiroto Nakasone (Kyoto University, Japan)
"ALMA Band 7 observations of water lines in the protoplanetary disk of V883 Ori"

7. Kotomi Taniguchi (NAOJ, Japan)
"Analyses of the aromatic infrared bands (AIBs) around the Wolf-Rayet Binary WR140"

8. Shota Notsu (The University of Tokyo, Japan)
"Synergies with PRIMA and GREX-PLUS - Observations of water line profiles from protoplanetary disks"

9. Toki Ikeda (Niigata University, Japan)
"The results of the protostar survey toward the outer Galaxy with ALMA: Detection of the protostellar outflows/jets and a hot molecular core"

10. Yao-Lun Yang (RIKEN, Japan)
"Organic ice chemistry in embedded protostars"

11. Yoshimasa Watanabe (Shibaura Institute of Technology, Japan)
"Oxygen isotope ratios in interstellar CH_3OH"

12. Hajime Tanuma (Tokyo Metropolitan University, Japan)
"Ion mobility measurements for H_3^+, D_3^+, HeH^+, and HeD^+ in He gas at 77.3 K"

13. Ryoma Kakuda (University of Toyama, Japan)
"Tentative assignment of the skeletal torsion excited state of methyl formate in the infrared spectra"

14. Kunihiro Okada (Sophia University, Japan)
"Commissioning of a new measurement system for ion—polar-molecule reactions under low-temperature conditions"

15. Arijit Roy (Physical Research Laboratory, India)
"Making the interstellar minerals behind the shock front"

16. Yuki Nakano (Hokkaido University, Japan)
"Sulfur-bearing species in molecular clouds and PPDs as possible precursors for hydrated and dehydrated minerals in meteorites"

17. Yuta Hirakawa (JAMSTEC, Japan)
"Analytical development for identifying femtomole-level organophosphorus compounds using IC/HRMS for organic astrochemical samples"

18. Ian F. Mochida (The University of Tokyo, Japan)
"Understanding the surface structure of amorphous water: quantifying the surface coverage of dangling OH bonds"

19. Rashida Aslam (University of Palermo, Italy)
"CO infrared band profiles as a probes of interstellar ice condensation conditions"

20. Reo Sato (The University of Tokyo, Japan)
"Three-step structural transformation of vapor-deposited ice (H_2O) at 120 K"

21. Satorre Miguel Ángel (Universitat Politècnica de València, Spain)
"Water ice: Experimental density and refractive index at low temperatures"

22. Yukiko Yarnall (NASA, USA)
"Laboratory measurements of band strengths and optical constants of D_2O ices along with new measurements on H_2O ices"

23. Yu-Jong Wu (NYCU/NSRRC, Taiwan)
"Visible absorption spectra of mass-selected cyanobenzene and iso-cyanobenzene cations in solid neon"

24. Anastassiia Topchieva (Russian Academy of Science, Russia)
"Modeling the composition of ices in protoplanetary disks with luminosity outbursts"

25. David Navarro-Almaida (CSIC-INTA, Spain)
"Fine-tuning the complex organic molecule formation: Sulphur and CO ice as regulators of surface chemistry"

26. Haruka Washinoue (RIKEN, Japan)
"Flare-driven X-ray ionization and chemistry in protoplanetary disks"

27. Yuto Komichi (The University of Tokyo, Japan)
"A simple and accurate framework for treating ortho-to-para ratio of molecular hydrogen in astrochemical models"

28. Alicja Bulik (Universitat Autònoma de Barcelona, Spain)
"CO_2 on interstellar iced grains: insights into adsorption and spectral features"

29. Debdatta Banerjee (IISER-Kolkata, India)
"Unveiling the physical properties of Fe-doped cosmic silicate nanostructures from a computational perspective"

30. Maria Murga (Institute of Astronomy of Russian Academy of Sciences, Russia)
"The impact of a multi-population dust model with temperature distributions on astrochemical simulations"

31. Gerard Pareras (Universitat Autònoma de Barcelona, Spain)
"Sulphur chemistry on transition-metal dust grains: Insights from CS hydrogenation"

32. Yu Komatsu (Ibaraki University, Japan)
"Quantum chemical surface reactions producing carbamic acid as a glycine precursor"

33. Guillermo M. Muñoz Caro (INTA-CSIC, Spain)
"Physical properties and photochemistry of interstellar ice analogs forming complex organic molecules with sulfur"

34. Kentaro Noguchi (The University of Tokyo, Japan)
"*In situ* measurement of the crystal structure of nanometer-sized vapor-deposited ice growing under polar mesospheric conditions"

35. Antonio Jiménez-Escobar (INAF-Osservatorio Astronomico di Palermo, Italy)
"Sinergy of VUV and X-ray radiation"

36. Arisa Iguchi (Hokkaido University, Japan)
"Methylamine formation by radical–radical reactions on diluted ice surface at 10 K"

37. Yu-Jung Chen (National Central University, Taiwan)
"Sulfur-chain growth and oxidation pathways in electron-irradiated H_2S and H_2O+H_2S ices"

38. Atsuki Ishibashi (The University of Tokyo, Japan)
"Molecular formation by transient diffusion of reaction products on cold ice surfaces"

39. Bruno Escribano (CSIC-INTA, Spain)
"X-ray Irradiation of H_2S-containing ice and analysis using density functional theory"

40. Carina Hobbs (University of British Columbia, Canada)
"Probing O(^{3}P) behaviour on interstellar ice analogues using the PSD-REMPI method"

41. Tamaki Endo (Hokkaido University, Japan)
"The surface diffusion of nitrogen atoms on amorphous solid water at low temperatures"

42. Héctor Carrascosa (CSIC-INTA, Spain)
"HMT derivatives as relics of the radicals formed at low temperatures"

43. Takuya Majima (Kyoto University, Japan)
"Fast heavy-ion-induced reactions on alcohol ice and droplet surfaces"

44. Carlos del Burgo Olivares (CSIC-INTA, Spain)
"Interstellar origin of complex molecules detected in meteorites: Experimental evidence from irradiated ices"

45. Yoichi Nakai (RIKEN, Japan)
"Interaction of low-energy CH_3^+ ion with methanol solid in low temperature environment"

46. Hiroshi Hidaka (Hokkaido University, Japan)
"Methanol formation via transient-diffusion-driven sequential reactions by methane deposition onto OH adsorbed amorphous solid water at low temperatures"

47. Hidemasa Teraoka (The University of Tokyo, Japan)
"Development of high-pressure RHEED and IR spectroscopy for understanding the structure of vapor-deposited ice under terrestrial atmospheric conditions"

48. Ziwei Zhang (RIKEN, Japan)
"Orion SrcI's disk investigated through sulfur-bearing molecules"

49. Shaoshan Zeng (RIKEN, Japan)
"Isomerism beyond thermodynamics: Discovery of cis-NMF in the ISM"

Oral Presentations

A molecular treasure trove in the Galactic Center: New discoveries toward the G+0.693-0.027 shocked molecular cloud

M. Sanz-Novo[1]

[1]*Center for Astrobiology (CSIC-INTA), Department of Astrophysics, Carretera de Ajalvir km 4, Torrejón de Ardoz, 28850 Madrid, Spain*

In recent times, the number of newly detected molecules in the interstellar medium (ISM) has skyrocketed, to the point that over one third of the current interstellar molecular census originates from discoveries made in the past five years. Two astronomical sources stand above the rest: the dark molecular cloud TMC-1 [1] and the molecular cloud G+0.693-0.027. The latter, a shock-dominated region located in the Galactic center (GC), appears as an "astronomical mine" for the detection of species harboring the six key elements for life (C, H, O, N, S, P), along with other refractory species (i.e., Si-, Mg-, and Na-bearing compounds), resulting in more than 20 first detections.

In this talk, I will showcase some of the latest discoveries enabled by the superb sensitivity of a broadband, ultra-deep spectral survey carried out with the Yebes 40m and IRAM 30m telescopes toward G+0.693, and discuss their astrochemical implications. Among these findings are glycolamide, the first interstellar glycine isomer detected in space [2]; carbonic acid (HOCOOH), also known as “tansan”, the first interstellar molecule containing three oxygen atoms and the third carboxylic acid detected in the ISM to date [3]; along with several sulfur-bearing species, such as thionylimide (HNSO), the first species detected in the ISM containing, simultaneously, N, S and O [4]; protonated carbonyl sulfide ($HOCS^+$) [5]; and dimethyl sulfide (CH_3SCH_3, DMS) [6], the predominant volatile organic sulfur compound in our oceans, previously considered as a unique biomarker in the search for extraterrestrial life.

Although we are currently living a new golden age of astrochemistry, these discoveries likely represent only a small fraction of the molecular inventory yet to be identified, possibly just the tip of the iceberg. This underscores the need for a fully coordinated, multidisciplinary approach that integrates laboratory experiments, astronomical observations, and theoretical modeling to enable the detection of increasingly complex molecules. This exciting journey will be key to unveiling the actual levels of chemical complexity in the ISM and assessing how widespread the fundamental prebiotic ingredients needed for the development of life are throughout space.

References

[1] G. Wenzel, I. R. Cooke, P. B. Changala et al., 2024, Science, 386, 6723.
[2] V. M. Rivilla, M. Sanz-Novo, I. Jiménez-Serra et al. 2023, ApJL, 953, L20.
[3] M. Sanz-Novo, V. M. Rivilla, I. Jiménez-Serra et al. 2023, ApJ, 954, 3.
[4] M. Sanz-Novo, V. M. Rivilla, I. Jiménez-Serra et al. 2024, ApJL, 965, L26.
[5] M. Sanz-Novo, V. M. Rivilla, I. Jiménez-Serra et al. 2024, ApJ, 965, 149.
[6] M. Sanz-Novo, V. M. Rivilla, C. P. Endres al. 2025, ApJL, 980, L37.

Exploring Molecular Complexity in the Low-Metallicity ISM

T. Shimonishi,[1] K.E.I. Tanaka,[2] Y. Zhang,[3] K. Furuya,[4] Y. Cheng,[5] and A. Sato[6]
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[2]*Department of Earth and Planetary Sciences, Institute of Science Tokyo, Japan*
[3]*Department of Astronomy, Shanghai Jiao Tong University, China*
[4]*Pioneering Research Institute, RIKEN, Japan*
[5]*Division of Science, National Astronomical Observatory of Japan, Japan*
[6]*Institut de Cie`ncies de l'Espai, Spain*

The Large Magellanic Cloud (LMC) provides a key laboratory for exploring the diversity of star formation and interstellar chemistry under subsolar metallicity conditions*. We here present the results of a hot core** survey toward 30 massive protostellar objects in the LMC using ALMA at 350 GHz [1]. Continuum imaging reveals 36 compact sources in total, among which line analyses identify 9 hot cores and 1 hot-core candidate. We detect CO, HCO^+, $H^{13}CO^+$, $HC^{15}N$, HC_3N, SiO, SO, SO^+, NS, SO_2, $^{34}SO_2$, $^{33}SO_2$, CH_3OH, $^{13}CH_3OH$, HCOOH, $HCOOCH_3$, CH_3OCH_3, C_2H_5OH, and hydrogen recombination lines from hot cores. All hot cores show stronger emission in a high-excitation SO line compared to non-hot-core sources, suggesting that its strong detection can serve as a useful hot-core tracer in the LMC. Chemical analysis reveals a spread of more than two orders of magnitude in CH_3OH abundances, with some sources deficient in complex organic molecules. In contrast, SO_2 is detected in all hot cores, and its abundance shows a good correlation with rotational temperature. The hot cores without CH_3OH detections are all located outside the LMC's bar region, where the metallicity is thought to be relatively low. These CH_3OH-poor hot cores also exhibit either high luminosity or active star formation in their surroundings. We speculate that a combination of locally low metallicity, active star formation in the vicinity, and high protostellar luminosity may jointly trigger the CH_3OH-poor hot core chemistry observed in some LMC protostars.

Note.
*Understanding the chemical evolution of the ISM in low-metallicity environments is important for unveiling the physical and chemical processes in past Galactic environments and in high-redshift galaxies, where the metallicity was significantly lower compared to the present-day solar neighborhood (see e.g., [2])

**Hot molecular cores are one of the early stages of star formation, and they play a key role in the chemical processing of interstellar molecules, especially for complex organic molecules.

References

[1] T. Shimonishi et al., submitted
[2] T. Shimonishi, 2025, to be published in the proceedings of the IAU Symposium 383, arXiv: 2411.04451

Predicting the composition of astronomical ices with machine learning

A. Megías,[1] I. Jiménez-Serra,[1] F. Dulieu,[2] J. Vitorino,[2] B. Maté,[3]
D. Ciudad,[4] W. R. M. Rocha,[5] M. Martínez Jiménez,[1] and J. Aguirre [1]

[1] *Centro de Astrobiología (CAB), CSIC-INTA, Spain*
[2] *LIRA, CY Cergy Paris Université, France*
[3] *Instituto de Estructura de la Materia (IEM), CSIC, Spain*
[4] *MasOrange, Spain*
[5] *Leiden Observatory, Leiden University, the Netherlands*

Current observations taken 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 H_2O, CO and CO_2, together with other minor species [1, 2]. Thanks to its sensitivity and spectral resolution, JWST has the potential to observe ice features towards hundreds of sources at different stages along the process of star formation. However, identifying the spectral features of the different species and quantifying the ice composition is not trivial and requires complex spectroscopic analysis [1, 2, 3].

We present AICE (*Automatic Ice Composition Estimator*), a new Python tool based on artificial neural networks. Given the infrared ice absorption spectrum between 2.5 and 10 μm, AICE predicts the ice fractional composition in terms of H_2O, CO, CO_2, CH_3OH, NH_3 and CH_4. To train the model, we used hundreds of laboratory experiments of ice mixtures from different databases like LIDA [4], which were reprocessed with baseline subtraction and normalisation.

Once trained, AICE takes less than 1 s in a conventional computer to predict the ice composition associated with the observed infrared absorption spectrum, with typical errors of ~3 % in the species fraction. We tested the performance of AICE in two spectra reported towards the NIR38 and J110621 background stars observed within the JWST Ice Age program [1], showing a good agreement with previous estimations of the ice composition. The fast and accurate performance of AICE enables the systematic analysis of hundreds of different ice spectra with a modest investment of time. In addition, this model can be enhanced and re-trained with more laboratory data, improving the precision of the predictions and enlarging the list of predicted species.

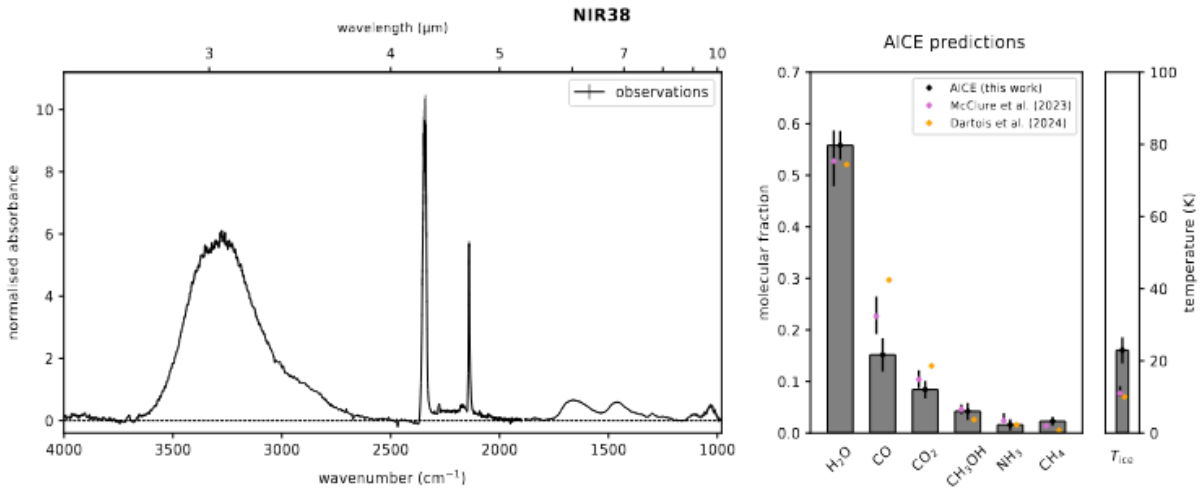

Figure 1: Absorption spectrum taken by JWST [1] and predictions of the ice composition by AICE.

References

[1] M. McClure et al., 2023, Nat. Astron. 7, 431.
[2] Z. L. Smith et al., 2025, Nat. Astron. 9, 883.
[3] E. Dartois et al., 2024, Nat. Astron. 8, 359.
[4] W. R. M. Rocha et al., 2022, A&A 668, A63.

Spectroscopy of astrophysical molecules with large amplitude motions

I. Kleiner[1]

[1]*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS, Université Paris Est Créteil et Université Paris Cité, France*

This talk will first give a short introduction to the spectroscopy of molecules containing one or two methyl internal rotors. One of the goals of our work is to describe with our theoretical method and codes the energy levels and then the line positions and intensities for this type of molecules. That way we can provide reliable predictions of line positions and intensities for astrophysical molecules containing one internal rotor CH_3, such as methanol CH_3OH, methyl formate $HCOOCH_3$, acetic acid CH_3COOH, acetamide CH_3CONH_2 or two internal rotors such as acetone CH_3COCH_3, dimethyl ether CH_3OCH_3 or methyl acetate CH_3COOCH_3 [1]

Internal rotors are present in any of the different phases leading the stellar and planetary formation from the molecular clouds to the star and its planets. Many complex molecules with internal rotors are not only detected in the interstellar medium (ISM), but also in comets, meteorites and asteroids. After a brief review of astrophysical internal rotors, I will show how high resolution spectra (mainly in the microwave, millimeter and sub-millimeter wave range) are achieved and what theoretical methods can be used to properly reproduce their spectra for astrophysics. Some recent results on an isotopologue of methanol will be given.

References

[1] I. Kleiner, “, Spectroscopy of interstellar internal rotors: An important tool for investigating interstellar chemistry”, ACS Earth and Space Chemistry, 3, 9, 1812-1842 (2019)

Low temperature gas-phase studies of collisional excitation, reactivity and cluster formation for astrophysical applications

I. R. Sims[1] and the CRESUCHIRP team

[1] *Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 Rennes, France*

Outside of artificially created laboratory environments, the coldest places in the Universe are to be found in dense interstellar clouds, and in particular pre-stellar cores, with temperatures as low as 5.5 K.[1] Observations reveal a rich inventory of molecules, evidence of a surprisingly active chemistry occurring under these extreme conditions. State-of-the-art astrochemical models often fail to predict accurately the observed abundances of these gas-phase (mainly) organic molecules, sometimes by many orders of magnitude. This is in part due to a lack of knowledge of important input parameters – the rate coefficients and in particular product branching ratios for formation and destruction reactions of these species, especially at low temperatures. Furthermore, transformation of radioastronomical detections into absolute abundances requires knowledge not only of radiative transitions but also collisional (de-) excitation by the most abundant species in these environments (hydrogen, helium, ..).

The CRESU technique (Cinétique de Réaction en Ecoulement Supersonique Uniforme or reaction kinetics in uniform supersonic flow)[2] employs carefully controlled expansions through Laval nozzles to recreate gas phase environments at such low temperatures. Using ultraviolet photolysis or infrared pumping combined with probes such as laser-induced fluorescence or chirped pulse Fourier transform millimeter wave spectroscopy, we can measure absolute cross sections or rate constants for a variety of reactive [2-4] and inelastic [5-7] molecular collisions to provide essential data for astrochemical models and astronomical observations. I will describe our latest measurements, including a focus on new measurements on collisional excitation and the determination of absolute rate constants for the formation of weakly bound complexes, the first stage in homogeneous nucleation, the key link between the gas-phase and condensed phases.

References

[1] A. Crapsi, P. Caselli, M.C. Walmsley, and M. Tafalla, 2007, A&A 470, 221.
[2] I. R. Cooke and I. R. Sims, 2019, ACS Earth Space Chem. 3, 1109.
[3] I. R. Cooke, D. Gupta, J. P. Messinger, and I. R. Sims, Benzonitrile as a Proxy for Benzene in the Cold ISM: Low-temperature Rate Coefficients for CN + C_6H_6, *Astrophys. J. Lett*. 891, L41 (2020).
[4] T. Guillaume, B. M. Hays, D. Gupta, I. R. Cooke, O. Abdelkader Khedaoui, T. S. Hearne, M. Drissi, and I. R. Sims, 2024, *J. Chem. Phys*. 160, 16, 204201.
[5] I. R. Cooke, I. R. Sims, in *Uniform Supersonic Flows in Chemical Physics: Chemistry Close to Absolute Zero Studied Using the CRESU Method,* A. Canosa, D. E. Heard, B. R. Rowe, Eds. (World Scientific, 2022), chap. 7, pp. 393-434.
[6] H. Labiad, M. Fournier, L. A. Mertens, A. Faure, D. Carty, T. Stoecklin, P. Jankowski, K. Szalewicz, S. D. Le Picard, and I. R. Sims, 2022, *Phys. Rev. A* 105, 6, L020802.
[7] B. M. Hays, D. Gupta, T. Guillaume, O. Abdelkader Khedaoui, I. R. Cooke, F. Thibault, F. Lique, and I. R. Sims, 2022, *Nature Chemistry* 14, 811.

Laboratory Spectroscopy of $^{13}CH_2DOH$ and its Astronomical Significance for Tracing the Formation of iCOMs

N. Sakai,[1] T. Oyama,[1] S. Zeng, [1] Y. Watanabe,[1, 2] and T. Sakai[1, 3]

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3Graduate School of Informatics and Engineering, The University of Electro Communications, Japan

Methanol, the most abundant saturated organic molecule in the interstellar medium, is considered the parent of many interstellar complex organic molecules (iCOMs). Its isotopologues are important tracers of chemical fractionation in star-forming regions and of the formation pathways of interstellar organic molecules. However, reliable studies require accurate laboratory spectroscopic data. In particular, precise transition frequencies and intensities are essential for deriving excitation conditions and column densities in astronomical sources[e.g. 1]. In this talk, I will present our latest laboratory measurements of methanol isotopologues obtained with the emission-type spectrometer SUMIRE[2], focusing on $^{13}CH_2DOH$[3], and further discuss the methanol isotopic ratios recently derived toward a young protostellar source.

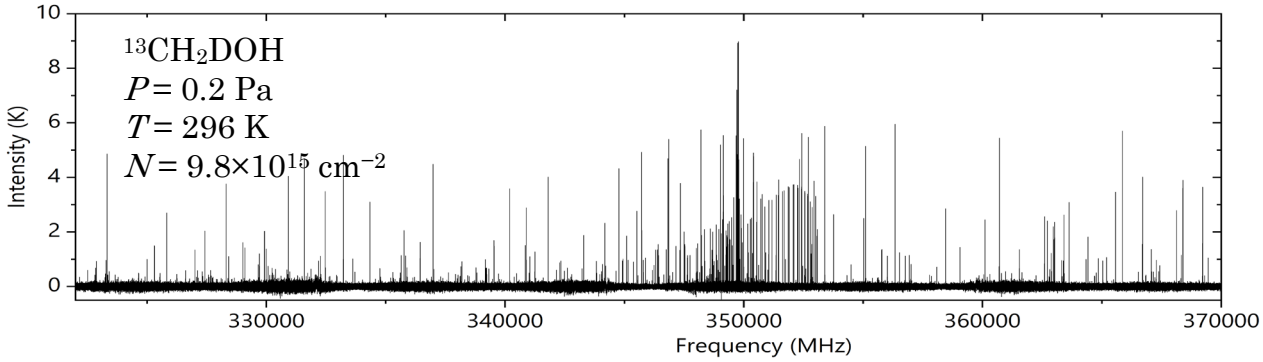

Figure 1: The spectrum of $^{13}CH_2DOH$ newly measured by SUMIRE in the ALMA-Band 7 frequency range.

References

[1] Oyama, T., Ohno, Y., Tamanai, A., Watanabe, Y., Yamamoto, S., Sakai, T., Zeng, S., Nakatani, R., and Sakai, N., 2023, ApJ, 957, 4.
[2] Watanabe, Y., Chiba, Y., Sakai, T., Tamanai, A., Suzuki, R., and Sakai, N., 2021, PASJ, 73, 372–393.
[3] Ohno, Y., Oyama, T., Tamanai, A., Watanabe, Y., Nakatani, R., Sakai, T., and Sakai, N., 2022, ApJ, 932, 101

Molecular Dynamics Simulations of Interstellar Chemical Reactions

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While exploration missions such as Hayabusa2 and recent advances in the ALMA radio telescope have accelerated the discovery of complex organic molecules relevant to life in the interstellar medium, it is essential to recognize that these molecules are the final products of a sequence of chemical processes. Identifying the specific reactions responsible for their formation in interstellar space is particularly challenging, as direct observations and measurements provide only limited insight into the underlying pathways. To address this issue, theoretical reaction dynamics simulations play a crucial role in elucidating the elementary processes, including reaction efficiencies and branching fractions.

Through collision simulations, we have investigated the thermal rate coefficients and branching fractions of several elementary reactions [1–7], focusing particularly on ion–molecule interactions of H_3^+ with ethylene (C_2H_4) [1], isocyanic acid (HNCO) [6,7], and methanol (CH_3OH). In the interstellar medium, H_3^+, widely regarded as a universal proton donor with strong proton affinity, plays a significant role in ion–molecule chemistry due to its high abundance. These reactions proceed efficiently in the absence of an entrance barrier and are primarily governed by strong attractive interactions such as charge–dipole and charge–induced dipole forces.

For the H_3^+ + HNCO branching reaction [6], the temperature dependence of the rate coefficients obtained from our collision simulations departs from the predictions of classical capture theory, including those based on the modified Arrhenius and Su–Chesnavich equations. This deviation arises because the interaction between H_3^+ and HNCO comprises both attractive and repulsive components.

In addition, we carried out collision simulations for the H_3^+ + HNCO, H_2D^+ + HNCO, HD_2^+ + HNCO, and D_3^+ + HNCO reactions to investigate the isotope effects [7]. In the H_2D^+ + HNCO and HD_2^+ + HNCO reactions, the abstraction of the lighter proton was preferred over that of the heavier deuteron at lower temperatures, owing to attractive interactions derived from the potential energy surface in these barrierless processes. These results suggest that, in barrierless reactions, the heavier deuteron–due to its greater mass and reduced mobility–is less likely to undergo efficient collisions with reactant molecules, thereby increasing the probability of proton abstraction relative to deuteron abstraction. This emphasizes the crucial influence of entrance channel dynamics in facilitating deuterium enrichment at low temperatures. The enrichment observed is attributed to a non-equilibrium isotope effect.

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Ion-molecule routes towards cycles in TMC-1

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The cyclopentadiene molecule (c-C_5H_6) is considered a fundamental building block in the formation of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM). [1] The synthesis of PAHs from simpler precursors is known as the "bottom-up" approach, which, so far, has been dominated by reactions between organic radicals. However, this theory fails when it comes to explaining the formation of the smaller cycles themselves (cyclopentadiene, benzene, etc.), and ion-molecule reactions have become promising candidates to explain the synthesis of these molecules.

In this work, we study the reaction between ethylene (C_2H_4) and the propargyl cation ($C_3H_3^+$) under the conditions of the ISM using *GRRM* [2], which automates the exploration of reaction pathways. Combined with DFT calculations, it allows us to map and understand the Potential Energy Surface (PES) of the system. Furthermore, we perform a kinetic analysis by computing the rate constants and branching ratios for these competing processes, so that they can be introduced into our astrochemical model and see the consistency of our calculations with respect to the observed data. This study reveals that the formation of the cation c-$C_5H_7^+$ by radiative association, which could eventually lead to cyclopentadiene, is not favoured, contrary to expectations. We also report the fragmentation of the system into c-$C_5H_5^+$ and H_2, in agreement with literature [3] and identify an additional channel that produces $C_3H_5^+$ and C_2H_2. The presence of these bimolecular reaction channels enables the exploration of new potentially relevant reaction pathways.

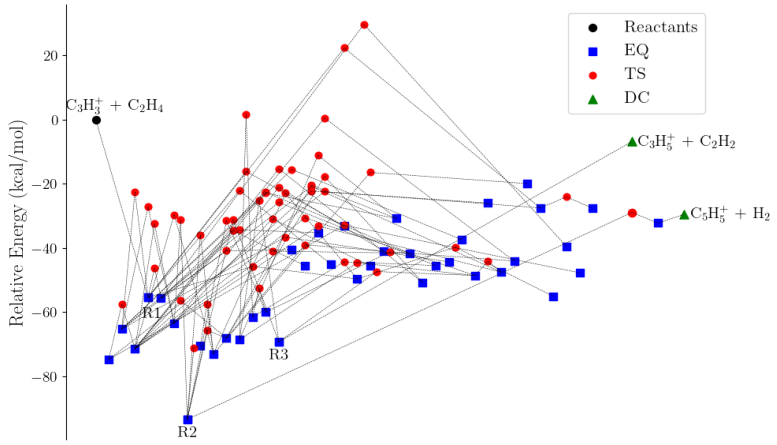

Figure 1: Reaction network of the C_2H_4 + $C_3H_3^+$ reaction built with automated path search and quantum chemistry calculations.

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Collisional excitation of H_2CO deuterated isotopologues by molecular hydrogen

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The deuteration fractionation is the molecular abundance ratio of a given hydrogenated molecule and its deuterated counterpart. It is a useful quantity to trace the physical and cheminal evolution of star-forming regions [1]. The interpretation of observational spectra through radiative transfer modeling is the knowledge base for determining these abundances. Accurate rate coefficients, induced by collisions with H_2, are required to interpret spectra of these deuterated species. In this work, we focus on the deuterated isotopologues of formaldehyde (H_2CO), being an important precursor to the formation of interstellar complex organic molecules such as methanol [2]. We report the first rate coefficients for rotational transitions of HDCO and D_2CO in collision with both *ortho*- and *para*-H_2. Based on an accurate five-dimensional potential energy surface [3], collisional cross sections and rate coefficients are computed with the time-independent close-coupling method over a temperature range of 5–300 K. Our calculations include the first 60 energy levels of *ortho*-D_2CO and *para*-D_2CO; and the first 100 levels of HDCO. General propensity rules are discussed. We found a significant isotopic substitution effect in the rate coefficients. The present collisional data have found good agreement with pressure broadening experiments. The impact of the new set of collisional data will be investigated in radiative transfer modeling of the HDCO and D_2CO emissions seen toward star-forming sources.

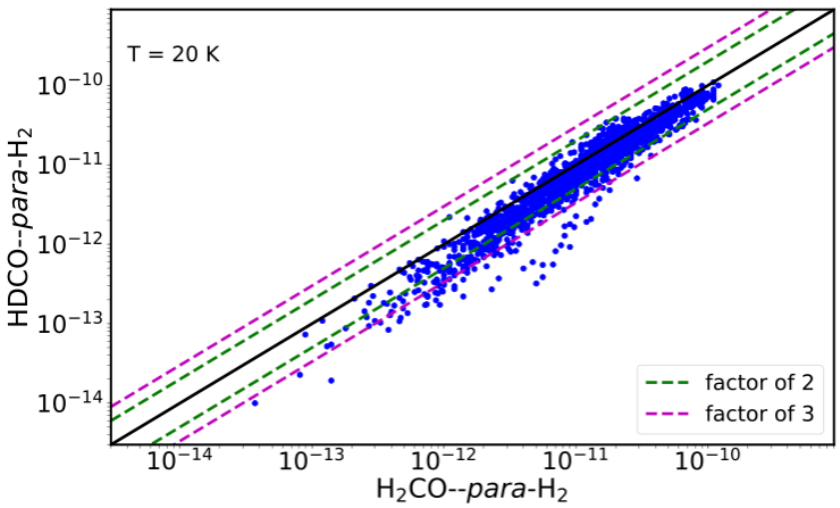

Figure 1: Systematic comparison of rate coefficients at 20 K between H_2CO and HDCO transitions induced by collisions with *para*-H_2.

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Astrochemical model: the good, the bad, and the ugly

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Astrochemical models are based on many uncertain physical and chemical data but also on uncertain formalisms of grain surface chemistry. Over the years, these models have been strongly improved to be more realistic. Some of the model predictions can reproduce general trends, for instance for observed ice composition, but not the detailed abundances. There are two main new types of processes that are currently strongly debated in the community, which are the non-diffusive chemistry and the radiolysis.
Non-diffusive chemistry is assumed to happen when two radicals are formed close by on the surface or in the bulk, they can react together without diffusing. Such process increases the efficiency of the formation of complex organic molecules or any molecules which diffusion is limited. Radiolysis is the chemistry driven by the interaction of cosmic-ray particles with ices. The collision of icy molecules with ices dissociates molecules and produces supra-thermal species.
I will present the latests developments of the Nautilus astrochemical model included those two processes. Each of the new features will be tested and compared to gas-phase and ice observations in cold cores.

Study on chemical evolution during molecular cloud formation based on 3-dimensional MHD simulations

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Molecular cloud formation is a pivotal process for both star formation and astrochemistry. One of the key triggers for cloud formation is the interstellar shock wave. Previous studies performed 3 dimensional (3D) magnetohydrodynamics (MHD) simulations of converging flows of atomic gas with reduced chemical networks (~ 10 chemical species). They revealed that forming molecular clouds have complex structures and turbulent mixing is essential for H_2 formation (e.g. [1][2]). Since molecular clouds are observed with various molecular lines of emission or absorption, we need to understand how these molecules form. However, it is computationally too expensive to solve 3D MHD and a detailed chemical network simultaneously.

We solve this problem by a two-step procedure. Firstly, we conduct 3D MHD simulations of converging flows with a reduced chemical network. We input tracer particles that move along the local velocity field and obtain the temporal variation of physical parameters (e.g., gas density) along their trajectories. Secondly, we calculate a detailed chemical network (~ 500 chemical species) along with them. We also calculate molecular abundances at each position with the physical parameters fixed at the final timestep of the 3D simulations, which we refer to as "static model" in contrast to the dynamical model stated above.

As for species in the reduced network, our result is consistent with previous studies; e.g. H_2 is formed in dense clumps and transported to lower-density regions due to turbulence, while CO exists only in dense regions. Results of the detailed chemical network and reduced network show reasonable agreement, which confirms the validity of our method. Abundances of various molecules that are used in observations, e.g. CCH and OH, are quite similar between the dynamical model and the static model in regions of $n < 10^3$ cm^{-3}, only if we fix the H_2 abundance of the static model referring to the dynamical model. This is possible since the chemical timescale is short, except for H_2 formation, which reflects the density variation along the flow. At higher densities, however, the chemical timescale is long, and ice formation becomes important.

We compare the column densities of CH, CCH, OH, and HCO^+ with observations of diffuse molecular clouds. We find that the column densities of CH, CCH, and OH show linear correlations with those of H_2, which supports the empirical relation used in the observations. On the other hand, the column densities of HCO^+ show non-linear dependence on the H_2 column densities, reflecting the difference in HCO^+ formation paths in CO-poor and CO-rich regions.

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Catalytic Pathways to Polycyclic Aromatic Hydrocarbons in AGB Stellar Envelopes

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the interstellar medium (ISM) and play a vital role in physical and chemical processes taking place in the ISM. Their primary formation site is believed to be the envelopes of asymptotic giant branch (AGB) stars, where conditions favor PAH growth. While gas-phase pathways for the formation of the first aromatic ring and subsequent growth have been extensively studied, the role of catalytic surfaces such as silicon carbide (SiC) and carbonaceous dust remain uncertain. Incorporating catalytic reactions could significantly alter predicted PAH abundances, size distributions, and their evolution in stellar environments.

In this work, we develop an astrochemical model to quantify PAH formation in AGB star envelopes. The model combines a high-temperature gas-phase reaction network, derived from literature data, with newly implemented surface reactions. These catalytic pathways involve sequential acetylene (C2H2) attachment to dust surfaces, forming C4H4 and C6H6 intermediates, followed by cyclization and desorption of benzene (C6H6). The kinetic parameters of surface reactions are determined via molecular dynamics simulations. The model self-consistently couples PAH chemistry with dust growth, treating SiC grains as nucleation seeds for carbonaceous accretion (e.g., acetylene and PAHs) and incorporating grain coagulation dynamics through a system of differential equations.

We apply the model to the dust formation region of the AGB star IRC+10216, accounting for periodic shock waves induced by stellar pulsations. Simulations comparing scenarios with and without catalytic surface reactions demonstrate that surface chemistry enhances PAH production and modifies their size distribution. Our results underscore the necessity of including catalytic pathways in astrochemical models to improve the accuracy of PAH abundance predictions in stellar envelopes.

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Isotopomer-Specific Carbon Isotope Ratio of Complex Organic Molecules in Star-Forming Cores

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The recent observation of complex organic molecules (COMs) in interstellar ices by the James Webb Space Telescope (JWST), along with previous gas-phase detections, underscores the importance of grain surface and ice mantle chemistry in the synthesis of COMs. In this study, we investigate the formation and carbon isotope fractionation of COMs by constructing a new astrochemical reaction network that distinguishes the position of ^{13}C within species (e.g., H^{13}COOCH3 and HCOO^{13}CH3 are distinguished). We take into account the position of ^{13}C in each species in gas and solid phase chemistry. This new model allows us to resolve isotopomer-specific ^{12}C/^{13}C ratios of COMs formed in the star-forming cores. We consider thermal diffusion-driven radical-radical reactions on the ice surface and non-thermal radiolysis chemistry in the bulk (surface + mantle) ice. We find that carbon isotope fractionation of the functional groups in COMs appears through both non-thermal radiolysis in cold environments and thermal diffusion in warm environments, depending on the COMs. In particular, COMs containing methyl groups show isotopomer differences in ^{12}C/^{13}C ratios that reflect their formation pathways and environments. These isotopomer-resolved fractionation patterns provide a diagnostic tool to probe the origins of COMs in star-forming cores. Our results suggest that future comparisons between high-sensitivity isotopic observations and isotopomer-specific models will be helpful for constraining the relative contributions of thermal and non-thermal formation processes of COMs.

c-C_3H_2 deuteration towards pre-stellar and starless cores in the Perseus Molecular Cloud

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Deuterium enrichment, which leads to higher D/H ratios than those in the local Interstellar Medium (ISM), occurs efficiently in cold, dense pre-stellar cores due to low temperatures and CO freeze-out. These conditions favor the formation and survival of H_2D^+, a key agent in transferring deuterium to other molecules [1,2]. This study investigates the deuterium fractionation of the small cyclic molecule cyclopropenylidene (c-C_3H_2) and its deuterated forms (c-C_3HD and c-C_3D_2) in pre-stellar cores within the Perseus molecular cloud. Cyclopropenylidene, being a small and early-type molecule with known deuterated variants, is ideal for probing deuteration processes in the gas phase [3].

The D/H and D_2/D ratios of c-C_3H_2 are derived from observations taken with the Yebes 40m, ARO 12m, and IRAM 30m telescopes towards Perseus starless and pre-stellar cores and compared to pre-stellar and starless cores in other molecular clouds. Moreover, the ortho-to-para ratios of c-C_3H_2 are also derived.

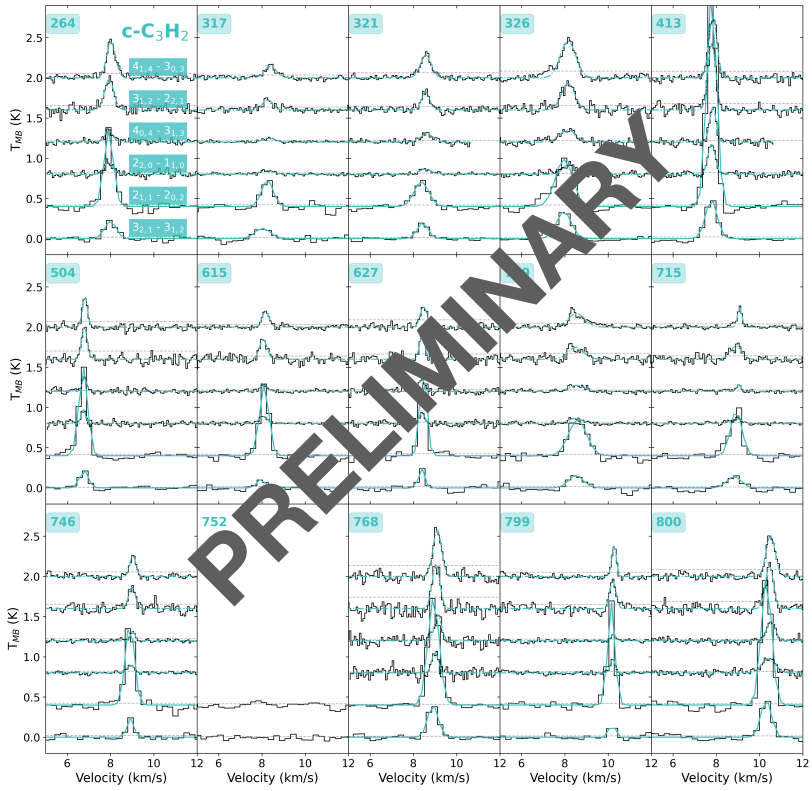

Figure 1: c-C_3H_2 detections towards fourteen Perseus molecular cloud cores.

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The trail of sulphur: from molecular clouds to life (SUL4LIFE)

Asunción Fuente

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Sulfur is the tenth most abundant element in the Universe and one of the six essential elements for life. It plays a critical role in biological systems and has been proposed as a key catalyst in the formation of amino acids in the interstellar medium. Sulfur is also fundamental to our understanding of the physical and chemical evolution of molecular clouds and star formation. Along with carbon, it is a major electron donor in the diffuse and translucent phases of the ISM, influencing the ionization balance and chemistry. However, unlike other key elements such as carbon and oxygen, the gas-phase abundance of sulfur remains uncertain by several orders of magnitude, particularly in dense molecular clouds where more than 90% of the expected sulfur is unaccounted for.

This significant gap in our understanding stems from both observational and theoretical challenges. Observationally, sulfur-bearing species commonly detected in millimeter surveys—such as CS, SO, and SO2—represent only a fraction of the possible sulfur reservoirs. Crucial species like SH, SH+, and H2S are difficult to detect and are often excluded from systematic studies. Furthermore, atomic sulfur, which may constitute a major component of the sulfur budget, is particularly challenging to observe in cold, quiescent environments due to its excitation conditions.

The SUL4LIFE project addresses these challenges by combining different approaches: (1) a comprehensive database of multi-wavelength observations—including recent JWST, ALMA, and NOEMA data—targeting a wide range of sulfur-bearing species; (2) upgrading chemical models with *ab initio* theoretical calculations to derive accurate reaction rates and laboratory experiments to constrain critical parameters such as the photodesorption efficiencies of sulfur species from dust grains; and (4) advanced 3D magnetohydrodynamical simulations with coupled gas-grain chemistry (chemo-MHD) to follow the chemical evolution of sulfur from diffuse clouds to planet-forming disks.

We present most recent results demonstrating the transformative potential of this approach. These include JWST observations of atomic sulfur in the Orion Bar PDR, a survey of H2S in hot corinos, new experimental measurements on SO2 photodesorption that clarify its role in UV-irradiated environments, and the detection of reactive ions SH+ and CO+, as well as S2H—the only molecule with a disulfide bond detected thus far—in the Horsehead Nebula. Together, these findings offer a new paradigm for sulfur chemistry in space and pave the way toward a complete and coherent picture of sulfur journey from clouds to life-bearing worlds.

Surface Chemistry of CN Radicals on Interstellar Ices: A Route to Molecular Complexity

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Nitriles are fundamental intermediates in prebiotic chemistry and are thought to have played a pivotal role in the chemical evolution that led to the origin of life in the Universe. In this contribution we present our latest DFT simulations on the surface reactivity of CN radicals, specifically amorphous water and carbon monoxide ices [1, 2].

Our results show that CN radicals, once adsorbed onto dust grain surfaces, exhibit high reactivity under cold interstellar conditions and can follow multiple reaction pathways that contribute to increasing molecular complexity budget of N-bearing species. We identify viable mechanisms for the formation of several astrochemically relevant species, including HCN, HNC, CH_3CN, CH_3NC, HOCN, HCOCN, $CH_3C(OH)NH$ (acetimidic acid), and a potential connection to CH_3CONH_2 (acetamide). The way CN radicals interact with the ice surface plays a crucial role in the emergence of many of these products, highlighting the active chemical role that interstellar ice matrices can have towards molecular complexity.

Finally, we have also investigated the hydrogenation pathways of HCN and HNC, demonstrating how these nitriles can be converted into methanimine and methylamine through reactions with both atomic and molecular hydrogen. We further examine the implications of these pathways for the formation of their deuterated analogues. Our findings are discussed in the context of existing literature, providing new insights into the role of grain-surface chemistry in shaping molecular complexity during astrochemical evolution.

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Theoretical studies of interstellar isomerism: formic acid and beyond

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In recent years, astrochemistry has entered what can truly be described as a golden era, driven by an unprecedented number of new molecular detections. A defining feature of these discoveries, compared with earlier ones, is the remarkable increase in molecular complexity. For instance, the detection of large polycyclic aromatic hydrocarbons (PAHs) [e.g., 1, 2] and complex organic molecules (COMs) [3, 4] has introduced significant challenges for interpreting their chemistry, both from theoretical and experimental perspectives. A natural consequence of this greater molecular complexity is the emergence of a large variety of isomers, species that share the same chemical formula but differ in their spatial arrangement. In this talk, I will discuss our recent efforts to address interstellar isomerism, focusing on one of the most studied cases: formic acid (HC(O)OH; Figure 1), a molecule on which we have carried out extensive work [5]. I will also introduce our new protocol designed to tackle the challenges posed by the increasing structural diversity of interstellar molecules. This approach combines automated exploration of the reactive landscapes of different isomers with the development of isomer-inclusive astrochemical models, paving the way toward a more comprehensive understanding of interstellar chemistry.

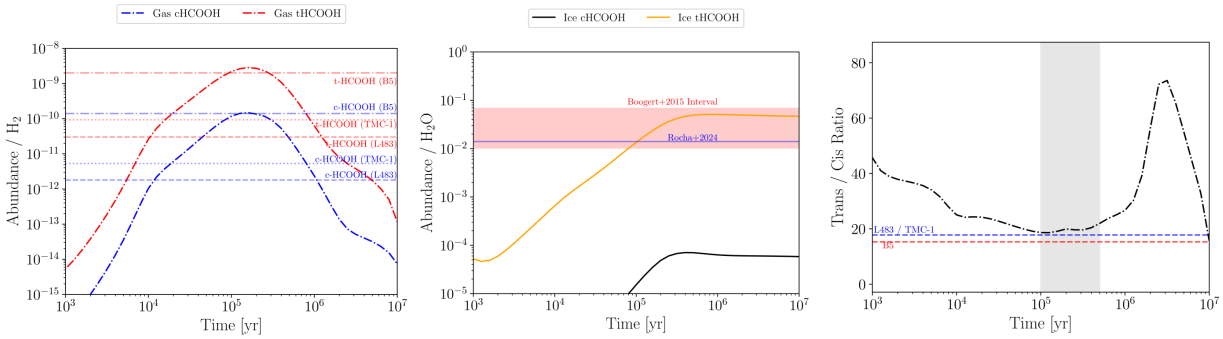

Figure 1: Isomer inclusive astrochemical models for the *cis* and *trans* formic acid. Left- Gas phase abundances compared with the abundances found in B5 [6], L483 [7] and TMC-1 [5]. Middle- Ice abundances in comparison with the literature [8,9]. Right- Gas phase *trans/cis* ratios.

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Theoretical investigation of low-energy glycine formation and spectral masking in star-forming regions

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The search for amino acids in the interstellar medium (ISM) has long motivated studies on the astrochemical origins of life. While glycine, the simplest amino acid, has been identified in meteorites and comets[1–3], its unambiguous detection in star-forming regions remains elusive[4,5]. In this presentation, I will introduce a theoretical approach where we employ quantum chemical simulations to investigate glycine formation on bare silicate grains—uncovered after water-ice sublimation during warm stages (>150 K) of star formation. Our results show that the classical Strecker-type synthesis is hindered by high activation barriers, rendering it inefficient under astrophysical conditions. Instead, we identify a low-energy, surface-induced neutral pathway involving formaldehyde, CO, and NH_3, which yields glycine in a spontaneous, exoergic process on forsterite (Mg_2SiO_4) surfaces. The formed glycine is strongly stabilized (binding energies >70 kcal mol^{-1}), preventing thermal desorption and favoring retention in dust aggregates and parent bodies. Moreover, vibrational analyses reveal that surface-bound glycine exhibits suppressed and shifted IR features compared to its gas-phase counterpart, providing a possible explanation for its persistent non-detection in astronomical surveys. These findings uncover a silicate-mediated route for glycine formation that links interstellar chemistry with the inventory of prebiotic organics delivered to planetary systems.

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Exploring Nondiffusive Pathways to Acetaldehyde Formation in Interstellar Ices: Insights from Computational Studies

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The detection of acetaldehyde (CH_3CHO) in cold astrophysical environments, such as dark clouds and prestellar cores, challenges standard grain-surface chemistry models, which rely on radical diffusion. At temperatures of ∼10 K, radical mobility is extremely limited, making these pathways inefficient. To explain the presence of iCOMs in these cold cores, various chemical mechanisms have been proposed, including those based on nondiffusive pathways [1-6]. In this work, we present a computational investigation of a nondiffusive three-body (3-B) formation mechanism for CH_3CHO on interstellar water ices. The mechanism involves the hydrogenation of CO to form HCO in close proximity to a CH_3 radical, enabling immediate reaction without requiring diffusion. Using static quantum chemical calculations, we characterized the potential energy surface, including competing channels such as hydrogen abstraction. To assess the efficiency of the mechanism under realistic conditions, we performed *ab initio* molecular dynamics simulations at 10–25 K on a crystalline water-ice surface. Our results show that CH_3CHO can form via this nondiffusive pathway, though alternative products (CH_4 + CO or stable HCO) are also possible, leading to a distribution of outcomes. These findings highlight the importance of nondiffusive chemistry for explaining iCOM formation in cold interstellar environments.

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Surface Hydrogenation of Interstellar Polyynes: Bridging the gap between observations of unsaturated carbon chains in TMC-1 and detection of linear alkanes in comet 67P

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Star systems similar to our Solar systems are formed from interstellar clouds of gas and dust. Prior to the formation of a protostar the temperature in the densest region of such cloud drops to as low as 10 K. The depletion of atoms and simple species from the gas-phase onto the dust surface results in rich chemistry triggered by various reactions between the accreting species. These ice coated dust grains provide the initial chemical inventory for the formation of various celestial bodies during the later stages of star formation [1].

This work is motivated by the recent breakthroughs in the detection of unsaturated carbon chain species in TMC-1 by QUIJOTE line survey [2] and the detection of saturated linear alkanes in the come of the comet 67P/Churyumov-Gerasimenko by the ESA's Rosetta mission [3]. We present the recent experimental results that provides the chemical link between these independent observations. We propose that under the conditions resembling those of molecular clouds, various unsaturated and semi-saturated carbon chains can participate in hydrogenation reactions on the surface of dust grains producing saturated linear alkanes as well as a number of other linear aliphatic organic compounds [4, 5, 6]. We also discuss the astrobiological implications of our results, the connection of our results with the detection of long saturated aliphatic chains in samples returned from asteroid Ryugu by Hayabusa2 mission, and the possibility to identify solid alkanes with JWST.

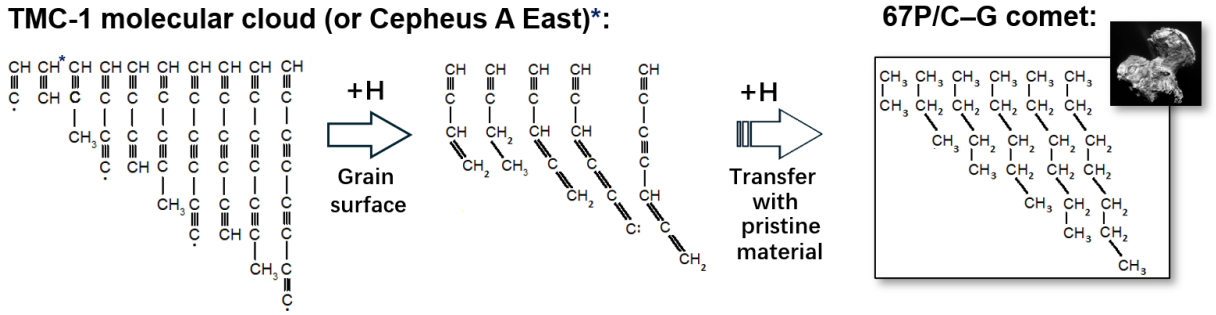

Figure 1: Schematic representation of the overall suggested mechanism on the example of polyynes hydrogenation. Various polyynes observed in dark clouds (e.g., TMC-1) are presented in the left part of the reaction scheme. Saturated alkanes observed at a comet 67P/Churyumov-Gerasimenko are shown in the right part of the scheme. The high saturation degree of hydrocarbons detected at comet 67P hints at their formation through surface hydrogenation mechanisms.

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The first detection of sulfur atom behavior on the silicate surface

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In molecular clouds (MCs), there is a long-time unsolved issue called "missing sulfur", that the observed abundance of S-bearing molecules in both gas and solid phases cannot match the cosmic abundance of S (~10^{-5} relative to H) [e.g., 1, 2]. The main reservoir of S remains unknown. Several experiments on the photolysis of ice containing H_2S have been performed and have found the synthesis of S-bearing molecules, but these cannot explain the missing sulfur issue. Although atomic S^+ ion was assumed to accumulate onto dust grains, being locked on the surface to cause the S depletion [3], no one can really verify this hypothesis. To clarify the fate of sulfur on dust grains, experiments for monitoring the behavior of S atoms on the materials of dust grains are highly desirable. However, a direct measurement of the S atom is difficult through the conventional experimental methods, such as IR spectroscopy and mass spectrometry.

In this work, we focus on the S atom itself using a recently developed method, PSD-REMPI, which has been applied to detect the atoms and radicals successfully [4, 5]. We monitor the behavior of S atoms on the silicate (Mg_2SiO_4) and amorphous solid water surface during the annealing process. By comparing the ratio, how many S atoms remain can be derived. We found that the S residue can remain in atomic form and survive even at room temperature, which shows a refractory property. In addition, the sulfur dimer S_2 is also detected, which is the main contribution of the S loss during annealing activities. These results could give evidence that embedded S atoms in the dust grain surface may be the source of missing sulfur in MCs

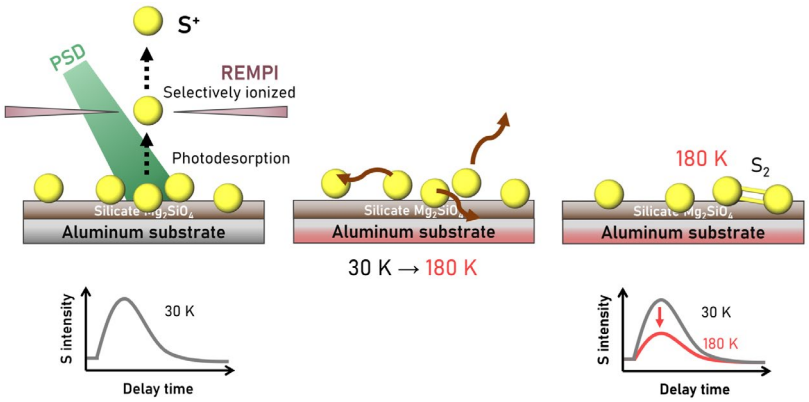

Figure 1: The cartoon figure of the PSD-REMPI method and experimental procedure.

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Chemical complexity driven by H_2 and carbon atoms: formation of sulfur-bearing molecules H_2CS and CH_3SH

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Molecular complexity in space develops through a combination of gas-phase and grain-surface reactions. The latter provide catalytic surfaces and efficient energy dissipation under the cold, dense conditions of molecular clouds. Although more than 330 molecules have been detected, mainly via rotational spectroscopy with facilities such as ALMA and NOEMA, recent JWST observations reveal that a rich chemistry is already present in pristine interstellar ices[1].

Despite extensive studies on atomic hydrogen addition, the role of molecular hydrogen (H_2) —the most abundant molecule in the universe—remains poorly understood. Theoretical work suggests that highly reactive carbon atoms could activate H_2 and open new non-energetic formation pathways for complex organic molecules (COMs)[2], but experimental tests are scarce.

We explore these routes for sulphur chemistry by investigating the formation of thioformaldehyde (H_2CS) and methanethiol (CH_3SH). Experiments were performed with the cryogenic ultra-high-vacuum setup SURFRESIDE[3], which co-deposits atomic (H/D, C) and molecular species onto cold gold substrates, monitored in situ by reflection-absorption infrared spectroscopy and analysed during warm-up by temperature-programmed desorption mass spectrometry.

These experiments provide new laboratory constraints for sulphur chemistry in cold cores and have implications for deuteration ratios and gas-phase abundances at later stages of star formation.

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X-ray Irradiation of H_2S-containing Interstellar Ice Analogues

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Observations show that gaseous sulfur in dense molecular clouds is depleted by three orders of magnitude relative to its cosmic abundance [1], pointing to an unseen reservoir. A plausible explanation is that sulfur is sequestered in icy dust-grain mantles and chemically reprocessed by energetic radiation [2]. However, this hypothesis lacks strong observational support—only OCS and tentatively SO_2 have been detected in interstellar ices so far [3]. To test this scenario, we irradiated H_2O:H_2S and CO:H_2S ices at 15 K with soft X-rays (150–1200 eV) on beamline BL08B at the National Synchrotron Radiation Research Center. Approximately 80% of H_2S was destroyed during the initial stages, leading to the formation of new sulfur-bearing products.

In H_2O-rich matrices, the dominant products are H_2S_2, SO_2, and HSO_4^-, whereas in CO-rich matrices, H_2S_2, OCS, CS_2, and SO_2 are mainly formed. In H_2O-rich ices, both reactant destruction and product formation proceed with larger cross sections, while in CO-rich ices the corresponding cross sections are smaller. Varying the mixing ratio further reveals that the relative abundance of components controls both the branching ratios and efficiencies of the reaction channels. These findings underline the critical role of the ice environment in shaping sulfur chemistry and support processed interstellar ices as potential reservoirs of the "missing" sulfur.

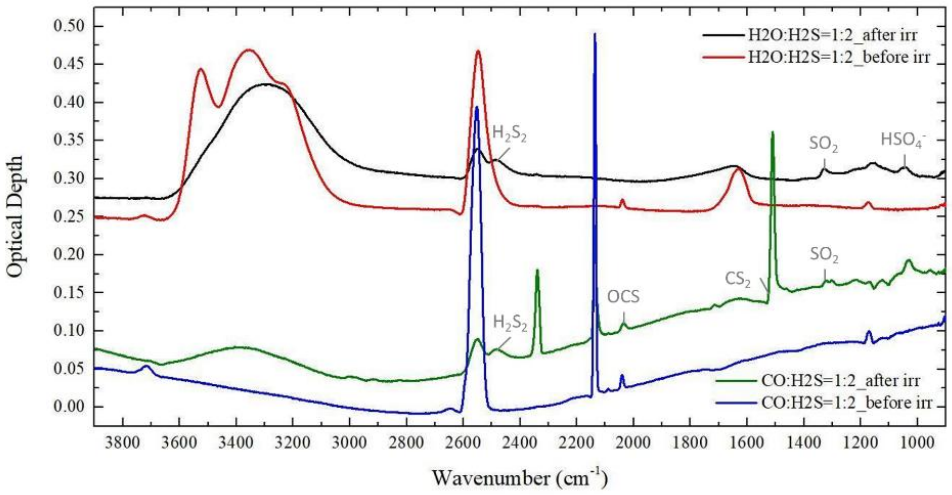

Figure 1: Mid-IR spectrum of H2O:H2S and CO:H2S ice mixtures before and after Soft-X-ray irradiation.

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Nucleobases in Bennu, Ryugu, and carbonaceous meteorites

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The presence of all canonical nucleobases (cytosine, uracil, and thymine, which are classified as pyrimidine bases, and adenine and guanine, which are classified as purine bases) in extraterrestrial materials has been recognized recently [1]. Given that organic molecules delivered by extraterrestrial materials may have played a pivotal role in chemical evolution on the early Earth [2], understanding the distribution of nucleobases in various kinds of extraterrestrial materials is a prerequisite for deciphering chemical evolution toward the emergence of genetic functions in that environment.

We had precious opportunities to analyze nucleobases in primitive materials of the Solar System collected at the carbonaceous asteroids (162173) Ryugu and (101955) Bennu by the Hayabusa2 and OSIRIS-REx missions, respectively, through the initial analyses of these samples, as well as JAXA's 3rd Announcement of Opportunity. In the present study, we will present the distribution of canonical nucleobases in Bennu and Ryugu samples and various classes of carbonaceous meteorites and discuss their formation pathways in relation to the concentration of ammonia (NH_3) in each parent body.

Samples: Samples returned from the asteroids Ryugu (A0106, C0107, A0480, C0370) and Bennu (OREX-800044-101, OREX-800107-108) were used for the analysis of nucleobases [3-5]. In addition, various classes of carbonaceous meteorites, including Murchison (CM2) [6], Yamato (Y)-791198 (CM2), Y-793321 (CM2), Aguas Zarcas (CM2), Orgueil (CI1), Oued Chebeika 002 (CI1), Kolang (CM1/2), Asuka-881828 (CR2), Y-002540 (CR2), and Tarda (C2-ung), were also analyzed. Detailed analytical conditions are referred to refs [1,3-7].

Results: All canonical nucleobases were detected in both Ryugu (A0480 and C0370 [4]) and Bennu samples (OREX-800044-101, OREX-800107-108 [5,8]). The distribution of nucleobases in carbonaceous meteorites varied between samples; except for Y-793321, Y-002540, Kolang, and Oued Chebeika 002, all canonical nucleobases were detected. These results strongly indicate that nucleobases are common in the primitive materials of the solar system. In addition to canonical nucleobases, various kinds of non-canonical nucleobases, such as isocytosine and hypoxanthine, were detected in the same extracts from the return samples and meteorites. The abundance of purine nucleobases relative to that of pyrimidine ones (Pu/Py) detected in the samples seems to have correlations with their NH_3 concentrations: CMs showed high Pu/Py (>1.7, except for Y-793321) with low NH_3 (<2 μmol g^{-1}), CRs moderate NH_3 (~6 μmol g^{-1}) with low Pu/Py (<0.2), and C2-ung Tarda very high NH_3 (49 μmol g^{-1}) with very low Pu/Py (0.1). We found that CIs, Bennu, and Ryugu are distributed in relatively low Pu/Py (<~1 or less) with the wide variations of NH_3 (0.2-43 μmol g^{-1}) regions, suggesting that the availability of NH_3 in each parent body may be one of the key factors to constrain the observed differences in nucleobase distributions.

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Laboratory investigation of shock-induced processing of cosmic carbon dust analogues

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Astrophysical shocks participate to the chemical evolution of the interstellar medium. These violent events strongly alter dust grains and lead to the release of new molecular species in the gas phase. Only a few studies on the shock processing of cosmic analogues have been conducted so far.

Shock-induced processing of dust components can be investigated using a shock tube[1,2], a tool commonly employed for fast thermal processing of gases and materials.

The destruction of the exposed carbon rich samples - such as fullerenes, polycyclic aromatic hydrocarbons and hydrogenated amorphous carbons - can be studied *in situ* and in real-time by optical emission diagnostics. Some further insights can be provided by molecular dynamics simulations. The analysis of volatiles collected after the shock can bring some additional support in the outlined scenario.

To get a more complete picture, the solid residues can be examined as well by a variety of analytical techniques including X-ray diffraction, transmission electron microscopy, Raman spectroscopy, and infrared spectroscopy, to help decipher the physical and chemical nature of the products.

These experiments provide some complementary insights into the lifecycle of carbon in space. This work illustrates the potential of shock tubes for laboratory astrophysics.

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Astrochemistry – The Final Frontier

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Over the last decade, ice-coated interstellar nanoparticles emerged as molecular factories in the synthesis of complex, often biorelevant organics in cold molecular clouds and in star-forming regions. An intimate understanding of the fundamental reaction mechanisms generating these nanoparticles along with complex organics on their surfaces in deep space requires new knowledge not only on fundamental gas-phase reaction pathways to carbonaceous nanostructures, but also on the processing of low temperature ices by (non)ionizing radiation present even deep inside cold molecular clouds.

This talk provides an overview on recent advances in gas phase molecular beams studies and novel surface science experiments of particular importance to the formation of astrobiologically important molecules within interstellar ices. These studies are aimed to decipher the underlying reaction dynamics and kinetics leading to polycyclic aromatic hydrocarbons (PAHs) as fundamental molecular building blocks and precursors to carbonaceous nanoparticles (gas phase) [1-4] and to complex organics (surface science) in deep space [5-8], many of which should not exist according to classical textbook knowledge. Novel developments focus on isomer selective vacuum ultraviolet photoionization (PI) techniques coupled with reflectron time-of-flight mass spectrometry (ReTOF-MS) exploiting single photon ionization in combination with the detection of functional groups via infrared spectroscopy (FTIR) with vacuum ultraviolet light generated by four-wave mixing and from synchrotrons. Facile low-temperature routes to complex aromatics signify a fundamental shift in the perception that aromatics can be only formed under high-temperature conditions on electronic ground state surfaces with novel mechanisms comprising excited state dynamics, submerged barriers, and unconventional concerted reactions between aromatic radicals.

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Cosmic-ray bombardment of icy troilite (FeS)

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The chemical evolution of sulfur during star and planet formation is not well understood due to the "missing sulfur problem"— where sulfur is often found to be depleted by 1–2 orders of magnitude in molecular clouds and protoplanetary disks relative to its cosmic abundance. A likely hiding place for the missing sulfur is in the solid phase, where sulfur may be trapped in refractory dust grains and/or within molecules condensed as ice.

One underexplored possibility is that the missing sulfur may be in the form of minerals, especially iron sulfides, which are ubiquitous in solar system materials and are of immense astrobiological interest. Troilite, an iron sulfide of the stoichiometric form FeS, has been found in asteroids and meteorites and is the primary form of sulfur found in chondrites [1]. Solid FeS is abundant in interplanetary dust particles (IDPs) within our Solar system [2], and has been suggested to explain infrared spectra of carbon-rich planetary nebulae and young stellar objects [3,4]. If present in the dust, FeS may play a role in the formation of sulfur-bearing molecules and in catalyzing reactions.

Our initial experiments aim to explore whether FeS could play a role in the formation of organosulfur molecules in interstellar or planetary ices. Ices were deposited on cryogenically cooled FeS substrates and irradiated with a 4-He+ ion beam (1—6 MeV) to investigate the release of sulfur, and its interaction with the molecules that compose the ice upon energetic processing. The experiments were conducted at the AStrochemical & Planetary materials IRradiation Experiment (ASPIRE) facility, a new end-station being developed at TRIUMF, Canada's particle accelerator centre. The residues from these experiments were collected and analyzed using liquid chromatography high-resolution mass spectrometry (LC-HR-MS) techniques. I will discuss the new facility at TRIUMF, our initial results from these experiments, and our plans for further investigating the role of "invisible" minerals in interstellar chemistry. I will highlight the prospect for future observations of interstellar iron sulfides and their wider astrobiological significance.

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Mass spectrometric analysis of sublimation products from silicate dust

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Molecules containing refractory elements have been detected along various lines of sight in star-forming regions. SiO is among the most important species, whose detection in molecular outflows has been commonly interpreted by sputtering of silicate dust in shock waves. Recently, SiO was also detected in the innermost disk of a massive protostar in the high-resolution observation using ALMA [1]. The possible production mechanisms of SiO in the inner disk include both non-thermal and thermal pathways: sputtering under shocks or radiation and sublimation under high temperatures ($\gtrsim$1500 K). The latter is of particular interest because this might be related to sublimation of planetary materials of the solar system recorded in primitive meteorites. However, it has been controversial whether the sublimation of silicate materials produces SiO [2,3]. In this study, we aimed to experimentally identify the sublimation products of forsterite (Mg_2SiO_4), which is a representative silicate mineral likely constituting dust.

We developed a new ultra-high vacuum apparatus consisting of a resistive heating system made of refractory metals and a quadrupole mass spectrometer with an electron-impact ionization source. Using this apparatus, we heated powdered forsterite at controlled temperatures (<2300 K) and detected the sublimated gas species under collision-free conditions. We identified Mg, SiO, and O as major products and MgO as a minor product (MgO/Mg~10^{-2}-10^{-1}) of sublimation of forsterite (Fig. 1). The Mg:SiO ratio was ~2:1, suggesting that the major sublimation reaction is Mg_2SiO_4 (s) → 2Mg (g) + SiO (g) + 3O (g). The identified products are different from the theoretical predictions based either on thermochemical calculations or kinetic experiments. The present detection of SiO as a major product indicates that SiO observed in the inner disk possibly traces dust sublimation, and thus, may be related to the sublimation of solar system materials studied through meteorites.

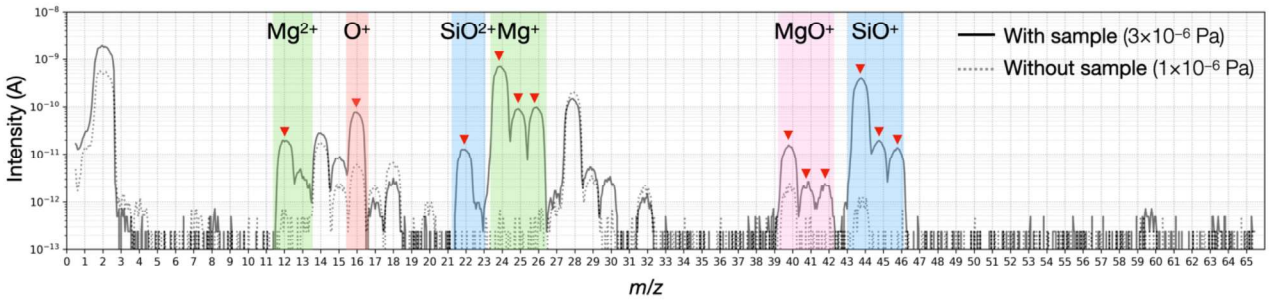

Figure 1: Mass spectrum of sublimation products of forsterite heated at 1900 K. The solid and dotted lines show the mass spectrum with and without the sample, respectively. The detected ions are indicated in the figure.

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Poster Presentations

Millimeter-wave spectroscopy of hydantoin in its vibrationally excited states

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Hydantoin (Imidazolidine-2,4-dione), a precursor to the amino acid glycine, is of astrobiological interest due to its detection in meteorites. [1] In a previous study, Alonso et al. [2] used laser ablation and FT-MW spectroscopy to determine the nuclear quadrupole coupling constants of the nitrogen nuclei in the vibrational ground state, while also assigning spectra of various decomposition products. Our previous work involved heating hydantoin to ~150°C to measure its pure rotational spectrum, determining precise rotational and centrifugal distortion constants for the ground and two excited states. [3] However, the study also revealed numerous unidentified spectral lines, leaving their assignment as an open problem. The present study, therefore, aims to assign these unidentified millimeter-wave lines and clarify the interactions among the excited vibrational states with the aid of theoretical calculations.

We have so far assigned approximately 3,000 rotational transitions of hydantoin in the millimeter-wave band, 865 of which are attributed to four novel excited vibrational states. To support our analysis, we performed structural optimization and force field calculations at the B3LYP/aug-cc-pVQZ level. The calculations show that among the 27 fundamental vibrations of hydantoin, the lowest in energy are, in order: ν_{27} (55 cm^{-1}, HCNC twist), ν_{26} (147 cm^{-1}, NCO twist), ν_{25} (367 cm^{-1}, HNCO wagging), and ν_{18} (393 cm^{-1}, CNC wagging). Among the six identified excited vibrational states, two states exhibit nearly identical rotational constants. These values are also consistent with the calculated vibration-rotation interaction constant for the ν_{27} mode. Accordingly, these two states were tentatively assigned as the tunneling-splitting components of the ν_{27} mode.

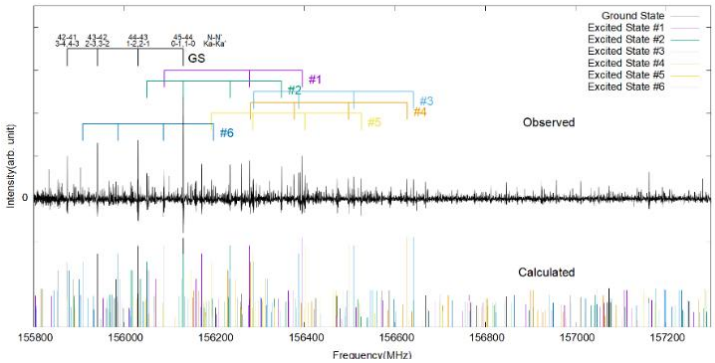

Figure 1 Observed & calculated spectrum of hydantoin around 156GHz

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Fourier-transform microwave spectroscopy of the fluorovinyl radical

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Reactions between acetylene and radicals play an important role in combustion chemistry and astrochemistry [1]. Halogenated vinyl radicals are considered intermediates in the addition reactions of acetylene with halogen atoms, and chlorovinyl radicals have been extensively studied both theoretically and experimentally [2,3]. In contrast, spectroscopic studies of fluorovinyl radicals have been limited to infrared spectroscopy in solid matrices [4,5]. In this study, we observed the pure rotational transitions of the fluorovinyl radical using a Fourier-transform microwave spectrometer. At the ae-RCCSD(T)-F12 level of calculation, the fluorovinyl radical was found to have three stable structures, α-H_2C=CF, β-*trans*-HFC=CH, and β-*cis*-HFC=CH, with the α-type being the most stable (Figure 1). The observed lines were analyzed using a doublet asymmetric rotor Hamiltonian, and the derived molecular constants agree well with values of *ab initio* calculations for β-type isomers. In this experiment, the most stable α-type was not detected. The fluorovinyl radical is considered to be formed via the addition of a fluorine atom, generated by discharge from fluoromethane, to the triple bond of acetylene, which produces the β-type isomers. Conversion from β- to α-type requires intramolecular hydrogen migration, which involves a high reaction barrier. Under the cryogenic conditions of the supersonic jet, this process is inhibited, explaining the absence of α-type isomer.

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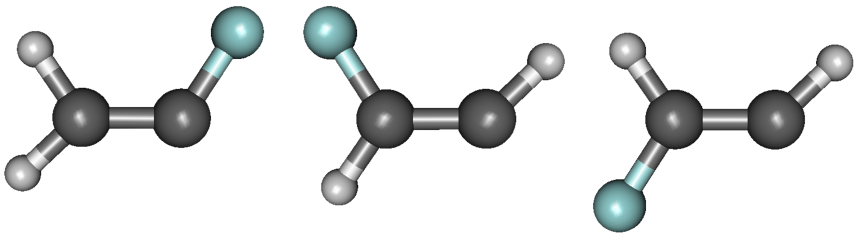

Figure 1. Three isomers of the fluorovinyl radical.

Enrichment and Spectroscopy of CH_3OD as a Step Toward the First Characterization of CH_2DOD

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In the interstellar matter (ISM), various complex organic molecules (COMs) have been identified. Among them, methanol (CH_3OH) is an important molecule for understanding chemical reactions related to the formation of COMs, as it has been considered as a seed molecules of COMs. Nevertheless, spectroscopic measurements of many CH_3OH isotopologue are still lacking. In particular, methanol exhibits significant variations in dipole moment depending on the transition, making it essential to determine transition intensities in terms of the dipole moment function. Thus, both frequencies and intensities of spectral lines must be measured. In this study, we carried out laboratory measurements of CH_3OD using the high-sensitivity emission-type spectrometer SUMIRE, developed at RIKEN.

A key experimental challenge is that, during vaporization, the hydrogen atom of the OH group in CH_3OD readily exchanges with residual water molecules inside the spectrometer. Therefore, highly deuterium-enriched samples are required. We established a simple method to prepare CH_3OD-enriched samples by repeated substitution of the OH hydrogen atom of CH3OH with deuterium in D_2O, followed by distillation. While the distillation technique itself is not novel, it provides a practical means of producing isotopically enriched samples suitable for spectroscopy. From the obtained spectra, we derived column densities of CH_3OH, CH_3OD, D_2O, and HDO, and determined their relative abundances. The results show that the abundance of CH_3OD increases with repeated distillation, whereas CH_3OH decreases. The CH_3OD fraction relative to total methanol increased from about 27% after the first distillation to 41% after the third (Figure 1).

In the future, we aim to apply the same methodology to synthesize CH_2DOD from CH_2DOH and D_2O Importantly, no spectroscopic measurements or molecular constants of CH_2DOD have ever been reported. Therefore, our planned measurements could represent the first spectroscopic characterization of this doubly deuterated isotopologue, providing highly novel and unique insights into the isotopic chemistry of methanol in star-forming regions.

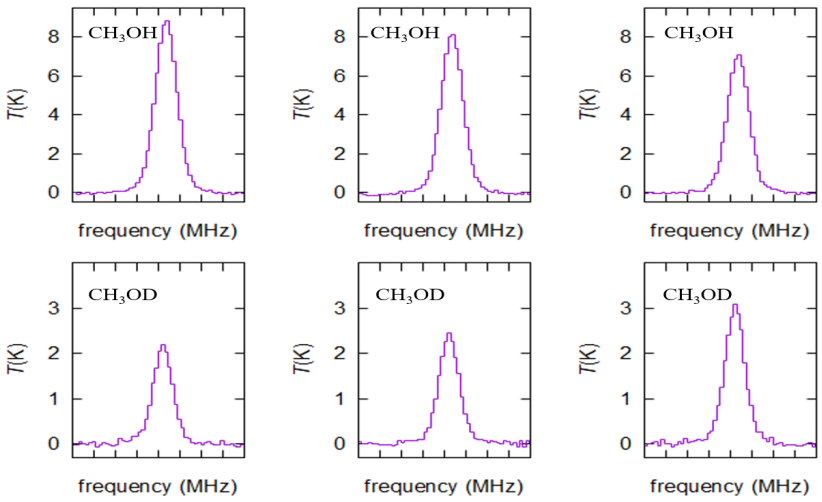

Figure 1. Top: Spectra of CH_3OH (5_0–4_0 E $v_t = 0$, 241700.16 MHz), from left to right: 1st, 2nd, and 3rd distillation. Bottom: Spectra of CH_3OD (5_0–4_0 A^+ $v_t = 0$, 226538.60 MHz), from left to right: 1st, 2nd, and 3rd distillation.

Microwave spectroscopy of Aminoacetonitrile

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Several types of amino acids, including glycine (NH_2CH_2COOH), which has the simplest molecular structure among them, have been detected in outer space [1] and in meteorites [2] that have arrived on Earth. Aminoacetonitrile (NH_2CH_2CN, AAN), the subject of this study, is regarded as a precursor to glycine.

In this study, the pure rotational spectrum of AAN was measured in the frequency range of 90–187 GHz. The frequency data obtained from the absorption spectra were assigned quantum numbers with reference to catalog data prepared based on previous studies [3,4], and the rotational constants and centrifugal distortion constants were determined.

To date, 5,126 spectral lines corresponding to thirty vibrational states have been assigned, including the ground state and unidentified vibrational excited states. For twenty of these states, rotational constants and quartic centrifugal distortion constants have been determined. Eighteen vibrational excited states were assigned, with the aid of rotational constants as well as the vibrational-rotation constants obtained by DFT calculations (B3LYP/aug-cc-pVQZ) as shown in Figure 1. The analysis of vibration-rotation interactions is ongoing.

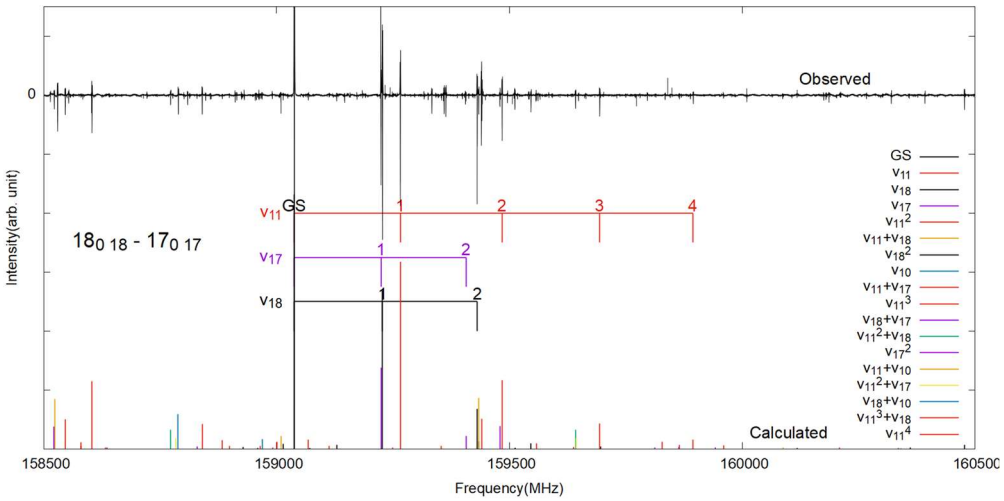

Figure 1: Observed and calculated spectra of AAN around 159 GHz.

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Rotational Spectroscopy of Deuterated Ethanol (CH_3CD_2OH) for Astronomical Detection

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Main isotopologue ethanol, as well as its singly-deuterated forms, have been detected in interstellar space, yet high-precision millimeter and sub-millimeter spectroscopic data for its doubly-deuterated isotopologues—especially CH_3CD_2OH—remain scarce. This limits secure identification of these species in astronomical spectra.

The rotational spectrum of CH_3CD_2OH in the 18 -42 GHz region was first reported in the 1960s [1,2], providing limited number of molecular constants. Later Su and Quade extended the measurement up to 70 GHz and improved the analysis of gauche-conformer [3]. In this paper, we report the microwave spectroscopy of the extended frequency range now routinely observed by facilities such as ALMA.

At the University of Toyama, 26 - 207 GHz region was recorded with the conventional frequency-modulation spectrometer [4]. At RIKEN, passive spectrometer (SUMIRE) [5] which is a powerful tool to provide absolute intensity was used to cover 216 - 264 GHz. The assignment was based on the previous study and ab initio calculations. A-reduced Hamiltonian fit for the trans-conformer is underway to further refine the spectroscopic constants. These new measurements clarify the influence of deuterium substitution on the internal rotation barrier and torsion–rotation coupling. We will prepare a high-accuracy spectral catalogue that will directly support millimeter- and sub-millimeter astronomical observations of CH_3CD_2OH.

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ALMA Band 7 Observations of Water Lines in the Protoplanetary Disk of V883 Ori

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The FU Orionis star V883 Ori provides a unique opportunity to probe the water snowline in a protoplanetary disk. During an accretion burst, the enhanced stellar luminosity heats the disk, sublimating ices and bringing volatile species into the gas-phase[1],[2],[3],[4]. The water snowline, located at ∼80 au in the midplane[3], represents a key boundary for dust growth and volatile delivery to forming planets.

We present Atacama Large Millimeter/submillimeter Array Band 7 observations of V883 Ori (PI: S. Notsu) that detect two targeted water isotopologue transitions: para-$H_2{}^{18}O$ $5_{1,5}$–$4_{2,2}$ at 322 GHz and HDO $3_{3,1}$–$4_{2,2}$ at 335 GHz. After correcting for Keplerian rotation, we detect HDO and $H_2{}^{18}O$ at 23.6σ and 9.3σ, respectively.

Rotational-diagram analysis using a Markov Chain Monte Carlo approach yields T_{rot} = 116.89 ± 12.81 K and N = (4.90 ± 1.69) × 10^{15} cm^{-2} for $H_2{}^{18}O$, and T_{rot} = 87.46 ± 4.95 K and N = (4.47 ± 0.62) × 10^{15} cm^{-2} for HDO. These results imply water vapor abundances of N_{H2O}/N_{H2} ∼ 3 × 10^{-7}–5 × 10^{-6} and an HDO/H_2O ratio of (0.4–2.0) × 10^{-3} near the snowline, broadly consistent with inheritance from protostellar envelopes.

The HDO line in Band 7 is significantly weaker than predicted from Band 6 extrapolation, showing only ∼26% of the expected strength. This attenuation can be explained by a more compact, hotter emitting region with an effective radius of ∼53 au and/or frequency-dependent dust absorption that enlarges the apparent inner cavity at higher frequency. Our results highlight both the diagnostic power of water isotopologue lines and the need for higher angular-resolution observations to resolve the snowline and test these scenarios.

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Analyses of the Aromatic Infrared Bands (AIBs) around the Wolf-Rayet Binary WR140

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Recent line survey observations toward the starless core Cyanopolyyne Peak in Taurus Molecular Cloud-1 (TMC-1 CP) have reported the detection of aromatic species with the nitrile bond [1,2]. Their derived abundances are surprisingly high ($\sim 10^{-10}$) and comparable with some classical carbon-chain species. However, their abundances cannot be reproduced by the standard chemical network simulations considering only a bottom-up mechanism that assumes that all of the carbon is initially in the form of C^+. Thus, some fraction of carbon may be inherited from the ISM in the form of polycyclic aromatic hydrocarbons (PAHs). Our science goal is to understand the lifecycle of carbon in the ISM; from evolved stars, through the diffuse ISM, to star-forming regions (*i.e.*, molecular clouds) [3].

We have analyzed data obtained from the James Webb Space Telescope (JWST) Mid-Infrared Instrument (MIRI) Medium-Resolution Spectrometer (MRS) toward the Wolf-Rayet binary WR140, where 17 nested circumstellar dust shells have been reported [4]. Our data covers the innermost dust shell (Shell 1; ~ 2100 au from WR140) and the subsequent dust shell (Shell 2; ~ 5200 au). We have analyzed spectra indicated in the left top panel of Figure 1 focusing on the aromatic infrared bands (AIBs) in the 6 – 11.2 μm region. These AIBs are generally considered to relate to PAHs.

We find that the observed spectral features around WR140 are different from typical class A-D AIB emission features in the ISM, as shown in right panels of Figure 1. We have compared the observed line widths (FWHM) and peak wavelengths of the 6 μm and 7.7 μm features, both of which come from the C-C stretching modes, to those of R Coronae Borealis (RCB) stars obtained with *Spitzer* [5]. The results indicate that FWHM and peak wavelengths of both features around WR140 are consistent with those of hydrogen-poor RCBs. We have also compared the observed spectra at the peak position on Shell 2 (S2) to those of the diffuse ISM toward the Galactic plane [6], as shown in the lower left panel of Figure 1. Although the peak wavelengths at S2 slightly different from those in the diffuse ISM, it is apparent that the two spectra are very similar.

Based on these results, it is proposed that hydrogen-poor carbonaceous material initially originates from the carbon-rich WR wind, and the hydrogen-rich stellar wind from the companion O star subsequently hydrogenates these carbonaceous materials. These hydrogenated carbonaceous compounds survive away from the WR star, and may be the origin of the interstellar PAHs after further processing by massive stars or in the diffuse ISM.

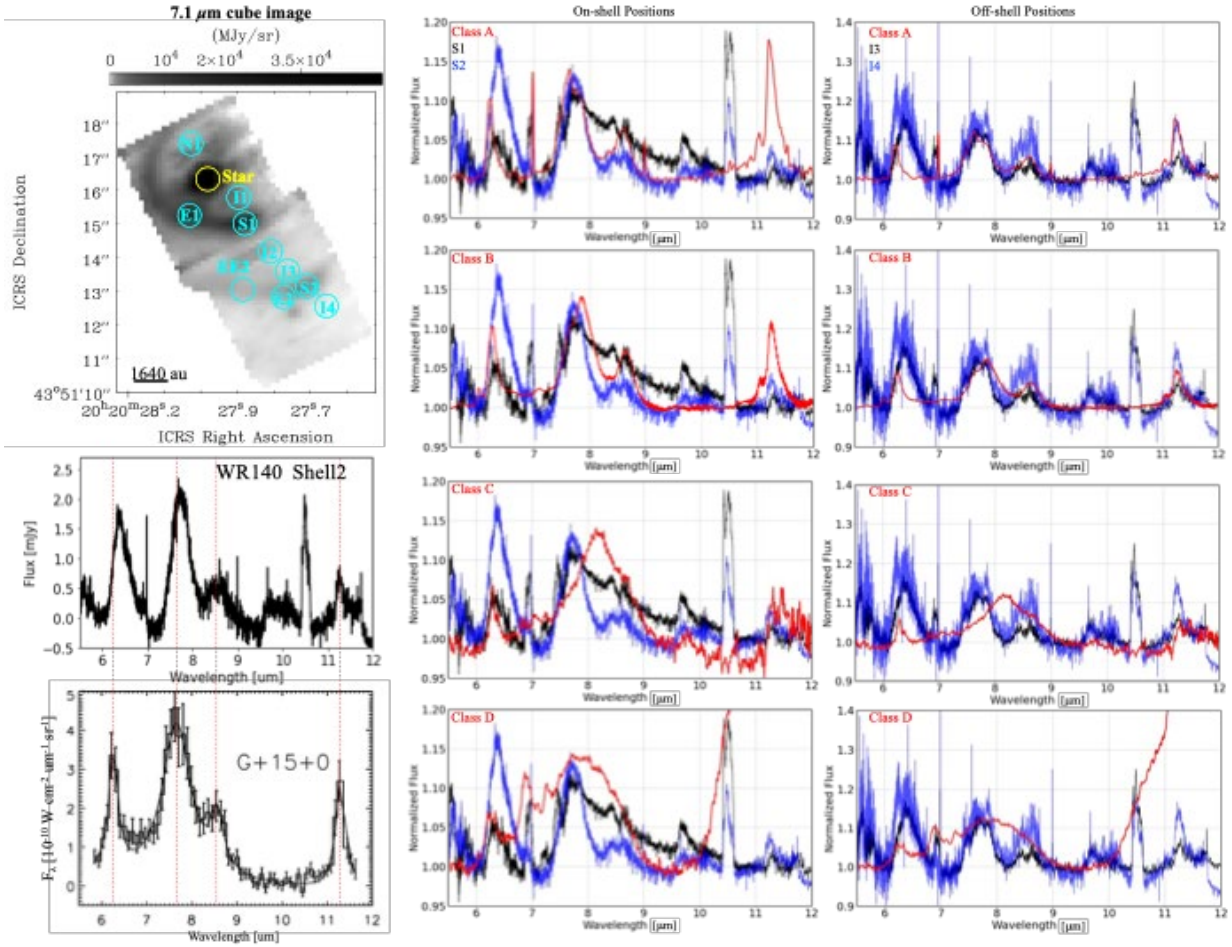

Figure 1: Left top panel shows the 7.1 μm cube image. The S1 and S2 positions indicate the peaks on Shell1 and Shell2, respectively. The left bottom panel shows comparison of the spectra at WR140 Shell 2 (upper) and the diffuse ISM toward the Galactic plane taken from [5] (lower). Right panels indicate comparisons of the observed spectra (black and blue) around WR140 and typical AIB emission features named classes A-D (red). These figures are taken from [7].

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Synergies with PRIMA and GREX-PLUS - Observations of water line profiles from protoplanetary disks

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Understanding the water vapor and ice distribution, including the water snowline position, in planet-forming disks (protoplanetary disks) will provide information on the origin of water in planetary systems, including our Solar System. Water can be delivered to rocky planets, including Earth, through icy pebbles, icy planetesimals, comets, and asteroids, supporting the emergence of life on these planets. Water gas abundance is high (~10^-4) within the water snowline, and it is relatively high (~10^-8 – 10^-7) in the hot surface layer and the photo-desorbed region of the outer disk, compared to its value (~10^-12) in the regions outside the water snowline near the equatorial plane (e.g., Walsh et al. 2012).

The PRobe far-Infrared Mission for Astrophysics (PRIMA) is a mission concept which is leaded by NASA and primed to provide a unique access to probe the dominant components of gas and dust in protostellar and protoplanetary systems for the community in the 2030 decade [1]. Recently, PRIMA-Japan working group have discussed potential unique science cases about star and planet formation as well. As one of PI Sciences, PRIMA will characterize the main reservoirs of warm and cold water vapor and the far-infrared crystalline and amorphous water ice features for around 200 protoplanetary disks, giving unique access to the time evolution of the water throughout the entire disk. In PRIMA, the spectral resolution of high-resolution mode with Fourier transform module (FTM) is R~λ/Δλ~ 4400 * (112 μm/λ), and it is R>10,000 at λ<40 μm and R~20,000 at the shortest wavelength coverage (λ~24 μm) of PRIMA/FIRESS. Thus, PRIMA will expect to resolve line profiles and/or measure the line widths with Keplerian rotation in the shortest wavelength water lines, especially λ<40 μm. By obtaining water line profiles and constraining the positions of the water snowline for around 200 disks within PI Science survey, PRIMA will trace the time evolution of the water snowline positions in the planet-forming disks which divide the regions between rocky and gas giant planet formation [1,2]. The cooperative observations (such as same target objects) with PRIMA and Japanese future infrared space telescope GREX-PLUS will be useful. GREX-PLUS will expect to obtain high spectral resolution spectra (R~30,000) towards 100 disks for λ=10-18 μm, where several candidate water lines such as the 17.75 μm line are included [2,3].

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The results of the protostar survey toward the outer Galaxy with ALMA: Detection of the protostellar outflows/jets and a hot molecular core

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The outer Galaxy (galactocentric distance (D_GC) >13.5 kpc) exhibits distinctive characteristics compared to the inner Galaxy, including low metallicity, reduced-gas density, and minimal perturbation from spiral arms and supernova explosions. These environmental conditions make it a crucial region for investigating the universality of star formation and chemical evolution across the Galaxy. Until recently, molecular detections of protostars in the outer Galaxy remained sparse, with only one reported (WB89-789 SMM1; [1]). Increasing the sample size of outer Galactic protostars is essential for unveiling the universality of physical and chemical properties of star-forming regions.

In this work, we carried out the protostar survey toward the 16 protostar candidates located in the five star-forming regions in the outer Galaxy (Sh 2-283/NOMF05-16/19/23/63; Z~1/3-1/4 Z_Sun) at the D_GC of 15.7-17.4 kpc with ALMA.

As a result, we newly detected 5 protostellar outflow sources with CO(3-2) emission, one of which exhibits jet components with bullet structures [2]. The morphological properties of these outflows and jets are similar to those observed in nearby sources, indicating the universality of star formation processes even in the outer Galaxy.

Moreover, we identified one protostar associated with a hot molecular core, in which high-excitation transitions (E_u > 100 K) of complex organic molecules such as CH3OH and CH3OCH3 were detected. A comparison of the fractional abundances relative to CH3OH between this protostar and WB89-789 SMM1 shows a remarkable similarity within a factor of ~2, and this result supports the idea that such chemical richness may be a common feature of hot cores, even in the outer Galaxy.
We will present a more detailed discussion of the physical and chemical properties of these sources.

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Organic Ice Chemistry in Embedded Protostars

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In recent years, common detection of gas-phase complex organic molecules (COMs) suggests extensive chemical reactions already taken place in the early phase of star formation. However, while some protostars have abundant gas-phase COMs, many protostars still show no sign of COM emission. This contrast of their gas-phase chemical signatures begs the question: Does the diverse gas-phase chemistry represent distinctively different chemical evolution? Ice not only represents the more pristine chemistry with minimum contamination from gas-phase reactions but also enables major formation pathways of COMs. While ALMA provides sub-100 au resolution, a resolution necessary to resolve sites of planet formation, to characterize gaseous COMs in nearby embedded protostars, measurements of chemical composition in ices had been limited by low-resolution and limited sensitivity spectroscopy until JWST. Thus, it is imperative to probe both gas and ice chemistry related to COMs, which can only be achieved with both ALMA and JWST. In this poster, I will highlight the latest JWST results on ice chemistry and the characterization of complex ice species in comparison with that detected in gas-phase by ALMA. Particularly, I will present the latest results from the CORINOS program, which aims to delineate the origin of COM diversity in gas-phase. We detect likely features of icy COMs regardless of the presence of gaseous COMs. Whereas JWST provides extremely sensitive spectra, interpretations of ice absorption features still face several challenges. The absorption features are intrinsically blended and isolating each species is not trivial. Furthermore, spectra of embedded protostars suffer from substantial extinction by dust and ice, which hinders straightforward measurements of absorption. I will also discuss the approaches we took to mitigate these challenges as well as the limitations.

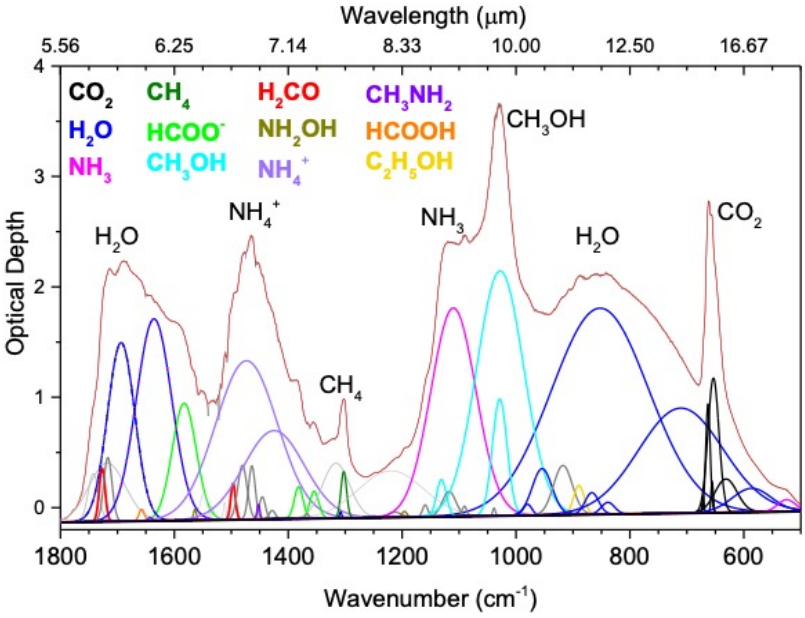

Figure 1: Ice absorption features and the identified species using our chemistry-driven framework (Turner & Yang et al., in prep.)

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Oxygen Isotope Ratios in Interstellar CH_3OH

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CH_3OH is a simple saturated organic molecule in the interstellar medium (ISM). It is also an important molecule in astrochemical studies because it is a seed molecule for complex organic molecules. We have performed comprehensive molecular spectroscopy experiments on various isotopologues of CH_3OH using the emission-type molecular spectrometer SUMIRE (Watanabe et al. 2019) to measure the frequency and empirical $S\mu^2$ values in the frequency band corresponding to ALMA Band 6 (e.g., Oyama et al. 2023, Tamanai et al. 2025). In particular, observation of $CH_3{}^{17}OH$ has been scarce because spectroscopic measurements of the isotopologue have been limited. Therefore, we search for $CH_3{}^{17}OH$ in the Orion KL region using ALMA archival data.

As a result, we identify eight a-type transition lines of $CH_3{}^{17}OH$ (J = 5 - 4) in the 236 GHz band (Figure 1). The $^{16}O/^{17}O$, $^{16}O/^{18}O$ and $^{18}O/^{17}O$ ratios are evaluated to be 2300±300, 650±70 and 3.5±0.3, respectively. Here, we use the column densities of $CH_3{}^{18}OH$ obtained from the ALMA archive data and those of CH_3OH obtained from IRAM PdBI by Peng et al. (2012). These values are consistent with the canonical isotopic ratios in the ISM of the solar vicinity. These results suggest that the oxygen isotopic ratios in the hot core region can be determined by using CH_3OH isotopologues. Since CH_3OH has many transitions in a narrow frequency band, multiple emission lines can be observed simultaneously with a single frequency setup with ALMA. Therefore, accurate column densities and isotope ratios can be estimated by using LTE/non-LTE analysis. The oxygen isotope ratios reflect the star formation history, such as star formation rate and initial mass function, and thus would be an important probe of the Galaxy evolution.

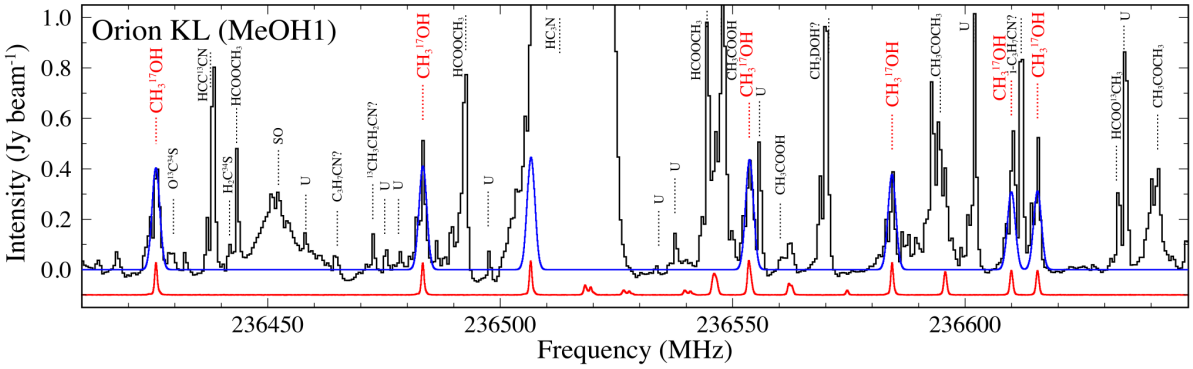

Figure 1: The spectrum of Orion KL observed with ALMA (black line), the laboratory spectrum of $CH_3{}^{17}OH$ measured with SUMIRE (red line), and the LTE model spectrum of $CH_3{}^{17}OH$ (blue line).

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Ion mobility measurements for H_3^+, D_3^+, HeH^+, and HeD^+ in He gas at 77.3 K

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H_3^+ is recognized as one of the most important molecules in interstellar space, having been observed in molecular clouds since 1996 [1]. On the other hand, HeH^+ is supposed to be the Universe's first molecule after the Big Bang, and was observed in the planetary nebula in 2019.

In this work, we have measured the ion mobility of H_3^+ and HeH^+ in He gas cooled by liquid nitrogen. We also performed measurements for their isotopologues, D_3^+ and HeD^+, to consider isotope effects in ion mobility in gas. The mobility of ions is directly related to the collision integral, which is the averaged momentum transfer cross-section and is regarded as the geometrical size of the ion.

As shown in Figure 1, the collision integrals of H_3^+ and D_3^+ are almost the same. However, those of HeH^+ and HeD^+ show a significant difference in the low T_{eff} region. These results suggest that the collision integral depends on the rotational constants of molecular ions, and the rotational excitation of H_3^+ and D_3^+ is not significant due to the relatively isotropic interaction potential with the He atom.

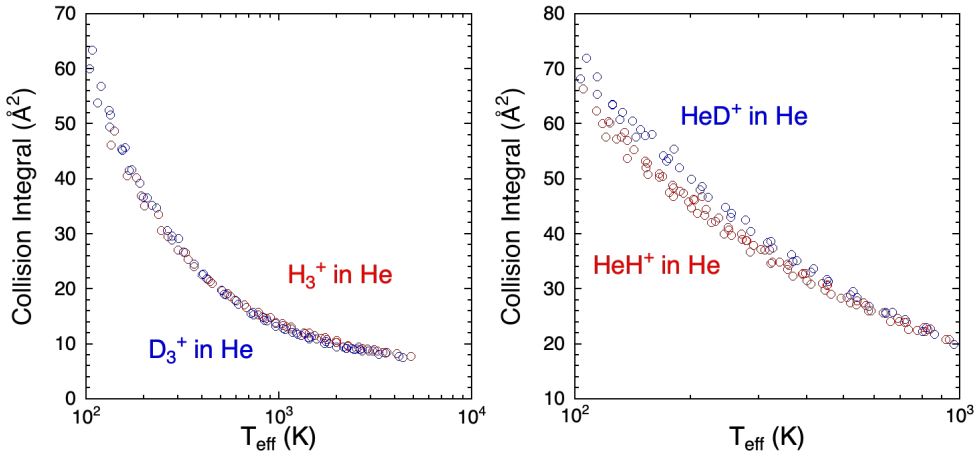

Figure 1: Collision integrals of H_3^+ and D_3^+ in He gas; those of HeH^+ and HeD^+ in He gas.

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Tentative assignment of the skeletal torsion excited state of methyl formate in the infrared spectra

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Methyl formate is one of the complex organic molecules abundantly present in interstellar space. The spectrum of this molecule is complicated because it splits into A and E species due to the internal rotation of the methyl group (corresponding to a torsion vibration). Over 1000 transitions, including those from the ground state and torsional excitation states, have been identified in interstellar space [1]. In observations of this molecule towards the Orion KL, the rotational temperature was about 200 K [2]. Considering this rotational temperature, lines of other low-lying excited states, such as the COC deformation (ν_{12}, 312 cm^{-1}) and skeletal torsion (ν_{17}, 332 cm^{-1}), become strong candidates for radio astronomical detection. We have already reported the laboratory assignment of pure rotational transitions in the COC deformation excited state using microwave spectroscopy. This vibrational assignment was confirmed through analysis of the vibration-rotation transitions observed with the Canadian Light Source [3]. The far-infrared spectrum is shown in Figure 1. Transitions between the skeletal torsion excited state and the ground state are also observed. In this paper, we report tentative assignments of this band.

The assignments were made based on the combination differences of A species in the ground state. We have completed the assignment of the K_c = 0,1series, and are currently extending the assignment to improve molecular constants. Future plans include extending the assignment of the COC deformation excited state, assigning pure rotational transitions in the skeletal torsional excited state, and conducting a search in interstellar space.

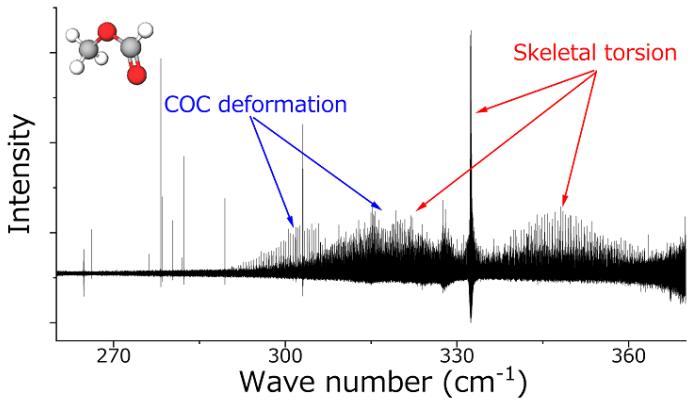

Figure 1: Far-infrared spectrum of methyl formate

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Commissioning of a new measurement system for ion—polar-molecule reactions under low-temperature conditions

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We have been developing an experimental apparatus designed to measure rate coefficients and branching ratios of ion—polar-molecule reactions in the low- to intermediate-temperature range. The system consists of a storage ion source (SIS) [1], a wavy/linear Stark velocity filter [2], and a cryogenic linear octupole radio-frequency (RF) ion trap (OPIT) [1]. The primary objective of this research project is to measure reaction rates of H_3^+ and hydrocarbon ions CH_n^+ (n = 0–5) with polar molecules. These reactions are believed to play crucial roles in the formation processes of interstellar molecules; however, only a limited number of reaction rate coefficients at low temperatures have been reported to date. In this context, hydrogen/methane gas was introduced into the SIS to produce H_3^+ and CH_n^+ ions, and a quadrupole mass spectrometer was used to selectively extract specific ion species. Figure 1 shows the mass spectrum of CH_n^+ ions detected at the end of the beamline through the OPIT (see Fig. 2). Based on the observed pressure dependence of the mass spectra, CH_5^+ is considered to be formed via the ion–molecule reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ in the SIS. In this poster presentation, we will report in detail on the production of low-energy H_3^+/ CH_n^+ ions using the SIS and discuss the optimization of beam transport and trapping of externally injected ions in the cryogenic OPIT via the sextupole RF ion beam guide.

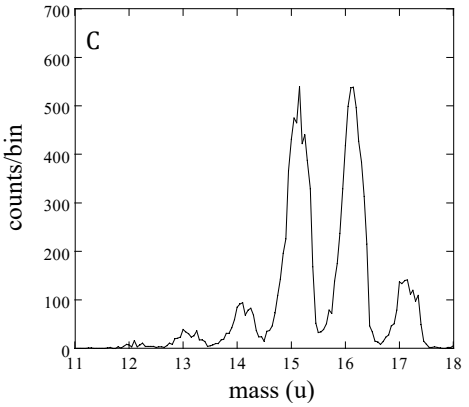

Figure 1: Mass spectra of CH_n^+ (n =0-5) obtained using a quadrupole mass spectrometer (SRS, RGA100) located at the end of the beamline.

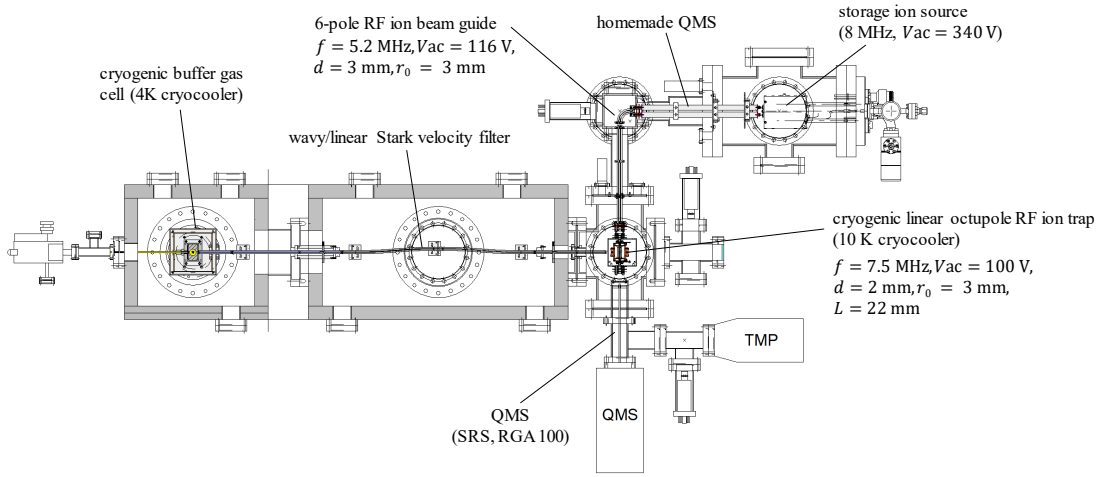

Figure 2: Schematic diagram of a new measurement system for ion—polar-molecule reactions under low-temperature conditions.

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Making the interstellar minerals behind the shock front

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Solid matter in the Interstellar Medium (ISM) has been detected in different astrophysical environments, and our solar system is typically classified into three categories: silicate-type minerals, carbonaceous dust, and ices [1]. A significant amount of interstellar minerals is thought to be produced via the gas phase condensation process in the extended envelope of the Asymptotic Giant Branch (AGB) stars [2]. The elemental abundance of these stars greatly affects these minerals' chemical compositions, especially the C/O abundance ratio. For the case of C/O <1, the dust grains are mostly oxides like olivine, pyroxene, spinel, etc.; for C/O >1, dust grains are carbonaceous like SiC, C_{60}, and other carbon allotropes [2]. However, our understanding of the formation pathways of these dust grains, especially for mineral dusts like olivine and SiC in stellar environments, is limited.

Shock waves are widely observed in different parts of ISM and, depending on its strength, can induce various events such as sputtering and shattering while interacting with dust grains [3]. The low-velocity shocks (3< M< 10) can enrich its propagating medium through thermal processing and enhance the molecular complexity of the ISM [3]. The low-velocity nebular shocks have also been proposed to be responsible for the formation of crystalline mineral dust in the comets [4]. In recent years' shock tubes have emerged as a new tool to mimic interstellar low velocity (3< M< 10) shocks in the laboratory [5, 6]. By utilizing the High-Intensity Shock Tube for Astrochemistry (HISTA) housed at the Physical Research Laboratory, we studied the shock processing of cosmic silicate [7], and SiC dust precursors. The processed samples have been analyzed using IR spectroscopy, XRD, FE-SEM, and HR-TEM imaging techniques. In this meeting, we will discuss some of the preliminary results of this experiment and their importance in cosmic mineral chemistry.

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Sulfur-bearing species in molecular clouds and PPDs as possible precursors for hydrated and dehydrated minerals in meteorites

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Chondritic meteorites are presumed to be fragments of planetesimals that formed in the solar protoplanetary disk (PPD). They nearly invariably contain hydrated and/or dehydrated minerals. The presence of those minerals is interpreted as evidence of aqueous or hydrothermal reactions between minerals and melted ice of interstellar origin during their evolution inside planetesimals [1, 2].

Conventionally, (pure) water ice is considered to be a sole source of aqueous fluid for the alteration reactions of minerals, owing to its high abundance in interstellar space [3, 4]. Thus, external heat sources that bring temperatures above zero Celsius are one of the necessary conditions for water-driven reactions to proceed. Recently a sulfuric acid (H_2SO_4-H_2O) that evolved from interstellar SO and SO_2 molecules through the PPD and planetesimal stages is proposed as a potential acidic alteration fluid at temperatures as low as -60°C, particularly for the planetesimal associated with Acfer094 chondrite [5].

Aqueous solutions of various electrolytes can simultaneously provide conditions of low temperature and a variable range in pH, thereby acting as different types of corrosive cryo-alteration agents within planetesimals. Here we report a possible cryo-alteration process that should work at high pH and is responsible for having formed tochilinite–cronstedtite mineral intergrowth commonly observed in CM chondrites.

We suspect two kinds of sulfur-bearing electrolytes as a potential cryo-alteration agent that should have given rise to the high pH in planetesimals. Ammonium hydrosulfide (NH_4SH) has been proposed to form at temperatures as low as 10K, from an ice mixture of ammonia (NH_3) and hydrogen sulfide (H_2S) [6]. Here we propose ammonium sulfide, $(NH_4)_2S$, as an alternative and more effective electrolyte to function as an alteration fluid in the CM parent asteroids. We carried out preliminary alteration experiments with mixed initial minerals of olivine + Fe-metal particles and ammonium sulfide solution as the alteration medium. The initial particles were immersed in the solution inside a microtube at room temperature for 1 to 4 weeks. After prescribed immersion period, a fraction of the solution was collected and dried on a Pt-grid. The residual minerals on the Pt-grid were observed with a transmission electron microscope to identify the precipitated minerals phases. A mixture of tochilinite and cronstedtite, as well as their separate phases, were identified on the surfaces of precursor minerals after one week under these experimental conditions. We are extending these experiments to conditions at -30°C using nanoparticulate olivine to further assess cryo-alteration processes.

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Analytical development for identifying femtomole-level organophosphorus compounds using IC/HRMS for organic astrochemical samples

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Phosphorus (P) -bearing organic molecules are believed to have played a pivotal role in the emergence of life on Earth; however, their origin and chemical evolution in cosmic environments remain poorly understood. Observations, meteoritic analyses, and laboratory simulations indicate that organophosphorus species can form abiotically under interstellar and asteroid conditions and may have been delivered to the early Earth [1–3]. However, the structural diversity and formation pathways of these molecules in astronomy have not been comprehensively characterized, limiting our understanding of phosphorus chemistry from the interstellar medium to the Solar System. To address these undescribed issues, we have developed a highly sensitive analytical method capable of identifying organophosphorus species using ion chromatography/high-resolution mass spectrometry (IC/HRMS) [4]. This technique enables the detection of femtomole-level organophosphorus compounds from matrices containing various interfering molecules (Fig. 1). By applying this approach to organic astrochemical samples, the molecular diversity and reaction networks of phosphorus species formed in interstellar ices, protoplanetary disks, and asteroids can be revealed. These results will provide new insights into the astrochemical evolution of primordial phosphorus and its potential contribution to the inventory of prebiotic molecules on the early Earth.

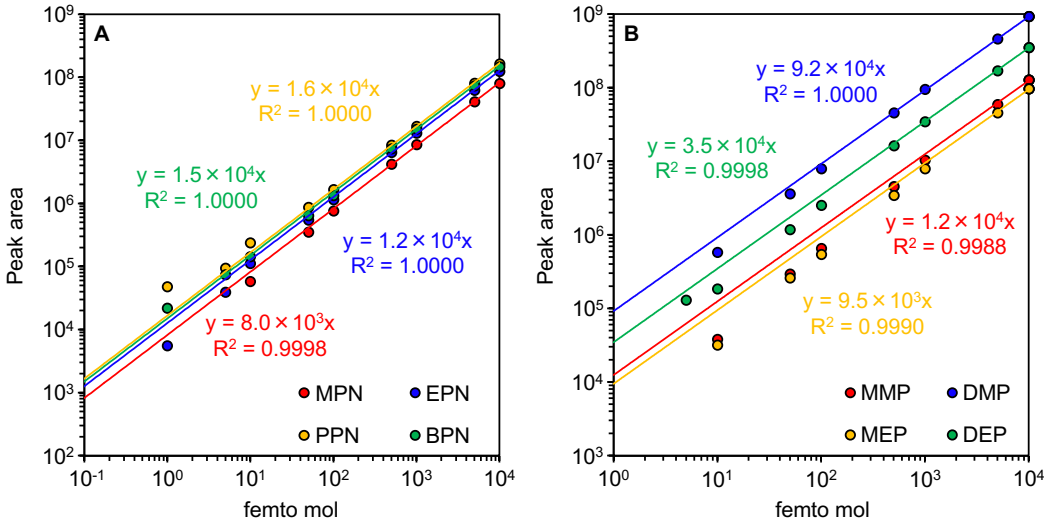

Figure 1: Calibration curves of organophosphorus standards [4]. The left and right figures show alkyl phosphonates and alkyl phosphates, respectively. Abbreviations: MPN, methyl phosphonate; EPN, ethyl phosphonate; PPN, propyl phosphonate; BPN, butyl phosphonate; MMP, monomethyl phosphate; DMP, dimethyl phosphate; MEP, monoethyl phosphate; DEP, diethyl phosphate.

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Understanding the surface structure of amorphous water: quantifying the surface coverage of dangling OH bonds

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Dangling OH (dOH) bonds, OH groups that do not form hydrogen bonds with other water molecules, are possible absorption and reaction sites on the surface of icy mantles of interstellar dust grains [1,2]. Although our group has recently quantified the column density of dOH bonds on vapor deposited amorphous water by estimating the absorption cross sections of dOH features (3720 cm^{-1} and 3696 cm^{-1}) at 20 K [3], the surface coverage of dOH bonds on the surface of amorphous water must be quantified to fully understand its surface properties as a reaction and absorption site. For crystalline ice Ih, a recent atomic force microscopy (AFM) study determined the coverage of dOH bonds to be around 10 %, which is less than half of the expected 25 % for an ideal 4-coordinated crystalline structure [4]. Although AFM effectively works for crystalline surfaces, it is experimentally challenging to apply AFM to the amorphous water surface due to its atomic-level roughness. Therefore, an alternative approach is required to determine the surface coverage of dOH on amorphous water. To this end, we estimated the surface coverage of dOH on amorphous water at 20 K and 90 K, using temperature-programmed desorption (TPD) and infrared multiple-angle incidence-resolved spectrometry (IR-MAIRS). The combined use of TPD and IR-MAIRS enabled us to obtain the surface coverage of dOH at 20 K and 90 K as 13 % and 9 %, respectively [5], both of which are close to the reported value for crystalline ice Ih (10 %) [4].

Additionally, our recent effort utilizing molecular dynamics simulation and a spectral simulation technique to understand the surface structure of vapor deposited amorphous water will be mentioned [6]. Our works would contribute to further understanding of the surface structure of icy dust grain in the interstellar medium.

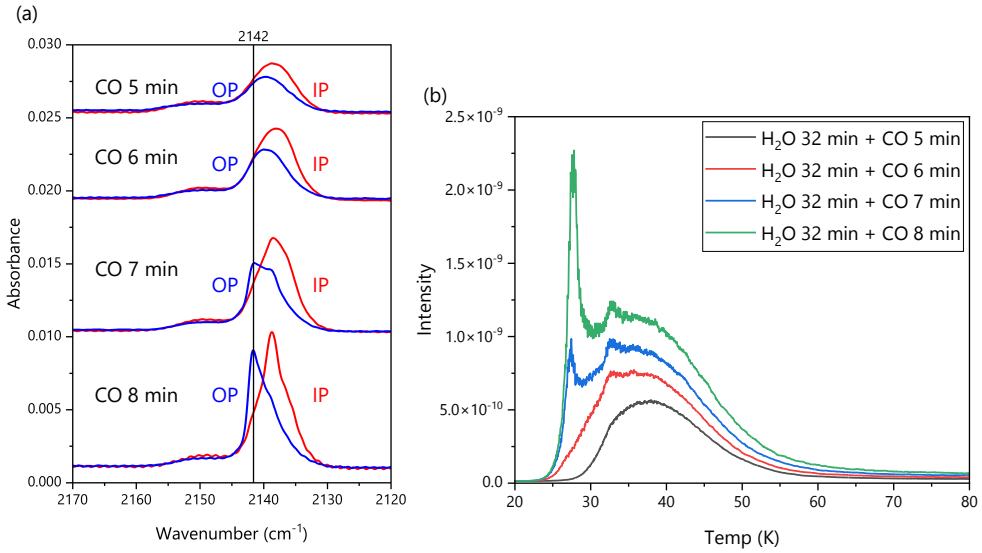

Figure 1: (a) Out-of-plane (OP) and in-plane (IP) spectra of CO deposited amorphous solid water at 20 K, with deposition times ranging from 5 to 8 minutes. Solid black guideline is 2142 cm^{-1}. (b) TPD spectra of amorphous solid water with different CO deposition time ranging from 5 to 8 minutes.

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CO Infrared Band Profiles as a Probes of Interstellar Ice Condensation Conditions

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Carbon monoxide (CO) is a fundamental component of interstellar ices, and its infrared absorption profile provides sensitive diagnostics of the molecular environment and ice structure. In this study, we deposited pure CO ice and CO mixed with H_2O, CH_4, and NH_3 in different ratios under controlled laboratory conditions, and investigated the resulting spectra using Fourier-transform infrared (FTIR) spectroscopy. Two different deposition procedures were employed: (i) direct deposition at the lowest attainable substrate temperature, and (ii) deposition during controlled cooling from higher temperature to the base temperature at a rate of 2K/min. In pure form, CO exhibits a sharp absorption near 2139 cm^{-1}, while the presence of H_2O, CH_4, and NH_3 produces distinct modifications of the CO band profile, including shifts in peak position, band broadening, and the appearance of asymmetric shoulders. The spectral variations depend on both the CO-deposited species and the deposition method, reflecting differences in ice morphology and intermolecular interactions. These results provide laboratory constraints on the interpretation of astronomical CO ice features observed toward dense interstellar clouds and protoplanetary disk. The study highlights the importance of ice composition and growth conditions in shaping the vibrational signatures of interstellar CO.

Three-step structural transformation of vapor-deposited ice (H_2O) at 120 K

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Water ice is ubiquitous not only in the earth's atmosphere but also in interstellar molecular clouds, where the birthplace of stars and planets under cryogenic and ultrahigh vacuum conditions [1]. In interstellar molecular clouds, non-crystalline ice (amorphous water) provides a field for heterogenous catalysis to produce molecules and will be transformed into crystalline ice by heating above 143 K. However, although the structure of water ice is important to discuss the physical properties of interstellar icy dust grains, the structure of water ice prepared by vapor-deposition is still not well understood even in laboratory studies.

In this study, we discovered the thickness-dependent structure of water ice prepared by vapor-deposition, using newly developed reflection high energy electron diffraction and infrared reflection absorption spectroscopy (RHEED-IRRAS) [2]. We prepared amorphous water by vapor-deposition at the substrate temperature of 120 K and at the water vapor pressure of 10^{-6} Pa. We confirmed the formation of amorphous water by the vague halo in the electron diffraction pattern (Fig. 1). After the deposition of water vapor for 120 min, a clear ring was shown in the electron diffraction pattern, which indicates the formation of polycrystalline ice even at 120 K. Moreover, the clear ring was transformed into another type of the ring after the deposition of water vapor for 420 min, which indicates the formation of a different structure of water ice. According to the structural analysis of water ice, not only amorphous water but also cubic and hexagonal ice could be appeared subsequently during vapor-deposition.

The vapor pressure of amorphous water is known as one order of magnitude higher than that of the bulk ice [3]. However, water molecules in the gas phase should not be equilibrated by collisions due to the ultrahigh vacuum conditions. Therefore, the thickness-dependent structure of water ice cannot be solely explained by differences in vapor pressure of water ice.

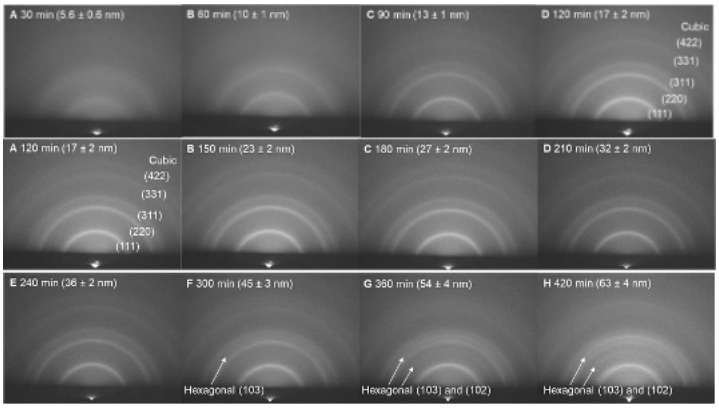

Figure 1: The electron diffraction analysis of water ice prepared by vapor-deposition at 120 K at 10^{-6} Pa.

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Water ice: Experimental density and refractive index at low temperatures

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Space presents water ice signatures from objects from our solar system to the interstellar medium. Our extensive laboratory work focuses on the physical properties of thin film ices grown by vapor background deposition. We obtain the refractive index in the visible spectrum (n) using double laser interferometry, as well as the ice average density (ρ) by measuring the mass deposited on the surface of a quartz crystal microbalance. Ice is grown at constant rates (0.2 – 3 nm s^{-1}) and temperatures (33-155 K) in a high-vacuum system. Interferometry also allows us to speculate about the relation between scattering and ice structure. The n and ρ values are used to obtain the Lorenz-Lorentz factor (L), commonly used to obtain the density from experimental n values. We also estimate the ice porosity from the obtained average density and the intrinsic density from diffraction experiments in the literature. Average density measurements are also important to constrain infrared band strength values, which have become more relevant as the capabilities of observational facilities improve (VLT, JWST).

The measured solid water densities vary between 0.48 g cm^{-3} at 33 K and 0.83 g cm^{-3} at 150 K. The visible refractive index at 532 nm grows from 1.15 to 1.32 in that temperature range. Distinct reproducible regimes are observed: a step-wise growth up to 80 K; a linear slope between 80 K and 110 K; a remarkable discontinuity at 115 K, indicating the formation of cubic ice crystals; and a steeper slope up to 155 K, when hexagonal structures appear. From these observations, we discuss the validity of the L factor; study the effect of deposition rates; estimate the porosity by temperature; and present updated band strength values.

Laboratory measurements of band strengths and optical constants of D_2O ices along with new measurements on H_2O ices

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Water is one of the more abundant molecules in cold extraterrestrial environments, such as the interstellar medium (ISM), comets, and icy planets and moons. Water is an essential molecule for biological activity and a fundamental material for chemical evolution. Many studies have been published on gas-phase water, including observations and identifications of isotopologues such as HD and HDO in the ISM [1, 2]. Theoretical studies of solid phase deuterium chemistry in ISM have also been published [3], but few laboratory studies on solid D_2O exist [4]. For such work, infrared (IR) spectroscopy is a powerful aid to observational, theoretical, and experimental studies, as each ice component exhibits a unique spectrum.

In the present laboratory study, we prepared D_2O ices and measured their IR band strengths at 10, 70, and 155 K with 1.0-cm^{-1} resolution, with corresponding measurements for solid H_2O. Additionally, we calculated IR optical constants for solid D_2O and solid H_2O as they are valuable for spectral modeling. This is the first study in which all of these physical properties - band strengths, refractive indices, and densities – were measured in the same laboratory.

Our new work can help to determine isotopic ratio in ices, unravel reaction chemistry, and support the analysis of observational spectra by the James Webb Space Telescope. Our study also will enable a better understanding of chemical evolution in cold extraterrestrial environments.

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Visible absorption spectra of mass-selected cyanobenzene and iso-cyanobenzene cations in solid neon

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We report the visible absorption spectra of mass-selected cyano-benzene ($C_6H_5CN^+$) and iso-cyano benzene ($C_6H_5NC^+$) cations isolated in solid neon at 3 K using the mass-selected matrix isolation spectroscopy technique [1]. The strong absorptions observed between 500 and 580 nm are assigned to overlapping $B\ ^2B_2 \leftarrow X\ ^2B_1$ and $C\ ^2B_1 \leftarrow X\ ^2B_1$ transitions of $C_6H_5CN^+$, in good agreement with recent gas-phase He-tagging measurements [2] and Franck–Condon simulations. Additional weak features around are attributed to $C_6H_5NC^+$, supported by the detection of a distinct NC stretching vibration at 2043.3 cm^{-1} in the IR spectrum and corroborated by quantum chemical calculations. Analysis of integrated IR intensities suggests that the iso-cyano benzene cation comprises only ~7–5% of the cyano-benzene cation population under our deposition conditions. The present work provides the first condensed-phase benchmark spectra of cyano-substituted benzene cations, expanding the spectroscopic database of aromatic cations at cryogenic conditions.

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Modeling the composition of ices in protoplanetary disks with luminosity outbursts

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Understanding the chemical composition of ices in protoplanetary disks is crucial for explaining the origin of water and organics in planetary systems. I present a comprehensive model that links the physical evolution of a disk with the chemistry of volatiles, with a special focus on the impact of FU Orionis-type luminosity outbursts.

Using the two-dimensional hydrodynamical code FEOSAD, we model disk evolution from cloud collapse to an age of 0.5 Myr, including dust coagulation and fragmentation, and phase transitions of volatiles (H_2O, CO_2, CH_4, CO) between the gas phase and ice mantles on dust grains of different sizes and pebbles [1]. Our results show that pebbles, covered in icy mantles, form as early as 50 kyr after disk formation. The ice composition on pebbles is significantly carbon-depleted (in CO and CH_4) compared to ices on small dust and in the gas phase and is dominated by H_2O and CO_2. This suggests a potential dominance of oxygen in the composition of planets formed from such pebbles. The outburst shifts the snowlines and leads to decomposition of pebbles, which are reformed several thousand years after the outburst.

Furthermore, using the ANDES astrochemical code, we investigate how luminosity outbursts disrupt this established picture [2]. Outbursts cause ice sublimation and release deuterated water (HDO) into the gas phase, allowing for a direct comparison of model predictions with ALMA observations of the FUor object V883 Ori [3]. We demonstrate that the observed high HDO/H_2O ratio in the V883 Ori disk cannot be explained by its current luminosity (~400 $L_\odot$). The best agreement with observations is achieved in scenarios involving more powerful past outbursts (2000 - 10000 $L_\odot$) or a series of consecutive outbursts. This indicates that the present-day chemical composition of ices is a consequence of the star's outburst.

In conclusion, our work shows that ices on pebbles have a distinct, oxygen-rich composition, and that luminosity outbursts are a critical mechanism that alters disk chemistry, revealing deuterated isotopologues and encoding the history of stellar activity into the observable ice composition.

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Fine-tuning the complex organic molecule formation: Sulphur and CO ice as regulators of surface chemistry

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Grain-surface chemistry plays a crucial role in the formation of molecules of astrobiological interest, including H_2S and complex organic molecules (COMs) [1, 2, 3]. These are commonly observed in the gas phase toward star-forming regions, but their detection in ices remains limited [4, 5]. Combining gas-phase observations with chemical modeling is therefore essential for advancing our understanding of their chemistry.

The goal is to investigate the factors that promote or hinder molecular complexity combining gas-phase observations of CH_3OH, H_2S, OCS, N_2H^+, and $C^{18}O$ with chemical modeling in two prototypical dense cores: Barnard-1b and IC348. To do so, we observed millimeter emission lines of CH_3OH, H_2S, OCS, N_2H^+, and $C^{18}O$ along strips using the IRAM 30m and Yebes 40m telescopes. We then used the gas-grain chemical model *Nautilus* to reproduce the observed abundance profiles, adjusting parameters such as initial sulfur abundances and binding energies.

H_2S, N_2H^+, and $C^{18}O$ gas-phase abundances vary up to one order of magnitude toward the extinction peak. The CH_3OH gas-phase abundance remains quite uniform. Our chemical modeling reveals that these abundances can only be reproduced assuming a decreasing sulfur budget, which lowers H_2S and enhances CH_3OH abundances. Decreasing binding energies, which are expected in CO-rich apolar ices [6], are also required. The sulfur depletion required to explain H_2S is generally higher than that needed by CH_3OH, suggesting an unknown sulfur sink. These findings highlight the intricate relationship between sulfur chemistry and COM formation, driven by the competition between sulfur and CO for hydrogen atoms.

The formation of COMs begins in the low-density envelopes of molecular clouds. The growth of CO ice and the progressive sequestration of hydrogen atoms are critical in determining whether chemical complexity can develop. Our study highlights that molecular complexity is closely tied to sulfur chemistry within dense cores, offering crucial insights into the early stages of star and planet formation.

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Flare-driven X-ray ionization and chemistry in protoplanetary disks

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Young stars often produce powerful explosions called flares—sudden releases of magnetic energy that generate intense X-ray radiation lasting for several hours. These X-rays play an important role in shaping the physical and chemical conditions of the surrounding protoplanetary disk. In particular, flares are a unique source of hard X-rays with energies above about 10 keV in a protoplanetary system. These high-energy photons can penetrate deep into the disk and ionize gas without undergoing absorption by disk materials [1]. While observations have indicated that time variability in stellar X-ray luminosity affects disk ionization [2], theoretical models [e.g., 3] have often neglected the detailed properties of individual flares and their hard X-ray emission.

In our study, we develop a model of time-varying X-ray emission from flares, based on solar/stellar observations and theories [4]. We combine this model with radiative-transfer and chemical network calculations to quantify how flare-driven X-rays change the ionization state and chemistry in the disk. Our results show that a single flare (energy ~10^{35} erg) can temporarily raise ionization rates to levels higher than those produced by galactic cosmic rays, leading to enhanced formation of molecules such as HCO^+ and N_2H^+. These findings highlight the importance of flare-driven X-rays as a driver of ionization and chemistry in protoplanetary disks. I will also discuss the potential impact of multiple flares and their role in the disk's chemical evolution.

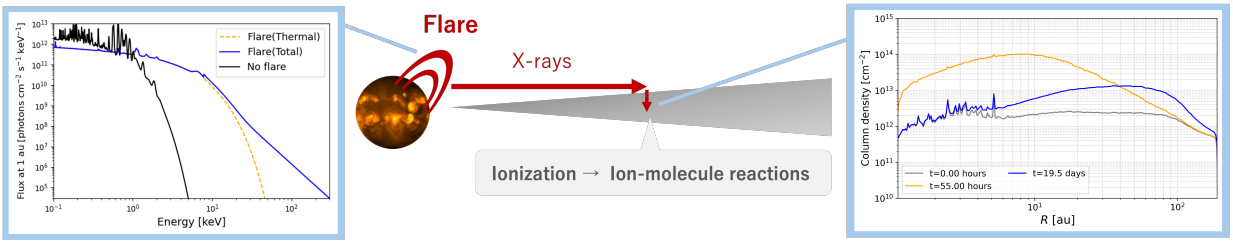

Figure 1: A schematic picture of this study. We model an X-ray spectrum of the stellar flare (left figure) and study the chemical responses (right figure: HCO+ column density before (gray line) and after the single flare (blue and orange lines)).

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A simple and accurate framework for treating ortho-to-para ratio of molecular hydrogen in astrochemical models

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Molecular hydrogen (H_2), which is a major constituent of molecular clouds, is classified into two types: ortho-H_2, whose spins are parallel, and para-H_2, whose spins are antiparallel. The energy difference between their ground states is approximately 170 K, which is significantly larger than the typical gas temperature of molecular clouds (~ 10 K). The abundance ratio of ortho-to-para-H_2 (the ortho-to-para ratio, H_2 OPR) affects both the thermal state of molecular gas and the efficiency of deuterium fractionation in interstellar molecules. Therefore, it is essential to estimate the H_2 OPR in molecular clouds.

Since the direct observation of H_2 OPR in cold molecular clouds is difficult, we need time-dependent chemical network models to estimate the H_2 OPR. However, such network models require a vast number of chemical reactions, because they treat ortho and para-H_2 separately.

In this work, we derive an equation for time evolution of H_2 OPR and develop a simple and accurate framework for treating the H_2 OPR within any chemical network models without increasing the number of reactions. Our framework appropriately considers the essential processes for the conversion between ortho and para states (e.g., two-body reactions with proton [1] and nuclear spin conversion on grain surface [2][3]) and does not require explicitly distinguishing the ortho and para-H_2. We compare the results of our framework with those obtained from the detailed chemical networks that treat ortho and para-H_2 separately and confirm that our framework gives results consistent with theirs. We will also discuss the applicability of our framework.

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CO_2 on interstellar iced grains: insights into adsorption and spectral features

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Dust grains covered by thick water-dominated ice mantles are present in the coldest and densest parts of the interstellar medium (ISM) and in protoplanetary disks during different stages of planetary formation. Until 2021 almost 300 species have been identified in the gas phase in the ISM, while only a fraction of these species has been detected in ices [1]. Since, observations of ices require a background-illuminating source for absorption, the available lines of sight for investigation are constrained. Further challenges arise when observations are compared with laboratory spectra, which is due to the influence of temperature, ice structure and the presence of other species. Some of these issues can be solved by employing quantum chemical calculations to simulate the infrared (IR) spectra. While, James Webb Telescope (JWST) has been already proven to be an excellent tool for detecting the chemical components of the icy mantles by means of IR spectroscopy, it requires precise spectral references [2]. In my work I use the ACO-FROST procedure to address the adsorption and IR spectral signature of CO_2, a third most abundant and astrochemically relevant icy species, on a model of an iced grain [3]. I will discuss the binding energy distribution and the IR spectral features of CO_2 in the context of experimental spectra and the findings from the JWST.

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Unveiling the physical properties of Fe-doped cosmic silicate nanostructures from a computational perspective

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One of the most intriguing challenges in astrochemistry revolves around the hunt for suitable reservoirs of the fundamental elements that are found to be depleted from gas phase observations in the interstellar and circumstellar environments [1]. Iron (Fe), the most abundant refractory transition metal is one such element whose possible existence in some form of condensed phase has been anticipated for a long time [2]. Numerous speculations and observations have identified several Fe-bearing compounds [3,4,5] in the astrochemical environment which may serve as potential candidates for sequestering the "missing iron" in the cosmos. In this regard, the structure of cosmic silicate dust grains (of olivine (Mg_2SiO_4) and pyroxene ($MgSiO_3$) stoichiometries) brings hope due to the compatibility of Fe substitution in its Mg-site. Not only that, the detection of Fe-bearing amorphous silicates [6,7] along with other astronomical findings offer strong evidence to consider the cosmic silicates as an effective confiscator of Fe. It is to be noted that these dust grains play a very crucial role in the cosmic life cycle of matter. Once released from the stellar outflows to the interstellar medium, they face a very challenging journey experiencing fragmentation and reformation by high energy particles and radiation. This results in a diversity of the sizes, shapes and chemistry. Subject to such processes, the cosmic silicates are very likely to be nanosized. Ultimately, they combine to form larger bodies in the planet forming disks. Hence, these nanosilicates can be considered important forerunners of planetary formation.

While Mg-bearing silicate dust grains dominate the cosmos, even small concentration of Fe can significantly modulate their physical properties. In this study we have investigated the influence of Fe (concentrations ranging from 0% to 50%) on the structural, electronic, magnetic and spectroscopic properties of nano-silicates using quantum chemical density functional theory. Our simulations indicate that the formation energy (at 0K) of these nanosilicates reduces in the presence of Fe, thereby demonstrating the potential of the nanoclusters to confiscate Fe. This study not only pinpoints the degree to which Fe amends the fundamental properties of these nanosilicates, but also provides insights into the spectroscopic properties which can aid in the gross estimation of Fe trapped in nanosilicates along various lines of sight in the cold interstellar medium.

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The Impact of a Multi-Population Dust Model with Temperature Distributions on Astrochemical Simulations

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Astrochemical models are becoming increasingly complex. The description of dust in these models has shifted from a single population to multiple dust populations. In this work, we aim to improve the accuracy of dust description in an astrochemical model. We use the model MONACO. We consider grains of different sizes, and the temperature of each grain is represented by a probability function rather than a single equilibrium value. The rates of reactions that depend on temperature and grain size have been corrected. These include reactions such as accretion, desorption, diffusion, and non-diffusion chemical reactions on the surfaces of dust grains. The temperature probability function for dust grains was calculated using a stochastic heating treatment, where heating is caused by ultraviolet photons and cosmic rays. Using our new multi-grain and multi-temperature model, we calculated the abundances of interstellar species under conditions corresponding to the dark cores of molecular clouds.

We compared the results obtained with the new version of MONACO and the one which includes only one dust grain. It was found that the simple molecules (e.g. CO, HCO+, etc.) are not sensitive to the dust description. Abundances of ice mantle components change in different ways: they can increase, decrease or remain the same with the new model in comparison with the classic one. The most prominent result is that the abundance of some complex organic molecules such as HCOOCH3, CH3OCH3, C2H5OH increases about an order due to elevated constant rates of the reactions of their formation during the short time periods when dust grains have elevated temperature. Herewith, large grains of radius ~0.1 mum or larger and the smallest graphite grains of radius <0.01 mum are the most favourable for proceeding of these reactions.

Considering the treatment of dust description in astrochemical models which includes multiple dust populations of different types and sizes and the temperature distribution for each dust grain may lead to increasing of abundance of complex organic molecules by approximately an order. However the variations are not the same for all molecules and depend on an exact molecule and reactions of its formation. The increase is present only for COMs which are formed in temperature-dependent reactions.

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Sulphur Chemistry on Transition-Metal Dust Grains: Insights from CS Hydrogenation

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The depletion of sulphur-bearing species in dense interstellar clouds remains a long-standing puzzle in astrochemistry. In this work, we investigate the catalytic role of Fe^0 single atoms embedded on amorphous SiO_2 surfaces ($Fe^0@SiO_2$) in the hydrogenation of carbon monosulfide (CS), a key sulphur reservoir. Using periodic DFT calculations and RRKM-based kinetic modelling, we show that CS strongly chemisorbs onto Fe sites, enabling efficient conversion into thioformaldehyde (H_2CS) and, under warmer conditions, methyl mercaptan (CH_3SH). The formation of H_2CS proceeds via low energy barriers and is kinetically viable at temperatures as low as 15 K, with quantum tunnelling enhancing reactivity. In contrast, CH_3SH formation requires significantly higher activation energies, becoming a kinetic bottleneck below 150 K. Binding energy analysis reveals that both reactants and products remain strongly adsorbed, suggesting that Fe-rich grains act as reactive sinks for sulphur species. These findings highlight the importance of transition-metal-induced astrocatalysis in shaping sulphur chemistry across star-forming environments.

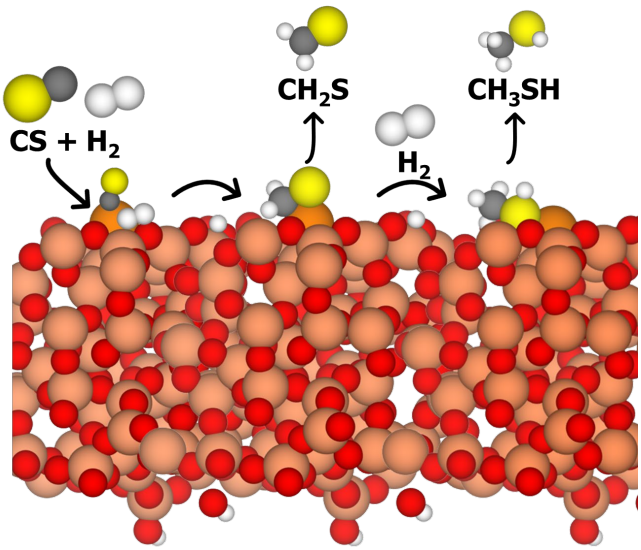

Figure 1: Schematic representation of the $Fe^0@SiO_2$ and the proposed reaction process.

Quantum Chemical Surface Reactions Producing Carbamic Acid as a Glycine Precursor

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Detecting glycine in space is a long-standing objective, but here we propose carbamic acid (H_2NCOOH) as a closer, mechanism-revealing target. Prior ice studies indicate that CO_2:NH_3 mixtures can yield carbamic acid together with its salt and dimer at low temperatures, and that their observables depend on the surrounding water environment [1,2]. These results suggest that specific mid-infrared bands (near the 9–10 μm region) remain promising under water-rich conditions and motivate a surface-reaction perspective.

We present quantum-chemical modeling that maps precursor pathways on dust/ice surfaces, focusing on CO_2 + NH_3 routes to carbamic acid, ammonium carbamate, and the dimer. Using transition-state searches on microhydrated cluster models, we characterize key elementary steps and quantify how local water stabilizes reactants and lowers barriers. We also predict environment-dependent vibrational signatures to aid interpretation of laboratory and astronomical spectra. The combined picture links feasible surface mechanisms with practical diagnostics and provides guidance for future observations of dense, water-rich ices.

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Physical properties and photochemistry of interstellar ice analogs forming complex organic molecules with sulfur

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This presentation covers the topics reported in our recent work with a similar title [1]. Radiation and thermally driven processes taking place on the bare dust, and particularly on dust particles covered by icy mantles, are mimicked in the laboratory. In addition to water, interstellar ice contains other simple species. We present our current knowledge on ice photochemistry and thermal processing that ultimately leads to the formation of complex organic molecules. Numerous complex organic molecules are of astrobiological interest and match those present in comets and asteroids. Upon impact of these minor bodies, water and complex organic molecules could have been delivered to the early Earth, which might have been vital for the first prebiotic reactions. The talk includes recent experimental results on ice properties (density, infrared spectroscopy, optical constants, morphology) supported by DFT calculations. It also presents some of the results obtained by irradiation of interstellar ice analogs leading to the formation of complex organic molecules, including sulfur-chemistry in the ice.

The harsh conditions in space (ultra-high vacuum, cryogenic temperatures, and radiation) are simulated in the laboratory to study ice properties and processes. UV photons/X-rays/ ions impact on the ice covering microscopic pre-cometary dust particles in dense interstellar clouds and protoplanetary disks prior to the formation of cometesimals by agglomeration of the icy dust. Radiation produces radicals and reactive species changing the initial composition of the ice (made of simple species like water, CO, CO2, CH3OH, NH3, etc) to form complex molecules of prebiotic interest (amino acids, nucleobases, sugars, …) in the laboratory. Many of these molecules were also identified in the Rosetta comet 67P, and the IR spectra of Ryugu samples delivered by Hayabusa2 are strikingly similar to our refractory residues made by ice irradiation [2].

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In situ measurement of the crystal structure of nanometer-sized vapor-deposited ice growing under polar mesospheric conditions

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Polar mesospheric clouds (PMCs), also known as noctilucent clouds, are the highest clouds in the Earth's atmosphere at the altitudes of around 83 km. Because the formation of PMCs is affected by important process such as increasing of greenhouse gases and atmospheric circulation, satellite observations and simulations have been conducted over long periods [1-3]. These studies suggest that PMCs consist of nanometer-sized water ice particles that heterogeneously nucleate on meteoric smoke at the temperature of 100~150 K and the water vapor pressure of 10^{-6} Pa. However, the detailed crystal structure of the water ice remains unknown. Recently, our group developed a novel experimental setup to monitor the ice film's structure using Reflection High-Energy Electron Diffraction (RHEED) and Infrared Reflection Absorption Spectroscopy (IRRAS). We found that the structure of the ice film growing at 120 K and 2×10^{-6} Pa is amorphous (ASW) for the first 15 nm, followed by metastable cubic ice I (Ic) up to 50 nm, and then finally hexagonal ice I (Ih) [4].

In this study, we further investigated nanometer-sized ice films growing at higher temperatures of 130~140 K and a water vapor pressure of 10^{-6} Pa. IRRAS spectra (Figure 1, left) indicate the formation of crystalline ice, and were fitted using the optical constants of crystalline ice [5] to determine the thickness. Because IRRAS alone cannot distinguish between Ic and Ih, we conducted RHEED measurements (Figure 1, center and right). This simultaneous measurement clearly demonstrates that the crystal structure of vapor-deposited ice is sensitive not only to substrate temperature and water vapor pressure, but also to the ice thickness. We confirmed Ic forms first before the thermodynamically more stable Ih emerges under mesospheric conditions. The present results strongly suggest that Ic can exist in PMCs and relevant environments near the polar mesopause, offering crucial insights into ice physics.

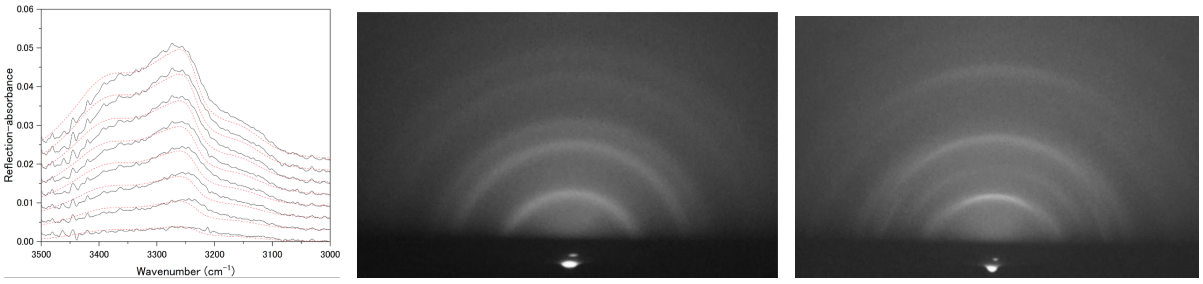

Figure 1: (Left) IRRAS spectra showing OH stretching vibration region for vapor-deposited ice growing at the temperature of 130 K and the water vapor pressure of 2×10^{-6} Pa, recorded between 30 and 240 minutes. The black solid and red dashed lines represent experimental and fitted spectra, respectively. (Center and Right) RHEED patterns of the ice grown for 60 min (6.2 nm) and 420 min (42 nm). Debye-Scherrer rings indicate that the crystal structure of the ice is polycrystalline Ic (Center) and Ih (Right), respectively.

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Sinergy of VUV and X-ray radiation

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Young stars are powerful emitters of VUV and X-ray radiation. The chemistry of inter- and circum-stellar ices has been extensively studied in the VUV regime, with less focus on X-ray radiation. This work investigates the combined effects of VUV and X-ray radiation on interstellar ices, particularly in terms of chemistry and photo-desorption.
To evaluate the synergy of both energy sources in a proto-planetary disk, we conducted single-source irradiation experiments using either VUV or X-ray radiation, as well as simultaneous VUV and X-ray irradiation. These experiments mimic the photon emission of a young star. We used a microwave-discharge hydrogen-flow lamp (MDHL) as VUV source and X-ray energies of 300, 550, and 900 eV. These experiments were performed at the national synchrotron radiation research center (NSRRC) in Taiwan.
The results obtained provide insights into the mechanisms and comparative effects of these distinct irradiation sources on circus-stellar ice analogues. They reveal how these sources influence the chemistry of the ice and the subsequent photo-desorption yields.

Methylamine formation by radical–radical reactions on diluted ice surface at 10 K

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Methylamine (CH_3NH_2) has been observed in interstellar space [1] and is considered as an important precursor of glycine. The formation pathways of CH_3NH_2 have been discussed and proposed in gas-phase reactions [2] and on grain surfaces.[3,4] In this study, we focused on the formation of methylamine by non-energetic processes on ice dust surfaces and experimentally studied the association reaction between CH_3 and NH_2 radicals on amorphous solid water (ASW).

To evaluate the possibility of methylamine formation on actual ice dust surfaces, experiments were conducted under very low reactant coverage on ASW, demonstrating interstellar ice environments. CH_3 and NH_2 radicals were produced by sequential deposition of CH_4 and NH_3 onto ^{18}OH adsorbed ASW at 10 K. The ^{18}OH adsorbed ASW was prepared by UV photolysis of ASW formed by $H_2{}^{18}O$ vapor deposition on an aluminum substrate at 30 K. The coverage of ^{18}OH was 1.0% and that of both CH_4 and NH_3 was 2.5% on ASW surfaces. To detect the small amounts of products, we performed our non-destructive and highly sensitive analysis method.[5] Figure 1 shows the variations of the parent radicals (^{18}OH and CH_3) and the product (CH_3NH_2). The surface temperature gradually increased from 10 to 60 K. Above 20 K, the intensities of parent radicals decreased due to CH_3 thermal diffusion, resulting in CH_3NH_2 formation. Surprisingly, CH_3NH_2 can be produced even on 10 K ice, although thermal diffusion of parent radicals is prohibited at this temperature. It is indicated that non-thermal radical–radical reactions occur at 10 K to produce methylamines.

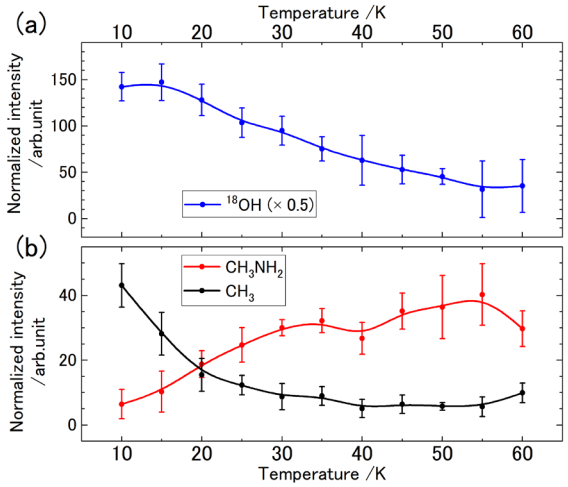

Figure 1: Temperature dependence of (a) ^{18}OH radical and (b) methylamine (red) and CH_3 radical (black). The intensity of ^{18}OH was multiplied by 0.5. NH_2 is not shown because it cannot be separated from CH_4.

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Sulfur-Chain Growth and Oxidation Pathways in Electron-Irradiated H_2S and H_2O+H_2S Ices

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Hydrogen sulfide (H_2S) is a crucial sulfur-bearing molecule in interstellar ices and a potential reservoir for the cosmic sulfur budget. To investigate its evolution under energetic processing, we irradiated pure H_2S and H_2O+H_2S ice mixtures deposited at 13 K with 1 keV electrons.

For pure H_2S ice, infrared spectra revealed amorphous features, and electron irradiation induced depletion through both chemical reactions and electron-stimulated desorption. Temperature-programmed desorption confirmed the formation of sulfur-chain products, including H_2S_2 and S_2, with desorption peaks near 86 K and 122 K, indicating chain growth in the solid phase. In contrast, H_2O+H_2S mixtures exhibited enhanced H_2S depletion and promoted oxidation chemistry. Infrared spectra identified SO_2 and HSO_4^- as dominant products, with desorption at higher temperatures due to stronger binding in water-rich matrices.

These results demonstrate that electron processing drives sulfur-chain growth in pure H_2S and oxidation in H_2O-rich ices, providing laboratory constraints on the distinct pathways regulating the fate of sulfur in astrophysical environments.

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Molecular formation by transient diffusion of reaction products on cold ice surfaces

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In molecular clouds, molecular evolution proceeds efficiently through physicochemical processes such as adsorption, diffusion, association, and reactions of atoms and molecules on interstellar dust surfaces. In particular, thermal diffusion of hydrogen atoms is a crucial process for forming simple molecules, which has been widely studied [1]. On the other hand, the formation of complex organic molecules (e.g., $HCOOCH_3$) would require association reactions between "heavier radicals (e.g., HCO or CH_3O)" than hydrogen atoms. However, on the cold ice surfaces of 10 K, thermal diffusion of these heavier radicals is inefficient. In contrast, non-thermal diffusion processes of radicals may play a role in the formation of complex organic molecules under cold molecular cloud environments as low as 10 K. We experimentally observed that radicals generated by surface reactions transiently diffuse, even at 10 K, during the process of dissipating reaction heat to the surface [2, 3], which is referred to as "transient diffusion."

In this work, we obtained information on transient diffusion by probing secondary reactions (S) of radicals (① HOCO, ② CH_3O) formed from primary reactions (P) between parent molecules (① CO, ② CH_3OH) and OH on 10 K ice surfaces, using a highly sensitive "ion pickup" apparatus [4,5]. Specifically, we investigated the following reaction sequence:

① P: $CO + OH \rightarrow HOCO^*$, S: $HOCO^* + OH \rightarrow CO_2 + H_2O$ [3]

② P: $CH_3OH + OH \rightarrow CH_3O^*$, S: $CH_3O^* + OH \rightarrow H_2CO + H_2O$ [2]

Here, "*" represents the transient state during the dissipation of reaction heat before thermalization at the surface temperature. The experimental procedure was as follows (Figure 1). First, trace amounts of OH (up to ~0.01 ML) radicals were produced by UV irradiation of the ice surface. After the irradiation, the parent molecules were deposited onto the OH-prepared ice surface at 10 K, which generated the radical products. Next, we detected products formed by secondary reactions between the generated radical products and another OH. Under the present experimental conditions, where the coverages of radicals were very low, the detection of secondary reaction products indicates the occurrence of transient diffusion, since the radical products and OH do not undergo thermal diffusion. By probing these secondary reactions, we obtained information on transient diffusion.

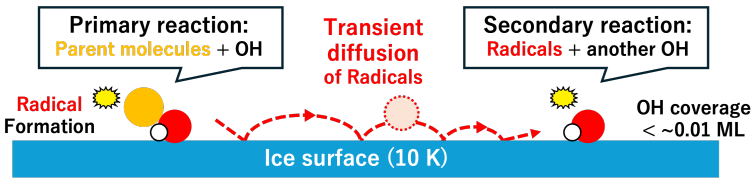

Figure 1: Schematic diagram of the present experimental procedure.

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X-ray Irradiation of H_2S-containing Ice and Analysis using Density Functional Theory

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The results on soft X-ray processing of pure H_2S and H_2S in ice mixtures will be discussed. These experiments were performed at the national synchrotron of Taiwan (NSRRC), where the ice samples were exposed to 300-1500 eV photons that simulate a protoplanetary disk environment in the vicinity of young stars. The formation of photoproducts is compared to that of previous ice processing experiments using UV photons for a similar dose in absorbed eV per molecule. While in other experiments using a different ice composition, the differences between X-ray and UV products were mainly quantitative, in these H_2S-ice experiments, some striking differences were found.

The resulting irradiated products were analysed using infrared (IR) spectroscopy and quadrupole mass spectroscopy. The IR analysis was complemented with density functional theory simulations. We present a novel general method for the prediction and confirmation of IR band strengths for any amorphous ice [1]. Simulated amorphous ices are generated using randomised initial positions of molecules in a cubical simulation box with periodic boundary conditions to simulate an infinite amorphous solid. Constant volume molecular dynamics is used to introduce temperature. IR spectra are generated according to density functional perturbation theory. Estimations for IR band strengths are presented for ices of astrophysical interest, including water, carbon dioxide, carbon monoxide, methane, ammonia, and methanol, as well as several sulphur-based molecules. The newly calculated band strengths are in good agreement with previous values obtained through experimental measurements.

The novel method can be applied in general to any amorphous ice, with especially good accuracy for bending vibrational modes. The method can also be applied to ices of unknown band strengths, including unstable species under Earth conditions, and to mixed or layered ices that contain more than one species.

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Probing O(^{3}P) behaviour on interstellar ice analogues using the PSD-REMPI method

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The triplet oxygen atom, O(^{3}P), is a product of the VUV photolysis of water. As a highly reactive and abundant species, involved in the formation of other abundant species, such as H_2O and O_2, understanding its surface diffusion and desorption is essential.

We used a combination of photostimulated desorption (PSD) and resonance-enhanced multiphoton ionisation (REMPI) techniques, known as the PSD-REMPI method, to selectively and sensitively monitor O(^{3}P) and O_2 photodesorption from amorphous solid water in the visible range (400-650 nm) [1, 2]. To produce O(^{3}P) radicals and minimise the interference of OH radicals, we deposited a thin layer (0.03 ML) of N_2O on H_2O ice (40 ML) and irradiated it at 193 nm. We observed a dependence of the PSD wavelength on temperature for O_2 and possibly for O(^{3}P). Both species desorbed more efficiently at longer wavelengths at lower temperatures.

Theoretical calculations are necessary to investigate how this observed trend relates to different types of binding sites on the ice surface. Further experiments are necessary to clarify the photodesorption efficiency of O(^{3}P) at varying wavelengths and temperatures with O(^{3}P) at steady state.
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The surface diffusion of nitrogen atoms on amorphous solid water at low temperatures

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Molecular clouds are the birthplace of stars and characterized by low temperature and low density. Despite such an unfavorable environment for chemical evolution, over 150 chemical species have been identified. This chemical diversity cannot be explained by gas-phase reactions alone, and it has been known that surface reactions on amorphous solid water (ASW) existing on interstellar dust grains play important roles. Due to high vacuum, in gas phases, reaction heat cannot be released as thermal energy. In surface reactions, ASW contributes as a heat sink. Furthermore, the surface also enhances the association efficiency of the reactants. In such reactions, radical reactions are particularly important because they proceed even under low-temperature conditions due to barrierless reactions.

The nitrogen (N) is the sixth most abundant element in space, but it is not obvious how N atoms are incorporated into molecules [1]. A large fraction of N atoms is thought to exist as N_2, but it is difficult to detect N_2 by observation. In addition, N_2 is thought to be produced on the surface of icy grains by the recombination reaction of N atoms. Therefore, to understand the formation processes of molecules containing N-atoms, including N_2, it is important to clarify the behavior of N atoms on ASW through quantitative experiments; in this work, we focused on the thermal diffusion of N atoms on ASW.

In the present experiments, to detect trace amounts of N atoms on ASW, we used the combination of photo-stimulated desorption and resonance-enhanced multiphoton ionization techniques: PSD-REMPI method. Using this method, radical on the surface of ASW were photo-desorbed by a weak nano-second laser pulse at 532 nm, they were selectively ionized by the REMPI laser, and the ions were detected by a time-of-flight mass spectrometer. When N atoms are deposited onto the ASW surface and detected using this method, the signal intensity is proportional to the surface number density of N atoms. Therefore, this method enables tracking the time evolution of the surface number density of N atoms.

When N atoms are continuously deposited onto ASW, we found that a steady-state, where the PSD-REMPI intensity became constant, was achieved. Under this condition, the supply rate of N atoms is balanced by the consumption rate, which is predominantly determined by the diffusive recombination reaction ($2N \rightarrow N_2$). The consumption rate increases at higher temperature due to enhanced thermal diffusion, resulting in the lower steady-state intensity. From the temperature dependence of steady-state intensities, we determined the activation energy for surface diffusion to be 930 ± 60 K. This value is significantly different from ~ 300 K predicated by quantum calculations [2] The discrepancy can be explained by considering that the experimental value represents the diffusion from the deepest potential sites, which is the rate-determining step for N-atom recombination, whereas the predicated value is an average from those from various potential sites. In fact, the calculated activation energy from the deepest potential site is approximately 900 K [2].

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HMT derivatives as relics of the radicals formed at low temperatures

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Hexamethylentetraamine (HMT) is a molecule known to be formed under experimentally simulated interstellar ice irradiation expected to occur in dense cloud interiors and cold protoplanetary environments. HMT could have played a significant role in the delivery of organic matter in the early Earth, as it can produce several aminoacids, being a relevant molecule for prebiotic chemistry and astrobiology. The formation pathways of HMT have been studied over the last years by several groups [1,2]. In this work [3], we have performed laboratory experiments to simulate realistic ice mantles (composed of H_2O:CH_3OH:NH_3) and study the formation of HMT-based species.

Up to 17 different HMT derivatives (HMT-R) have been detected from the GC-MS analysis of the residues left by the UV-irradiated ice mantles at room temperature, 11 of them are detected for the first time [4]. Analysis of different residues over the last decades have shown considerable differences in the detected products for similar experiments, suggesting that the analytical procedure and, as we will discuss also the storage time of the samples, play a key role in the species which are detected in the chromatographic analysis.

We propose that the abundance of the different HMT-R species is indicative of the abundance of the R groups at lower temperatures. Even though there are some considerations that should be pointed out, the idea of using these species as tracers of the radical abundances in the irradiated ice at low temperatures seems to be an interesting point that will be addressed during the talk.

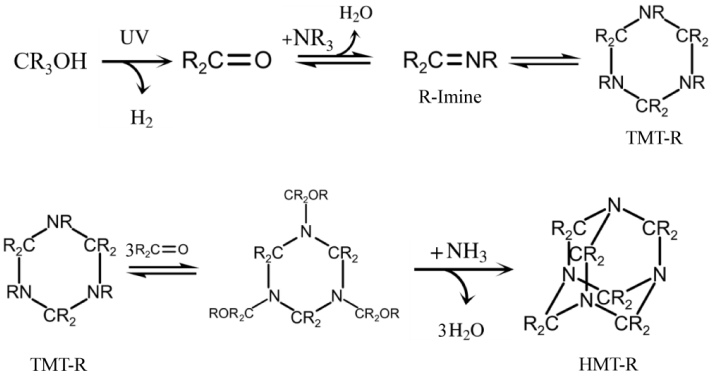

Figure 1. Synthesis of HMT-R. The proposed pathway has been modified from the accepted pathway towards the formation of HMT, showing how HMT-derivatives can be obtained.

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Fast heavy-ion-induced reactions on alcohol ice and droplet surfaces

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Ion–molecule reactions are widely recognized as key processes in astrochemistry. While most studies have focused on gas-phase reactions, these processes are also expected to play a significant role in condensed phases. Nevertheless, their investigation remains challenging, and many aspects are still unclear. In particular, anion–molecule reactions have not been fully explored, and some important pathways may still be overlooked.

From the perspective of radiation chemistry, we have investigated the positive and negative secondary ions emitted from microdroplet surfaces under fast heavy ion impacts using mass spectrometry. Experiments using alcohol droplets have revealed characteristic features of reactions in the condensed phase [1] and suggested molecular growth pathways driven by previously unidentified anion–molecule reactions, such as $CH_3O^- + CO \rightarrow C_2H_3O_2^-$ [2]. Since such reactions are also expected to occur at ice surfaces, we have recently extended our experiments to alcohol ices, aiming to contribute to astrochemical studies.

Figure 1 shows the positive secondary ion mass spectrum obtained from a methanol ice surface irradiated with 1.5 MeV C^+ ions. In addition to protonated cluster ions, fragment ions and reaction products involving more than one molecule are clearly observed. It was found that these ion distributions closely resemble those obtained from alcohol droplets. In this presentation, we will also report results for negative ions and for other alcohol targets.

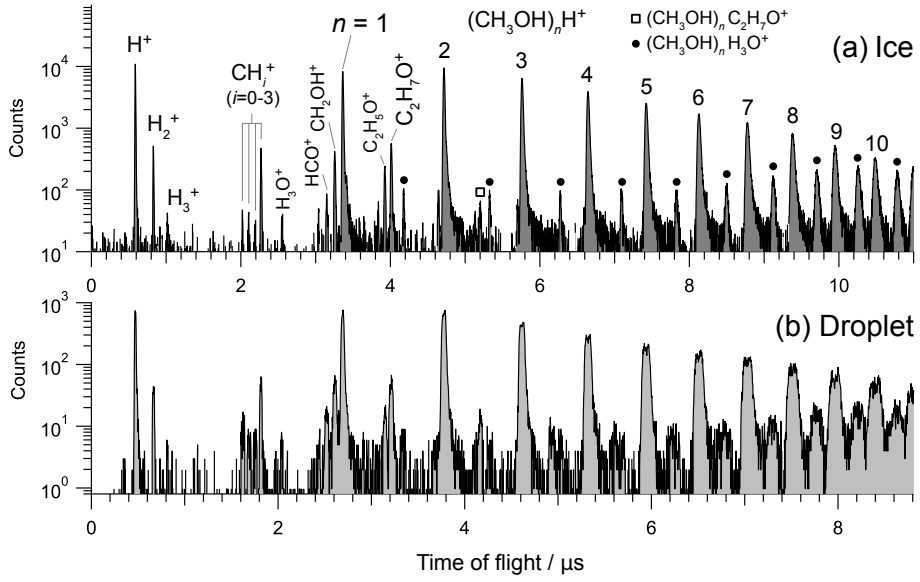

Figure 1: Time-of-flight mass spectra of positive ions from the methanol (a) ice and (b) droplet [2] surfaces.

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Interstellar Origin of Complex Molecules Detected in Meteorites: Experimental Evidence from Irradiated Ices

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In the coldest regions of molecular clouds, interstellar dust grains are covered with layers of ice composed mainly of simple volatile molecules. Exposure to secondary UV photons and subsequent heating in regions such as hot cores induce increasing chemical complexity in these ices. The resulting organic matter evolves from molecular clouds to protoplanetary discs, contributing to the formation of Solar System bodies, such as primitive chondritic material and, ultimately, planets.

Laboratory experiments are fundamental to understanding the origin and evolution of this organic matter. In this work [1], we performed UV irradiation followed by warming to room temperature of H_2O:CH_3OH:NH_3 ice mixtures deposited at 80 K. Some of the products generated are stable at room temperature and form a refractory organic residue rich in organic compounds, many of which are of astrobiological interest.

Using gas chromatography coupled with mass spectrometry (GC-MS), we have identified relevant compounds, including new derivatives of hexamethylenetetramine (HMT, $(CH_2)_6N_4$) and five-membered nitrogen heterocycles. Some of these compounds have already been detected in comets and meteorites [2], reinforcing the hypothesis of their interstellar origin. In addition, the detailed mass spectra we present open up new possibilities for the identification of HMT-based molecules in pristine materials from the Solar System.

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Interaction of low-energy CH_3^+ ion with methanol solid in low temperature environment

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Despite extremely low temperatures of approximately 10 K within molecular clouds, existence of numerous types of molecules has been known. These molecules are thought to form through various reaction pathways, beginning with reactions involving atoms and simple molecules including ionic species. Elucidating these reaction processes and physical mechanisms is also strongly linked to understanding the physical and chemical properties of interstellar matter. Ion-molecule reactions in the gas phase are considered the most important mechanism for molecular synthesis. However, these alone could not explain the abundance of even relatively common molecules like hydrogen, water, and methanol molecules. Therefore, neutral reactions involving radicals on the surfaces of icy grains have also been recognized as important. In particular, the importance of hydrogen-atom addition reactions has been experimentally demonstrated at low temperatures below approximately 20 K [1, 2]. Radicals heavier than hydrogen atoms diffuse very slowly below 20 K and thus will contribute to molecular synthesis in a higher temperature environment, otherwise as a result from non-thermal diffusion driven by energetic processes like photodissociation.

In the past decade, theoretical calculations using computational chemistry methods have proposed another type of molecular formation by reactions between low-energy ions and amorphous ice surfaces [3-5]. To verify these theoretical predictions, we developed a new experimental apparatus employing reactive scattering ion mass spectrometry (also known as the ion pickup method) for detecting chemical species on surfaces [6, 7]. Using this apparatus, we investigated the formation of methanol molecules from the reaction of CH_3^+ with amorphous solid water surfaces at very low temperatures [8]. Recently, we have been conducting experiments for the reaction of CH_3^+ with methanol solid surfaces to investigate the reaction between methanol formed on icy grains and low-energy ions. To the best of our knowledge, no theoretical predictions exist for this reaction. The experiments using methanol with natural isotope abundance suggest the potential formation of formaldehyde and dimethyl ether (or ethanol). We are also performing experiments using isotope labeling to investigate the origin of constituent atoms in the reaction products. We will report about these experiments.

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Methanol formation via transient-diffusion-driven sequential reactions by methane deposition onto OH adsorbed amorphous solid water at low temperatures

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Recently, sequential reactions have been experimentally observed at 10 K as a result of transient surface diffusion of radicals driven by the heat of reactions [1,2]. We propose that such transient diffusion of radicals may play an important role in various reactions. In this context, we investigated the association reaction between CH_3 and OH as a formation pathway for CH_3OH at 10 K. Under the preset experimental condition, this reaction is expected to proceed via the transient diffusion of CH_3 radicals, facilitated by the heat of preceding reaction of $CH_4 + OH \rightarrow CH_3$. In addition, the temperature dependence of CH_3OH yield were measured at surface temperatures up to 60 K.

The experiments employed the highly sensitive Cs^+ pickup method, a powerful technique for mass-analyzing trace amounts of adsorbates on amorphous solid water (ASW) [1]. In this method, surface species (X) on ASW are identified as ionic complexes (Cs^+-X) by mass spectrometry following low-energy Cs^+ beam irradiation. Figure 1 shows the pickup mass spectra of (a) photolyzed ASW and (b) photolyzed ASW with CH_4 deposition at 10 K. Signals corresponding to CH_3 (148u) and CH_3OH (165u) were observed only after CH_4 deposition onto photolyzed ASW. This indicates that CH_3OH is formed via the $CH_3 + OH$ reaction, since the direct reaction of $CH_4 + OH \rightarrow CH_3OH + H$ is highly endothermic (+58.8 kJ/mol) [3]. Furthermore, CH_3OH yields measured at various initial OH coverages exhibited a square dependence on OH concentration, providing further evidence that CH_3OH produced through the association of OH and CH_3. This is consistent with the fact that CH_3 is the product of preceding hydrogen abstraction of CH_4 by OH.

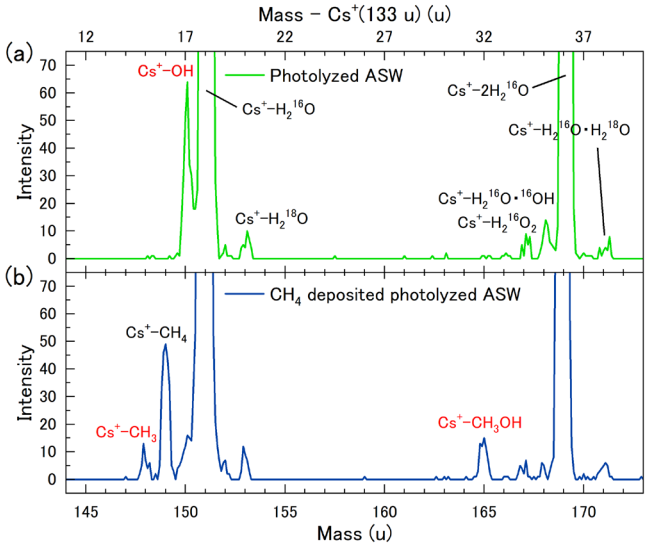

Figure 1: The pickup mass spectra for (a) photolyzed ASW and (b) CH_4 deposited on photolyzed ASW. The deposition time of CH_4 was 15 minutes (coverage 0.17).

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Development of high-pressure RHEED and IR spectroscopy for understanding the structure of vapor-deposited ice under terrestrial atmospheric conditions

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Water (H_2O) ice has many forms. Twenty-one different crystalline structures have been observed, named ices I-XIX. Water is ubiquitous in the universe. In the extra-terrestrial space, it is an abundant intersteller molecule. Ice covers the surface of dust grains in molecular clouds, which are cold (10 K) and dense (10^4 molecules cm^{-3}; 10^{-12} Pa) interstellar regions. Water ice also exists in the Earth's atmosphere [1]. Polar mesospheric clouds, also known as noctilucent clouds, are the highest clouds in Earth's atmosphere, which occur at the heights of about 82 km at temperature below about 145 K under partial vapour pressure of 10^{-7}–10^{-5} Pa. The formation of polar mesospheric clouds is a topic of intense research because they are beneficial to understanding the physics and chemistry of the mesosphere and lower thermosphere and also serve as potential indicators of global climate change.

Recently, we developed an experimental apparatus for the in situ structural analysis of vapour-deposited ice through a combination of reflection high energy electron diffraction (RHEED) and infrared reflection−absorption spectroscopy (IRRAS), and reported that the structures of the growing ice under polar mesospheric temperature (120 K) and vapour pressure (10^{-6} Pa) conditions differ depending on the ice size (thickness), that is, the ice appeared to grow in three steps during vapour deposition, being amorphous water for the first 15 nm, then cubic ice Ic up to 50 nm, and finally hexagonal ice Ih subsequently [2]. Although the current RHEED-IRRAS apparatus powerfully works to study the structure of vapour-deposited ice, it requires a high vacuum condition to protect the turbo molecular pump in the vacuum chamber and the electron gun for RHEED from damaging. Thus, the current apparatus cannot simulate the total pressure in the mesosphere (about 1 Pa). In addition, it is impossible to study the ice structures in other Earth's clouds, such as polar stratospheric clouds, important factor of ozone depletion, which form at below 188 K at heights of 17−31 km under partial vapour pressures of 10^{-3}–10^{-2} Pa with the total pressures of 10^3–10^4 Pa [3,4,5,6].

For understanding the structure (amorphous water, cubic ice Ic or hexagonal ice Ih) of ice in the Earth's clouds, we are now constructing a new apparatus to study the ice structures under higher pressure conditions using a combination of high-pressure RHEED and IR spectroscopy. Two-stage differential pumping system is employed to protect the filament of the gun from burning out even when the pressure of the sample chamber reaches 10 Pa. The distance between the electronic gun and the screen is designed to be shorter than the mean free path of electrons under 10 Pa for RHEED measurements. A silicon (Si) substrate is used for RHEED and IR measurements. The substrate can be cooled down to 77 K using liquid nitrogen, and heated by a heater up to 230 K, at which the vapour pressure of ice Ih reaches 10 Pa [5]. Our new apparatus will be able to simulate polar mesospheric conditions including its total pressure (1 Pa). Simulating the partial vapour pressure and temperature of polar stratospheric conditions is also possible for studying the ice structures of polar stratospheric clouds.

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Orion SrcI's Disk Investigated through Sulfur-bearing Molecules

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Sulfur-bearing molecules are effective probes of heated and shocked environments in star-forming regions, such as the centrifugal barrier in low-mass protostars. In massive sources, both volatile (e.g., SO) and refractory (e.g., SiS) sulfur-bearing species are commonly detected and utilized to study their physical and chemical structures. Here, we present a case study of sulfur-bearing molecules (SO, SO2, and SiS) in Orion SrcI with high frequency ALMA observations (Band 8 and 9), focusing on the disk/outflow surface region. Moreover, the physical conditions, such as temperature and density, are constrained through NLTE analysis of multiple transitions of the detected species. Clear stratification is observed both chemically and physically in the disk. It is demonstrated that sulfur-bearing species are good tracers of the physical and chemical properties of massive young stellar objects. Furthermore, with both the volatile and refractory species considered, we could better estimate sulfur abundance, assisting in addressing the high depletion rate of sulfur- the "missing sulfur" problem.

Isomerism beyond thermodynamics: Discovery of cis-NMF in the ISM

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Isomerism in complex organic molecules provides key insights into the formation mechanisms and physical conditions of the interstellar medium (ISM). Among the C_2H_5NO isomers, only acetamide and trans-N-methylformamide (trans-NMF) have been detected in space. The recent detection of higher-energy isomers in other chemical families raises questions about the formation and abundance of less stable isomers. We used ultra-sensitive wide-band spectral surveys obtained with the Yebes 40 m and IRAM 30 m telescopes to search for cis-NMF towards the Galactic Centre molecular cloud G+0.693-0.027. We present the first detection of cis-NMF in the ISM, with new transitions identified based on extrapolated spectroscopic data. The resulting trans/cis-NMF isomeric ratio deviates significantly from thermodynamic expectations, suggesting that kinetic non-equilibrium processes and stereospecific chemical pathways are responsible for the formation of cis-NMF in this environment. The detection of cis-NMF expands the known inventory of interstellar C_2H_5NO isomers and challenges the assumption that isomer abundances strictly correlate with thermodynamic stability. Laboratory and theoretical studies propose formation via CH_3NCO hydrogenation or spin-forbidden reactions involving CH_2 and NH_2CHO, though these may not reflect typical ISM conditions. This finding highlights the need for further investigation into isomerisation mechanisms and constrains astrochemical models of complex organic molecules.

References

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