Workshop on Interstellar Matter 2021

Book of Abstracts

17-19 November 2021

Institute of Low Temperature Science,
Hokkaido University, JAPAN

Program

In Japan Standard Time (UTC+9)

17th, Wed.

9:00-9:05 Opening remarks: Naoki Watanabe (Hokkaido University, Japan)

Morning Session 1　　Chair: Tomoya Hirota

9:05-9:45 Brett McGuire (Massachusetts Institute of Technology, USA) Invited
"The PAH Revolution: Cold, Dark Carbon at the Earliest Stages of Star Formation"

9:45-10:05 Yuki Okoda (The University of Tokyo, Japan)
"Compact Distributions of N-bearing species and HCOOH in the Protostellar Source B335"

10:05-10:25 Giseon Baek (Kyung Hee University, Korea)
"Complex organic molecules detected in twelve high mass star forming regions with ALMA"

10:25-10:40 Coffee break

Morning Session 2　　Chair: Brett McGuire

10:40-11:00 Zwei Zhang (RIKEN, Japan)
"Hot Disk Chemistry in Massive Star forming Regions"

11:00-11:20 Takashi Shimonishi (Niigata University, Japan)
"ALMA Discovery of Chemical Complexity at the Edge of our Galaxy"

11:20-11:40 Nadia Murillo (RIKEN, Japan)
"Studying the factors that determine multiplicity and chemical complexity in Perseus"

11:40-12:00 Hideko Nomura (NAOJ, Japan)
"Formation of complex organic molecules through ice mantle reactions"

12:00-14:00 Lunch

Afternoon Session 1 Chair: Germán Molpeceres

14:00-14:20 Victor Manuel Rivilla Rodriguez (CSIC/INTA, Spain)
"Molecular precursors of the RNA-world in the interstellar medium"

14:20-14:40 Laura Colzi (CSIC/INTA, Spain)
"The GUAPOS project: A comprehensive study of peptide-like bond molecules"

14:40-15:00 Albert Rimola (Universitat Autònoma de Barcelona, Spain)
"Quantum Chemical Simulations to Unveil the Interstellar Grain Surface Chemistry. Insights at an Atomistic Scale"

15:00-16:30 Poster session

Afternoon Session 2 Chair: Thanja Lamberts

16:30-17:10 Germán Molpeceres (Universität Stuttgart, Germany) Invited
"Machine Learning Meets Surface Astrochemistry"

17:10-17:30 Stephan Schlemmer (Universität zu Köln, Germany)
"MissIons: Missing Ions in Laboratory"

17:30-17:50 Frederik Doktor S. Simonsen (Aarhus Universitet, Denmark)
"Formation of water ice clusters on graphite"

17:50-18:00 Coffee break

Afternoon Session 3 Chair: Kensei Kitajima

18:00-18:40 Brian Hays (Université de Rennes 1, France) Invited
"The measuring the formation of products from reaction at low temperatures using chirped pulse Fourier transform spectroscopy in uniform flows"

18:40-19:00 Cristina Puzzarini (Universitá di Bologna, Italy)

"Theory and Experiment for Elucidating Chemical Evolution in Space"

19:00-19:20 Jesús Antonio Lique-Urrutia (Universtitat Autònoma de Barcelona, Spain)
"Glycolaldehyde Formation on Interstellar Water Ice Surfaces. A Computational Quantum Chemical Approach"

18th, Thu.

Morning Session 1 Chair: Kenji Furuya

9:00-9:40 Rob Garrod (University of Virginia, USA) Invited
"Cold chemistry in hot cores: Non-diffusive grain-surface chemistry and its role in forming complex organic molecules in star-forming regions"

9:40-10:20 Masashi Tsuge (Hokkaido University, Japan) Invited
"Icy grains are not spherical nor ellipsoidal"

10:20-10:40 Y. L. Yang (University of Virginia, USA)
"Chemistry of Embedded Disks in Perseus: Prevalent Complex Organic Molecules and Shock-excited Sulfur-bearing Molecules"

10:40-12:20 Poster session

12:20-14:00 Lunch

Afternoon Session 1 Chair: W.M.C. Sameera

14:00-14:20 Izaskun Jimenez-Serra (CSIC/INTA, Spain)
"Formation, Abundance Distribution and Evolution of Complex Organic Molecules in Starless/Pre-stellar Cores"

14:20-14:40 Juan García de la Concepción (Centro de Astrobiología, Spain)
"Formation of phosphorus monoxide (PO) in the interstellar medium: insights from quantum-chemical and kinetic calculations"

14:40-15:00 Joan Enrique Romero (Universite Grenoble Alpes, France)
"A systematic computational study of radical–radical reactions on interstellar ice surfaces"

15:00-15:20 Ni-En Sie (National Central University, Taiwan)
"The thickness and UV absorption effect on UV photolysis of CH_4 ice"

15:20-16:30 Poster session

Afternoon Session 2 Chair: Yuri Aikawa

16:30-16:50 Thanja Lamberts (Universiteit Leiden, The Netherlands)
"Carbon atom addition reactions in interstellar ices: How to marry laboratory and computational chemistry"

16:50-17:10 Aurèle Germain (Università degli studi di Torino, Italy)
"Application of the Tight Binding GFN-xTB Method to Model Large Interstellar Amorphous Icy Grains"

17:10-17:30 Stefano Ferrero (Universitat Autònoma de Barcelona, Spain)
"The energy dissipation process of hydrogenation reactions of atomic nitrogen on water ice surfaces"

17:30-17:50 Coffee break

Afternoon Session 3 Chair: Masashi Tsuge

17:50-18:30 Jean-Hugues Fillion (LERMA - Sorbonne Université et Obserbatoire de Paris, France) Invited
"Photon Stimulated Desorption from interstellar ice analogs: recent results using synchrotron radiation"

18:30-19:10 Emmanuel Dartois (Institut des sciences moléculaires d'Orsay, France) Invited
"Non-thermal desorption of ice mantles: cosmic rays desorption of complex organic

molecules"

19:10-19:30 Kenji Furuya (NAOJ, Japan)
"Quantifying the chemical desorption of H_2S and PH_3 from water ice surface"

19th, Fri.

Morning Session 1　　Chair: Ralf Kaiser

9:00-9:40 Susanna Widicus Weaver (University of Wisconsin-Madison, USA) Invited
"The role of UV photolysis and thermal processing in interstellar ice chemistry"

9:40-10:00 Atsuki Ishibashi (Hokkaido University, Japan)
"Water-promoted formation of methyl formate from methanol via methokxymethanol on ice"

10:00-10:20 Zhen-Dong Sun (Shandong University, China)
"Calculation of the ortho-para conversion rate of gaseous methanol by the internal axis method"

10:20-10:40 Coffee break

Morning Session 2　　Chair: Kaori Kobayashi

10:40-11:20 Ralf Kaiser (University of Hawaii, USA) Invited
"An Aromatic Universe - Low Temperature Molecular Mass Growth Processes to Polycyclic Aromatic Hydrocarbons (PAHs)"

11:20-12:00 Shogo Tachibana (The University of Tokyo, Japan) Invited
"Hayabusa2 returned samples from C-type near-Earth asteroid (162173) Ryugu: Preliminary report of initial analysis"

12:00- Concluding remarks: Nami Sakai (RIKEN, Japan)

Posters

In Japan Standard Time (UTC+9)
17th Wed. **15:00-16:30**
18th Thu. **10:40-12:20, 15:20-16:30**

1. Yuri Aikawa (The University of Tokyo, Japan)

"HCO^+ and ionization structure observed by ALMA"

2. Mitsunori Araki (Tokyo University of Science)

"Testing Dust-Surface Formation Model of Prebiotic Molecule CH_3NCO in Star-Forming Cores Sagittarius B2 (M) and (N)"

3. Gianni Cataldi (NAOJ, Japan)

"Can grain-surface chemistry explain the surprisingly low C/CO ratio in the HD 32297 debris disk?"

4. Izumi Endo (The University of Tokyo, Japan)

"Nitrogen inclusion in organic dust in novae revealed by laboratory synthesis of Quenched Nitrogen-included Carbonaceous Composite (QNCC)"

5. Izuru Fukuda (Tokyo University of Science, Japan)

"Development of Cavity Enhanced Absorption Spectrometer Aiming to Measure Optical Absorption Bands of Interstellar Molecules"

6. Tetsuya Hama (The University of Tokyo, Japan)

"Experimental measurement of the absorption cross section of dangling OH bonds in water ice"

7. Tomoyuki Hanawa (Chiba University)

"Cloudlet capture model for the origin of asymmetric molecular line emissions from in the young stellar objects"

8. Tomoya Hirota (NAOJ, Japan)

"Submillimeter H_2O masers in high-mass star-forming regions"

9. Hoga Furukawa (University of Toyama, Japan)
"Microwave spectroscopy of isothiazole"

10. Chao-Hui Huang (National Central University, Taiwan)
"Energetic processes caused by sub-keV electrons impacting on H_2O+CO ice mixtures"

11. Hyeon-Deuk Kim (Kyoto University, Japan)
"Anomalous Properties of Condensed Hydrogen Molecules under Extreme Thermodynamic Conditions Revealed by the Non-Empirical Quantum Molecular Dynamic Simulation Method"

12. Kensei Kitajima (Hokkaido University, Japan)
"A new electrochemical property of ice: negative charge transport triggered by reactions of surface OH radicals with electrons"

13. Beatrice Kulterer (University of Bern, Switzerland)
"Mono-deuterated methanol in prestellar cores"

14. Signe Kyrkjebø (Aarhus University, Denmark)
"Early stages of water cluster growth observed with low-temperature scanning tunnelling microscopy"

15. Berta Martínez-Bachs (Universitat Autònoma de Barcelona, Spain)
"Computational Investigation on the Potential Energy Surface of the Formation Route of Formamide from Reaction between NH_2 and H_2CO on Interstellar Water Ice Surface"

16. Ayane Miyazaki (Hokkaido University, Japan)
"Detection of photodesorption OH radicals from H_2O ice surface by visible light"

17. T. Nagasawa (The University of Tokyo, Japan)
"An infrared spectroscopic approach towards understanding the orientation of dangling OH bonds on amorphous solid water"

18. Yoichi Nakai (RIKEN, Japan)
"Methanol production via interactions of low-energy CH_3^+ ions with ASW surface: experimental investigation of ion-surface reactions"

19. Thanh Nguyen (Hokkaido University, Japan)
"Experimental and computational studies on the physicochemical behavior of phosphine induced by reactions with H and D atoms on interstellar ice grains"

20. Shota Notsu (RIKEN, Japan)
"X-ray-induced chemistry of water and related molecules in low-mass protostellar envelopes"

21. Naoki Numadate (The University of Tokyo, Japan)
"First direct detection of OH radicals photodesorbed from liquid organic surface by using laser-induced fluorescence technique"

22. Satoshi Ohashi (RIKEN, Japan)
"FAUST III. Misaligned rotations of the envelope, outflow, and disks in the multiple protostellar system of VLA 1623$-$2417"

23. Kunihiro Okada (Sophia University, Japan)
"Experimental study toward the measurements of rotational state dependence of interstellar ion-polar molecule reactions at low temperatures"

24. Yoko Oya (The University of Tokyo, Japan)
"Chemical Differentiation and its Relation with the Physical Structures in Disk-Forming Regions of Young Low-Mass Protostellar Sources"

25. Anshika Pandey (Banaras Hindu University, India)
"Formation of 3-Pyrolline in Interstellar Space: A Computational Study"

26. Akant Vats (Banaras Hindu University, India)
"DFT study on hydrogenated and deuterated derivatives of interstellar fullerenes"

27. Jessica Perrero (Universtitat Autònoma de Barcelona, Spain)
"Formation of acetaldehyde on mixed-ice grain surfaces"

28. P. V. G. M. Rathnayake (The University of Sydney, Australia)
"PyQMMM for modelling chemical processes in the interstellar medium"

29. Eri Saiga (The University of Tokyo, Japan)
"Star Formation Feedback to a Parent Cloud: The Elias 29 Case"

30. Nami Sakai (RIKEN, Japan)
"Measurements of Microwave Spectra of Methanol Isotopologues in ALMA Band 6 Frequency Range"

31. R. Sato (The University of Tokyo, Japan)
"Development of the RHEED apparatus for in situ structural analysis of water ices in low-temperature and ultrahigh vacuum conditions"

32. Richard Schömig (Universität Stuttgart, Germany)
"A Theoretical, Neural-Network Assisted Study of Methane Formation under Astrophysical Conditions"

33. Taha Selim (Radboud University, The Netherlands)
"Unraveling Molecular Collisions in Protoplanetary Disks"

34. Bethmini Senevirathne (University of Gothenburg, Sweden)
"H and D diffusion on interstellar water ices"

35. Atsuki Ishibashi (Hokkaido University, Japan)
"Development of a high-sensitivity and non-destructive detection system for trace amounts of adsorbates on ice"

36. Satyam Srivastav (Banaras Hindu Univ, India)
"Interstellar Branched Chain Molecules"

37. Kotomi Taniguchi (NAOJ, Japan)
"Nitrile Chemistry in a Disk Structure around the G24.78+0.08 A1 Hyper-compact HII region"

38. Lorenzo Tinacci (Univerisitè Grenoble Alpes, France)
"A New Approach to the Compute Accurate Binding Energy Distribution of Molecules at Ice Interstellar Grain Models: the Case of NH_3"

39. Takuto Tomaru (Hokkaido University, Japan)
"STM and Non-Contact-AFM observation of Si(111) by a self-made Qplus sensor at low temperatures"

40. Masashi Tsuge (Hokkaido University, Japan)
"Diffusive hydrogenation of CO embedded in amorphous solid water at temperature up to 70 K"

41. Masashi Tsuge (Hokkaido University, Japan)
"Ortho-to-para nuclear spin conversion of H_2 on interstellar bare grain analogues"

42. Withdraw

43. Yoshimasa Watanabe (Shibaura Institute of Technology, Japan)
"Development of Spectrometer Using Superconductor Mixer Receiver (SUMIRE)"

44. Tomohiro Yoshida (NAOJ, Japan)
"A new measurement method of isotopologue ratios in protoplanetary disks: a case study of the $^{12}CO/^{13}CO$ ratio in the TW Hya disk"

45. Yichen Zhang (RIKEN, Japan)
"Multi-tracer Observations for Multi-scale Accretion Structures in Massive Star Formation"

46. Shaoshan Zeng (RIKEN, Japan)
"Inventory of Nitrogen-bearing organics towards G+0.693-0.027"

47. Akemi Tamanai (RIKEN, Japan)
"Experimental Molecular Emission Spectroscopy of Ethylene Oxide in ALMA Band 6"

Oral Presentations

The PAH Revolution: Cold, Dark Carbon at the Earliest Stages of Star Formation

Brett A. McGuire[1,2]

[1]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA
[2]National Radio Astronomy Observatory, Charlottesville, VA, USA

Polycyclic Aromatic Hydrocarbons (PAHs) have been implicated as a large reservoir of reactive carbon in the interstellar medium since the 1980s. PAHs have been widely attributed as the carriers of the unidentified infrared bands where their aggregate vibrational emission spectra are extremely well matched to the observed line signals. Only in the last year have individual PAHs been detected in the ISM for the first time [1–3], however, allowing us to begin to investigate the detailed chemical pathways for the formation and destruction of these molecules. In this talk, I will discuss our detections of PAH molecules via their rotational transitions using Green Bank Telescope observations of TMC-1 from the GOTHAM collaboration [4]. I will discuss the efforts to model the chemistry of these PAHs, the necessity of complementary laboratory kinetics work such as the elegant single-collision studies being carried out by R. Kaiser and co-workers [5], our application of novel machine learning approaches to exploring the chemical inventory in TMC-1 [6], and finally the benefits of unbiased reaction screening studies in the laboratory with Microwave Spectral Taxonomy [7, 8].

References

[1] B. McGuire et al. 2021, Science 371, 1265
[2] A. Burkhardt et al. 2021, ApJL 908, L11
[3] J. Cernicharo et al. 2021, A&A 649, L15
[4] B. McGuire et al. 2020, ApJL 900, L10
[5] S. Doddipatla et al. 2021, Science Advances 7, eabd4044
[6] K. Lee et al. 2021, ApJL 917, L6
[7] M. McCarthy & B. McGuire 2021, JPCA 125, 3231
[8] M. McCarthy et al. 2020, JPCA 124, 5170

Compact Distributions of N-bearing species and HCOOH in the Protostellar Source B335

Y. Okoda,[1] Y. Oya,[1] M. Imai[1], N. Sakai[2], Y. Watanabe[3], A. López-Sepulcre[4],
and S. Yamamoto[1]

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[2] *RIKEN Cluster for Pioneering Research, Japan*
[3] *Materials Science and Engineering, College of Engineering, Shibaura Institute of Technology, Japan*
[4] *Univ. Grenoble Alpes, CNRS, IPAG, France*
Institut de Radioastronomie Millimétrique, France

Molecular-line distributions around newly born protostars provide us an important clue to understanding chemical processes as well as physical structures such as a disk/envelope or an outflow. B335 is a Bok globule harboring the Class 0 protostellar source (T_{bol}=37 K), IRAS 19347+0727, whose distance is reported to be 90-120 pc. A number of Complex Organic Molecule (COM) lines were detected in the vicinity of the protostar with ALMA (Atacama Large Millimeter/submillimeter Array), and hence, this source contains a hot corino at a few 10 au scale [1].

We have conducted ALMA observations toward this source at a high spatial resolution of ~3 au. The CH_3OH and CH_2DOH line emission have an extended distribution with the radius of ~10 au around the protostar. In contrast, the N-bearing molecular lines, NH_2CHO and HNCO, show a more compact distribution within a radius of ~6 au or less. These characteristic features have been reported for other sources [2][3]. Interestingly, the HCOOH lines show a similar distribution to the N-bearing molecular lines, despite being an O-bearing species. This trend has also been seen in a high-mass source [4]. We derive the rotation temperature around the protostar under the assumption of the LTE condition using multiple lines each for CH_3OH, CH_2DOH, NH_2CHO, and HCOOH. Figure 1 shows the temperature distribution along the disk/envelope system. The temperature is derived to be ~250 K at the continuum peak, and decreases with increasing the distance from it. The derived temperatures in the vicinity of the protostar within 3 au are all similar. However, it depends on molecules at 6 au. This may suggest the complex structure of the disk/envelope system. Further works are in progress.

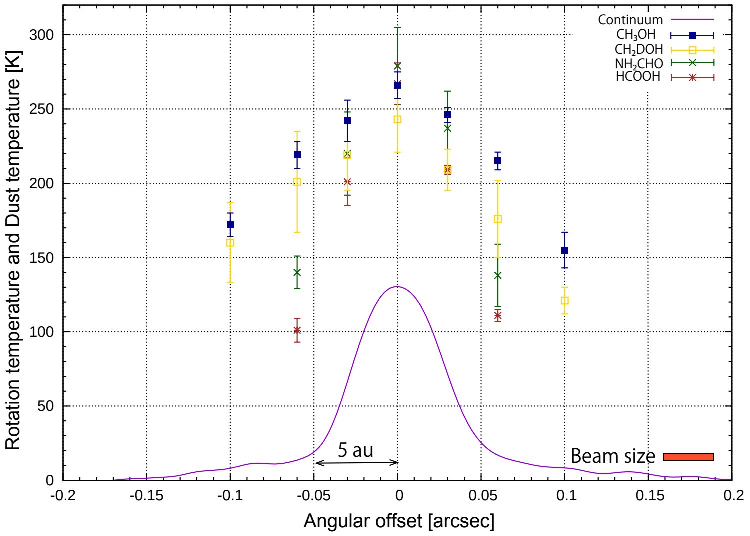

Figure 1: The blue, yellow, green, and orange marks represent the rotation temperatures derived from the CH_3OH, CH_2DOH, NH_2CHO, and HCOOH lines, respectively, along the disk/envelope system. The vertical bars indicate the error bars. The purple line represents the dust continuum distribution.

References

[1] Imai, M., Sakai, N., Oya, Y., et al. 2016, ApJL, 830, L37
[2] Colzi, L., Rivilla, V.~M., Beltrán, M.~T., et al. 2021, AAP, 653, A129
[3] Okoda, Y., Oya, Y., Abe, S., Komaki, A., et al. 2021, arXiv:2110.00150
[4] Csengeri, T., Belloche, A., Bontemps, S., et al. 2019, AAP, 632, A57

Complex organic molecules detected in twelve high mass star forming regions with ALMA

Giseon Baek,[1] Jeong-Eun Lee,[1] Tomoya Hirota[2,3], Kee-Tae Kim[4]
and KaVA Star-Formation Science Working Group
[1]*School of Space Research, Kyung Hee University, Korea*
[2]*Mizusawa VLBI Observatory, National Astronomical Observatory of Japan (NAOJ), Japan*
[3]*Department of Astronomical Sciences, SOKENDAI (The Graduate University for Advanced Studies), Japan*
[4]*Korea Astronomy and Space Science Institute (KASI), Korea*

Recent astrochemical models and experiments have explained that complex organic molecules (COMs; molecules composed of six or more atoms) are produced on the dust grain mantles in cold and dense gas in prestellar cores [1]. However, the chemical networks and the roles of physical conditions on chemistry are not still understood well. To address this question, hot cores in high mass young stellar objects are great laboratories due to their strong emissions and larger samples than those of low-mass counterparts. In addition, CH_3OH masers, which have been mostly found in high mass star forming regions, can provide constraints due to their very specific emerging conditions. We investigate the chemical diversity in richness and complexity of twelve high mass star forming regions using the ALMA band 6 observations. They are associated with 44/95 GHz class I and 6.7 GHz class II CH_3OH masers, implying that the active accretion processes are ongoing [2][3]. For these previously unresolved regions, 63 continuum peaks are detected. Among them, we found 28 cores emitting COMs and specified 10 cores associated with 6.7 GHz Class II CH_3OH masers. We identified up to 19 COMs including oxygen- and nitrogen-bearing molecules and their isotopologues in a core and derived their abundances. We found that (1) oxygen-bearing molecules appear to be richer in abundance and more complex in molecular structures than those of nitrogen-bearing species, (2) COMs detection rate steeply grows with the gas column density, above the threshold of $\sim 10^{24}$cm^{-2}, which can be attributed to the effective COMs formation in dense cores, and (3) cores associated with class II CH_3OH maser tend to emit larger number of COMs. Therefore, from our analysis, we conclude that the chemical diversity among hot cores could be originated by the degree of the accretion of each source as well as different physical conditions of cores.

References

[1] K. Öberg & E. A. Bergin, 2021, PhR, 893, 1
[2] J.-H. Kang, D.-Y. Byun, K.-T. Kim et al. 2016, ApJS, 227, 17
[3] B. Hu, K. M. Menten, Y. Wu et al. 2016, ApJ, 833, 18

Hot Disk Chemistry in Massive Star Forming Regions

Z. E. Zhang[1], Y. Zhang[1], K. Tanaka[2], Y. Kawashima[1], P. C. Stancil[3], B. H. Yang[3], N. Balakrishnan[4], and N. Sakai[1]

[1]*Star and Planet Formation Lab, RIKEN, Japan*
[2]*Department of Astrophysical and Planetary Sciences, University of Colorado, USA*
[3]*Department of Physics and Astronomy, University of Georgia, USA*
[4]*Department of Chemistry, University of Nevada, USA*

During the embedded phase of massive star formation, the surrounding materials of protostars experience vigorous physics and chemistry, resulting in intense physical conditions, such as high temperature and density. As a consequence, various high excitation molecular lines have been detected and used to probe the physical properties of these massive protostellar systems (e.g., Orion Source I [1][2]). Recent ALMA observations have unveiled the unusual structure of the inner region of IRAS 16547–4247 (an O-type binary protostellar object) with rovibrationally excited "hot-disk" tracing molecules, e.g., NaCl, SiS, and H_2O [3]. We present non-local thermal equilibrium (NLTE) analysis of the detected species to constrain the physical properties of this circumbinary system. The effects of physical conditions (e.g., temperature, density, and radiation) on the excitation of these detected molecules are explored with NLTE modeling. Furthermore, we discuss the unique chemistry for refractory species and sulfur in the massive star forming regions. Such study is essential to the evaluation of the potential of these rovibrationally excited molecules as "disk-tracers", as well as to the investigation of detailed physical and chemical structures of massive protostars.

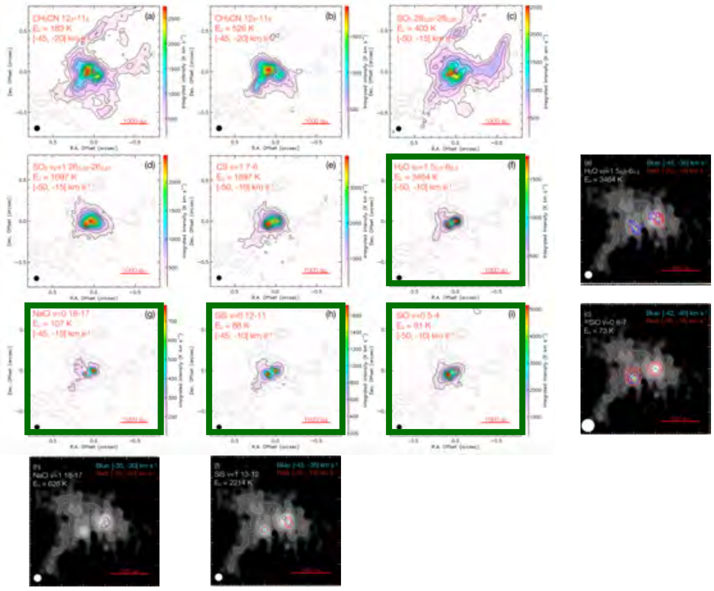

Figure 1: Integrated intensity maps of emission lines overlaid with the 1.3 mm continuum emission. The velocity maps for representative molecules are attached in grayscale.

References

[1] Tachibana, S. et al. 2019, ApJL, 875, 2, L29.
[2] Wright, M. et al. 2020, ApJ, 880, 2, 155.
[3] Tanaka, K. et al. 2020, ApJL, 900, 2, L2.

ALMA Discovery of Chemical Complexity at the Edge of our Galaxy

T. Shimonishi,[1] N. Izumi,[2] K. Furuya[3], and C. Yasui[4]

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[2]*Institute of Astronomy and Astrophysics, Academia Sinica, Taiwan*
[3]*National Astronomical Observatory of Japan, Japan*
[4]*National Astronomical Observatory of Japan, California Office, USA*

Interstellar chemistry in low metallicity environments is crucial to understand chemical processes in the past metal-poor universe. Here we report the first detection of a hot molecular core in the extreme outer Galaxy, which is an excellent laboratory to study star formation and interstellar medium in a Galactic low-metallicity environment [1]. The target star-forming region, WB89-789, is located at the galactocentric distance of 19 kpc. Our ALMA observations have detected a variety of carbon-, oxygen-, nitrogen-, sulfur-, and silicon-bearing species, including complex organic molecules (COMs) containing up to nine atoms, towards a warm (>100 K) and compact (<0.03 pc) region associated with a protostar (~8x10^3 Lsun) (Fig.1). Deuterated species such as HDO, HDCO, D2CO, and CH2DOH are also detected. A comparison of fractional abundances of COMs relative to CH3OH between the outer Galactic hot core and an inner Galactic counterpart shows a remarkable similarity. The presence of a great molecular complexity in a primordial environment of the extreme outer Galaxy suggests that the interstellar condition to form the chemical complexity might exist from the early history of the Universe.

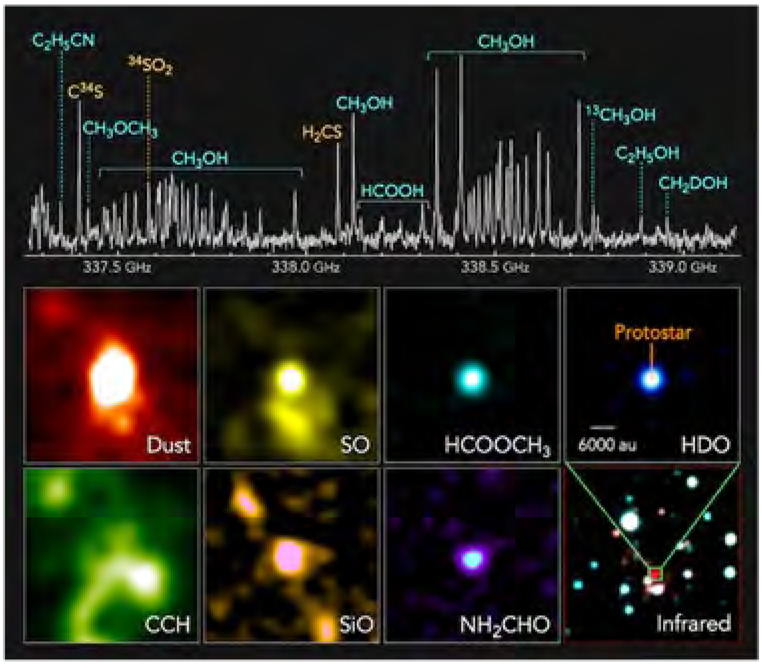

Figure 1: Examples of ALMA submillimeter spectrum (up) and molecular line distributions (bottom) for a newly-discovered hot molecular core in the extreme outer Galaxy [1].

References

[1] T. Shimonishi, N. Izumi, K. Furuya, & C. Yasui, 2021, ApJ, in press, arXiv/astro-ph: 2109.11123.

Studying the factors that determine multiplicity and chemical complexity in Perseus

N. M. Murillo,[1] and N. Sakai[1]

[1]Star and Planet Formation Laboratory, RIKEN, Japan

Star formation involves a wide range of physical and chemical processes. To fully comprehend and build a picture of star formation and evolution, we need to understand how each process influences the final outcome. While models provide some insight into this question, observational constraints are needed to fully understand this topic.

Two aspects of protostellar systems that are of interest are their multiplicity and chemical complexity. Multiple protostars are common at all stages and masses of star formation. The chemical complexity of protostellar systems significantly varies among systems. A curious observational occurrence in low-mass star formation is that almost all, if not all, chemically complex systems are multiple protostellar systems (e.g., IRAS16293, NGC1333 IRAS4), but not all multiple protostellar systems are chemically complex (e.g., VLA1623, L1448 N). In addition, within multiple protostellar systems the chemical complexity can vary among components.

Observations of protostellar systems from molecular cloud to disk scales are needed to study which physical and chemical processes determine multiplicity, chemical complexity, and whether there is a relation between both. A large sample including multiple and single protostellar systems is necessary to obtain statistically significant results. The Perseus molecular cloud (d ~ 300pc) is ideal for such studies, given the extensive available data which covers dust continuum, molecular lines, and magnetic fields for a range of scales.

In this talk, a large sample of Perseus protostellar systems observed with the Nobeyama 45m Telescope, Atacama Pathfinder EXperiment (APEX), and Atacama Large Millimeter/submillimeter Array (ALMA) will be presented. Our observations trace scales from molecular cloud to the protostellar envelope (few 100 AU). The spectral set-up includes a range of molecular species that can trace gas distribution, kinematics and temperature toward each protostellar system to study the impact of heating, mass, and accretion on multiplicity and chemical complexity. Further information from smaller scales is obtained from previous studies. Our results suggest that multiplicity is determined by mass, while how that mass is accumulated may be related to chemical complexity.

Formation of complex organic molecules through ice mantle reactions

C.-E. Wei[1], H. Nomura[2], P. Theulé[3], and C. Walsh[4]

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[2]Divison of Science, National Astronomical Observatory of Japan, Japan
[3]Laboratory of Astrophysics of Marseille, Aix-Marseille Université, France
[2]School of Physics and Astronomy, University of Leeds, UK

Recent solar system exploration missions, such as Rosetta mission, have found various complex molecules in solar system objects. Some of these materials are thought to be pristine and produced before the solar system objects are formed. Meanwhile, recent development in astronomical observations, for example, by ALMA, as well as in chemical model calculations have brought us new knowledge on formation of complex organic molecules in protoplanetary disks, natal place of planet formation [1][2][3].

In interstellar clouds it is believed that complex organic molecules are mainly formed through grain surface reactions. Meanwhile, laboratory experiments suggest that ice mantle reactions can proceed in certain conditions, and produce more complex species [4]. In this work we have constructed a formula of mantle reaction rate based on the recent laboratory experiments which show ice chemistry proceeding through the thermal process inside the ice bulk. Also, we introduced the obtained reaction rates to chemical reaction network with three phase model including gas-phase, grain surface, and ice mantle reactions. We performed model calculations with different physical conditions, which show that the mantle reactions can proceed efficiently when the temperature is higher than ~120K.

In addition, we adopt some physical conditions of protoplanetary disks in early evolution phase, taking account of the temperature increase caused by FU Ori type outbursts, and investigate the effect on formation rate of COMs via mantle reactions. We especially focus on the formation rates of the materials detected on the comet 67P/Churyumov-Gerasimenko in the Rosetta mission, and found that the mass accretion rate of 10^{-5} solar mass per year is required in order to produce the ammonium carbamate found in the comet 67P/C-G efficiently at comet forming region in protoplanetary disks [5].

References

[1] C. Walsh, T.J. Millar, H. Nomura et al. 2014, A&A 563, A33.
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Molecular precursors of the RNA-world in the interstellar medium

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The question of the origin of Life has intrigued human beings for centuries. We still do not understand how simple molecules combine together to form large molecules essential for living organisms. Recent prebiotic experiments, based on the RNA-world hypothesis for the origin of Life, have suggested that the three basic macromolecular systems (nucleic acids, proteins and lipids) could have formed from relatively simple precursors. The detection of some of these molecules in space, thanks to the unprecedented capabilities of current astronomical facilities, has opened a new window for Astrobiology from the Astrochemical point of view.

In this talk I will present an overview of the most recent results of a ultradeep unbiased spectral survey towards the Galactic Center molecular cloud G+0.693-0.027 with the Yebes 40m and the the IRAM 30m telescopes. Among the more than 120 molecules detected, we have discovered in the last three years 9 new interstellar species towards this cloud (see Figure 1). These molecules include key precursors of RNA nucleotides such as hydroxylamine [1] (NH_2OH) or cyanomethanimine [2] (HNCHCN), proteins, such as ethyl isocyanate [3] (C_2H_5NCO), and lipids, such as ethanolamine [4] ($NH_2CH_2CH_2OH$). This amazing chemical complexity, which might be only the tip of the iceberg, means that interstellar chemistry offers an extremely rich feedstock for triggering prebiotic chemistry.

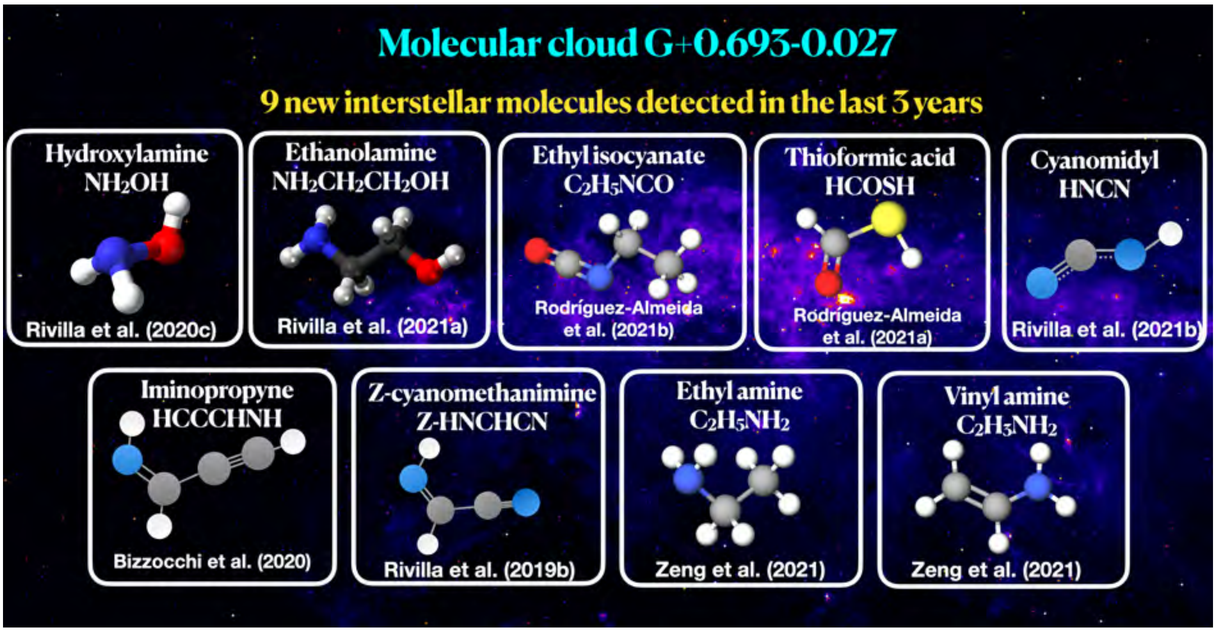

Figure 1: New interstellar molecules detected towards the molecular cloud G+0.693-0.027 using a deep unbiased spectral survey conducted with the Yebes 40m and IRAM 30m telescope.

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The GUAPOS project: A comprehensive study of peptide-like bond molecules

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Complex organic molecules (COMs), i.e. molecules containing carbon with 6 or more atoms, have been detected ubiquitously in the interstellar medium (ISM) towards low- and high-mass star-forming regions (e.g. [1]). Among prebiotic COMs, those containing peptide-like bonds (NCO backbone) are of great interest because they can participate in the link of amino acids forming proteins (e.g. [2]).

Here I present a study of HNCO, $HC(O)NH_2$, CH_3NCO, $CH_3C(O)NH_2$, CH_3NHCHO (Fig. 1) towards the chemically rich hot core G31.41+0.31, where these molecules have been observed together for the first time in the disk of our Galaxy, outside the Galactic Centre ([3]). This work is part of the GUAPOS (G31 Unbiased ALMA sPectral Observational Survey) project, which is a sensitive spectral survey conducted with the ALMA (Atacama Large Millimeter/submillimetre Array) observatory towards the star-forming region G31.41+0.31, covering the whole Band 3, that is from 84 to 116 GHz, and with an angular resolution of 1.2'' (~750 au, see [4]).

From the comparison with other sources, we find that molecular abundance ratios towards different sources are found to be consistent between them within one order of magnitude, regardless of the physical properties (e.g. different masses and luminosities), or the source position throughout the Galaxy. Correlations have also been found between the abundances of these molecules. These results suggest that all these species are formed on grain surfaces in early evolutionary stages of molecular clouds, and that they are subsequently released back to the gas-phase through thermal desorption or shock-triggered desorption.

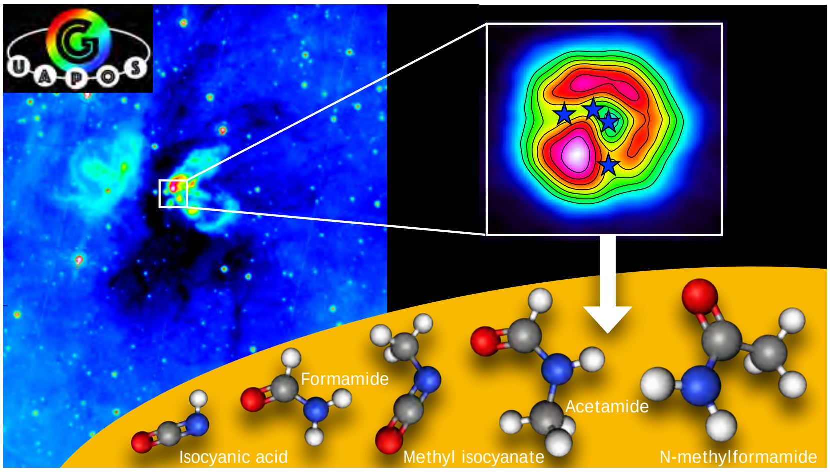

Figure 1: G31.41+0.31 at 8 μm (IRAC4, Spitzer space telescope, left panel) and ALMA 0.2'' resolution integrated emission maps at 1.4 mm of $HC(O)NH_2$ (right panel, see [3]). The blue stars indicate the position of protostars that are forming within this region. In the bottom the chemical structure of the peptide-like bond molecules studied are shown.

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Quantum Chemical Simulations to Unveil the Interstellar Grain Surface Chemistry. Insights at an Atomistic Scale

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The Universe is molecularly rich [1]. Its chemical diversity and complexity is reflected by the more than 250 molecular species detected in the gaseous phase by means of radioastronomy [2] and the different solid-state phases in the form of dust grains [3]. The presence of the gas-phase molecules cannot be explained uniquely by reactions taking place in the gas phase but chemical reactions occurring on the surfaces of grains are essential to rationalize the interstellar chemistry. However, combining astronomical observations with astrochemical modelling and laboratory experiments is not enough to fully unveil the grain surface chemistry and its contribution to the chemistry of space because they hold some intrinsic limitations [4,5,6]. Quantum chemical simulations can partly alleviate this as they provide reliable, quantitative atomic-scale information (structure, energetics, and dynamics) of chemical processes taking place on the surface of grains, this way allowing us to determine the actual role of the grains on them, that is, as chemical catalysts, reactant concentrator and/or third bodies. This contribution aims to present some of the potentialities of current state-of-the-art computations developed in the *QuantumGrain* group to obtain unique and fundamental information that help improving our know-how on the grain surface chemistry. To this end, examples on the modelling of realistic grain surfaces for ices and silicates [7], on simulations dealing with the adsorption of astrochemically-relevant species [8] and with chemical reactions forming ethanol from CCH reacting with water ice [9], and finally on the fate of the extra energy released in an exothermic reaction (here the H_2 formation, [10]) will be presented.

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Machine Learning Meets Surface Astrochemistry

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Surface reactions play a vital role in the chemistry occurring on interstellar mediums (ISM). In particular, under the cold conditions of a molecular cloud (~10-20 K), adsorbates (atoms, radicals and molecules) accrete, diffuse, react and desorb on top of ice-covered dust grains [1]. The chemical composition of these ices is varied and depends on the cloud's evolutionary stage, e.g. water ice dominates the early stages [2]. At the same time, CO and CO_2 are prevalent in later stages. Moreover, interstellar ices are usually amorphous, presenting a wide range of binding sites for adsorbates to perform the aforementioned processes [2]. It appears evident that, given the complexity of the substrates, the dynamics of adsorbates on interstellar ices are essentially non-local, meaning that a particular process depends significantly on the binding site under consideration. This condition imposes a constraint on computational studies of interstellar surface chemistry, requiring extensive sampling and considerably increasing the computational cost for constructing reliable models. Several approaches are employed in the literature to reduce this cost, i.e. cluster models [3], periodic models, [4] QM/MM models [5] and recently, machine-learned models [6]. In this contribution, I will present our recent efforts in the application of neural-network potentials [7] to surface astrochemistry, putting the focus on the simulation of:

1. Adsorption and desorption (calculation of sticking coefficients and desorption rate constants) [6];
2. Diffusion (estimation of diffusion coefficients and hopping rate constants) [8];
3. Reaction (chemical desorption vs energy dissipation) [9].

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MissIons: Missing Ions in Laboratory

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Ions play a key role in the chemical evolution of our universe. The process of star and planet formation is tightly connected to the presence and abundance of these species. Their spectra are diagnostic tools for various astrophysical environments and their temporal evolution. However, laboratory spectra of most ions relevant to astrophysics are not available. Moreover, predicted spectra from ab-initio theory are not nearly accurate enough to guide astrophysical searches. Therefore, laboratory spectra of molecular ions are needed.

We will report on progress towards recording high-resolution spectra from the microwave to visible range using our unique and innovative light induced reactions (LIR) methods in ion traps [1]. It is molecule specific through mass selection, many orders of magnitude more sensitive and less complex due to buffer gas cooling as compared to conventional methods. Examples concern the molecule first observed in space, CH^+ [2] but also ions which can play an important role in the chemical development producing more complex species, e.g., C_3H^+ [3] and $C_3H_2^+$ [4]. For many reasons H_3^+ is the corner stone in ion chemistry. It gives away its proton to most other species. As a result, protonation of more complex species, like methanol, could be another key towards the formation of complex organic species, molecules which are observed with today's telescopes but how they come into existence is under debate. We will discuss the tools to record the spectra and to understand the relevant reactions in the laboratory.

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Formation of water ice clusters on graphite

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In cold regions of the interstellar medium (ISM) icy mantles may form on the surface of cold dust grains and act as heterogeneous catalysts for the formation of complex organic molecules (COMs) [1].

In recent years the "onion model", which describes icy mantles as thick layered structures of polar molecules underneath apolar molecules, has been challenged by several groups, e.g. [2][3]. Arguments are made for partly ice-covered grains with exposed bare grain surfaces which themselves are complex and porous structures, stressing the importance of the grain-ice interface. The structure of the grains and their ices will likely impact the COM production as diffusion, adsorption and possible reaction barrier characteristics are influenced [4].

Here we examine sub-monolayer water ice formation on highly oriented pyrolytic graphite (HOPG), using a low-temperature scanning tunnelling microscope (LT-STM) functioning at 5 K. Sub-monolayer amounts of water were deposited onto an HOPG surface kept at ≈ 40 K.

Presented in Figure 1 is an example of water ice clusters grown at 40 K via molecular deposition on the HOPG surface. We argue for diffusion limited aggregation (DLA) [5] growth which is visible from the fractal structure of the clusters, both near step edges and for individual nucleation sites.

DLA leads to low densities and an amorphous and porous structure which with growth may form the reputed amorphous solid water of icy grain mantles.

Finally, water was deposited at varying surface temperatures, offering a unique look into non-heat-treated water ice clusters formed under slightly different, but controlled, conditions.

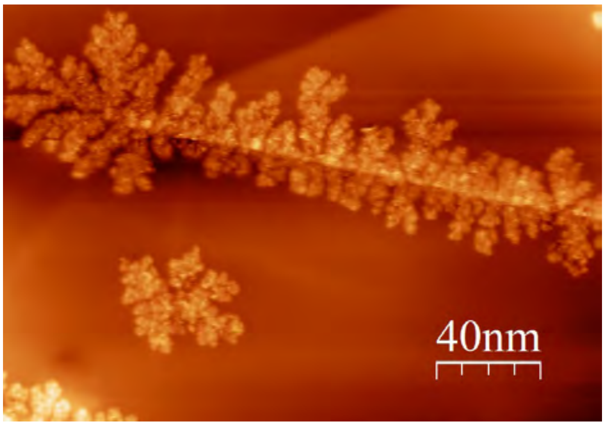

Figure 1: LT-STM image of water ice clusters on HOPG (4.5 V, 15 pA). The image shows a cluster on the terrasse of HOPG and aggregation of water along a step-edge on the HOPG surface.

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The measuring the formation of products from reaction at low temperatures using chirped pulse Fourier transform spectroscopy in uniform flows

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The formation of complex molecules in the interstellar medium often proceeds at very low temperatures. Predicting the formation mechanisms of these molecules depends heavily on experimental measurements of the rates of reaction at low temperatures. While experiments are available to measure these rates at low temperatures using the CRESU (French acronym for Reaction Kinetics in Uniform Supersonic Flow) technique, the products of these reactions and their branching ratios are usually not measured. This leaves a large gap in astrochemical kinetics databases concerning the product branching ratios of reactions.

The CPUF (Chirped Pulse in Uniform Flow) combines the revolutionary chirped pulse Fourier spectroscopy technique with the CRESU environment, using rotational spectroscopy to unambiguously identify the products of reaction at low temperatures. A new chirped pulse Fourier transform millimeter wave spectrometer was adapted to continuous uniform flow apparatus available in Rennes. The products of fast CN radical reactions with ethane and acetylene were directly observed in the uniform flow, showing proof of concept results from this instrument.

The Fourier transform spectra were heavily affected by the buffer gas used in the CRESU technique in interesting ways. This provided a unique opportunity to explore intermolecular dynamics between the buffer gas and other molecules, specifically the elastic and inelastic scattering of these species. HCN and HNC spectra were compared in the low temperature He environments, where the collisional excitation of these two molecules were found to be very different, especially at low temperatures relevant to molecular clouds. Finally, the CPUF apparatus was extended to sample the uniform flow using a newly developed secondary expansion chamber, where the product branching ratios could be measured from reaction. Future developments will allow for the CPUF technique to be extended to even colder temperatures and more molecular systems.

Theory and Experiment for Elucidating Chemical Evolution in Space

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Understanding the chemical evolution of the universe is one of the main aims of Astrochemistry, with the starting point being the knowledge whether a molecule is present in the astronomical environment under consideration and, if so, its abundance. In this context, molecular spectroscopy plays the central role. The astronomical observation of the spectroscopic features of a given molecule is the definitive, unequivocal proof of its presence in the astronomical environment under consideration, with the overwhelming majority of gas-phase chemical species being discovered via their rotational signatures.

Among the goals of astrochemistry, the detection of prebiotic COMs in astrophysical environments is fundamental in view of possibly understanding the origin of life. While the evidence for molecular complexity in the universe is undisputed, there is still much to be understood about what prebiotic molecules are present and how they are formed in the typically cold and (largely) collision free environment of the interstellar medium. By means of selected examples, it will be shown that: (*i*) the interplay of experiment and theory in the field of rotational spectroscopy is a powerful tool in astrochemistry [1-3]; (*ii*) state-of-the-art computational approaches allow for deriving formation pathways able to explain the molecular abundances derived from astronomical observations [3-5]; (*iii*) a rationalization of interstellar chemistry in terms of class of reactions might be a feasible way [5].

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Glycolaldehyde Formation on Interstellar Water Ice Surfaces. A Computational Quantum Chemical Approach

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Astrochemists of diverse disciplines aim to unfold the intricate chemical mechanisms that occur in space to get insight on one of the primordial questions we have today: what is the origin of life? To evolve from dead chemical matter into living beings, there are some essential chemical compounds that must be present for that to occur, such as amino acids [1] and complex sugars [2]. Focusing on sugars, glucose is one of the main targets. However, its presence has not been confirmed in space while this is indeed the case of its closest relative, glycolaldehyde (GLA, $HOCH_2CHO$) [3]. In this contribution, we present results dedicated to GLA formation on surfaces of interstellar water ice adopting the formose reaction, $2\cdot H_2CO \rightarrow$ GLA, and its radical derivation $H_2CO + CHO^* + H^* \rightarrow$ GLA. Reactions in the gas phase (i.e., absence of water ice) have been used for a benchmarking study, in which CCSD(T) results were compared with those obtained at the more approximated DFT theory level. With the latter, calculations of the GLA formation reactions have been carried out on cluster models for water ice (see Figure 1), in which the energy features of the reactions (i.e., reaction energy and activation energies) are provided. Additionally, simulations also help us to understand the role of the ice surface in this synthetic route.

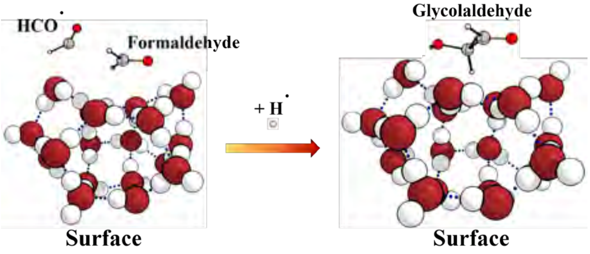

Figure 1: Glycolaldehyde formation by reaction of HCO with H_2CO followed by H addition simulated on a cluster model mimicking the surfaces of interstellar of water ice.

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Cold chemistry in hot cores: Non-diffusive grain-surface chemistry and its role in forming complex organic molecules in star-forming regions

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Reactions on dust-grain surfaces are responsible for the production of many important interstellar molecules, including gas-phase H_2, grain-surface ice species such as water, ammonia and methanol, and arguably some of the most complex molecules detected in star-forming regions. However, our view of the temperature dependence of this chemistry has recently been changing. A major driver in this shift is the gas-phase detection of complex organic molecules (COMs) such as methyl formate in cold pre-stellar cores. These detections have pushed back the astronomical clock on COM production, to a time much earlier than the warm proto-stellar stage in which they are usually detected (albeit in much greater abundance). Experimental evidence also suggests that COMs may be formed on very cold surfaces (~10 K), through mechanisms that do not require thermal diffusion of the reactants. Past models that rely solely on diffusive reaction mechanisms now appear inadequate.

I will discuss new modeling treatments [1,2] that adopt a more comprehensive framework for grain-surface and ice-mantle chemistry, allowing reactants to meet in a variety of ways that do not rely solely on diffusion. This allows COMs to form as the ice mantles grow, while processing of the ices by external and cosmic-ray-induced UV fields can also lead to COM production. The period when the water-dominated ices desorb from the grains (Fig. 1, dashed lines) also allows trapped radicals to meet and react on the warm ice surfaces, prior to desorption. Gas-phase chemistry can further enhance COM production in some cases. In combination, these processes allow COMs to form over a range of temperatures, through a variety of mechanisms. I will discuss the implications of this new picture of COM chemistry.

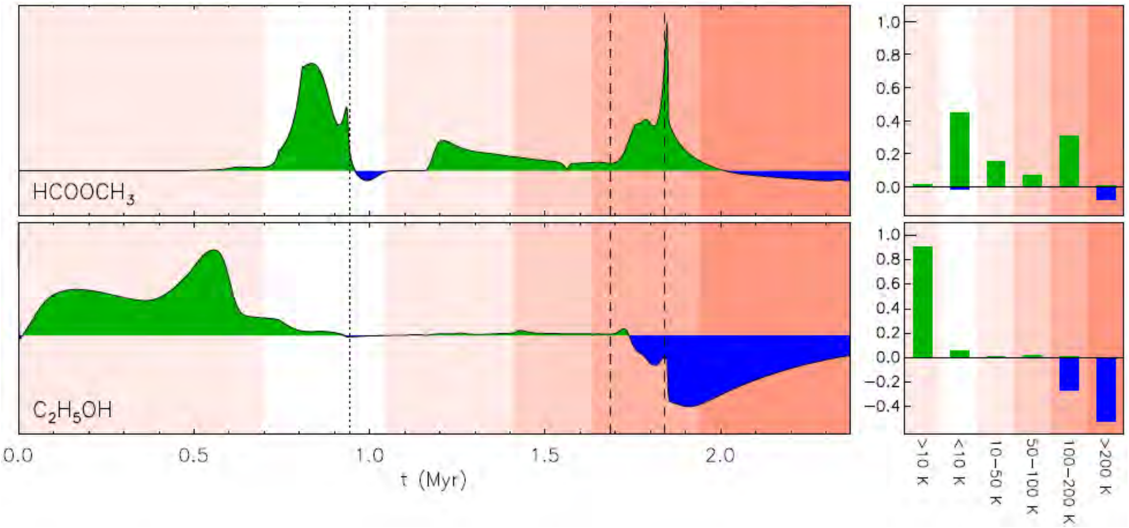

Figure 1: Net rates (arb. units) of molecular formation/destruction (green/blue), summed over all chemical phases (gas + surface + ice), from the collapse of a cold core through its evolution to a hot molecular core.

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Icy grains are not spherical nor ellipsoidal

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In the astrochemical community, it has been assumed, without experimental validations, that ices on grains in molecular clouds and proto-planetary disks are formed by homogeneous layers regardless of their composition or crystallinity (Figure 1A). To verify this assumption, we investigated the H_2O deposition onto refractory substrates and the crystallization of amorphous ices (H_2O, CO_2, and CO) using an ultra-high-vacuum transmission electron microscope [1]. Upon heating the samples deposited at 10 K, which are uniform layer of amorphous H_2O (a-H_2O) on refractory substrates, amorphous CO on a-H_2O, and amorphous CO_2 on a-H_2O, we found that the uniform thin films of a-H_2O and amorphous CO became three-dimensional islands of polyhedral crystals while amorphous CO_2 became a thin film of nano-crystalline CO_2 covering a-H_2O. Our observations indicate that crystal morphologies greatly depend on not only the ice composition but also the substrate material. Using experimental data and the crystallization timescale of amorphous ices, we conclude that icy grains in molecular clouds and proto-planetary disks are not spherical nor ellipsoidal; in molecular clouds, a-H_2O covered the refractory grain uniformly, CO_2 nano-crystals were embedded in a-H_2O, and a polyhedral CO crystal was attached to a-H_2O at temperatures as low as 10 K (Figure 1B); in proto-planetary disks, one thin CO_2 I crystal on a-H_2O (1C) or one ice I crystal on organics (1D). Important implications for the chemical evolution of molecules, non-thermal desorption, collision of icy grains, and sintering will be presented.

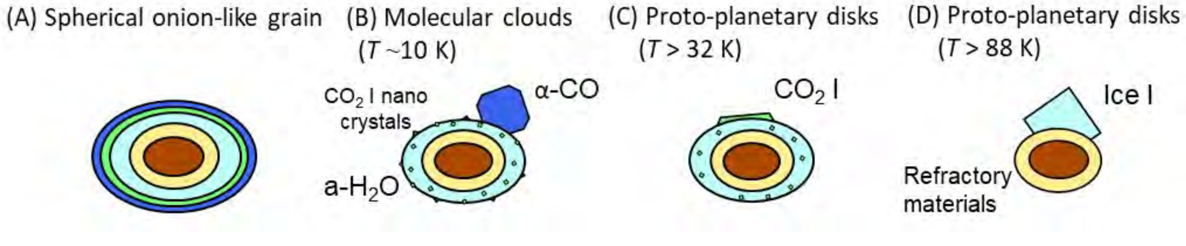

Figure 1: The schematic of icy grains (cross-section): (A) spherical onion-like grain as hitherto assumed, (B) in molecular clouds (T ~10 K), (C) in proto-planetary disks ($T > 32$ K), and (D) in proto-planetary disks ($T > 88$ K). Respective colors show the chemical compositions: red—core; yellow—refractory material; green—CO_2; light blue—a-H_2O; dark blue—CO.

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Chemistry of Embedded Disks in Perseus: Prevalent Complex Organic Molecules and Shock-excited Sulfur-bearing Molecules

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In recent years, observations discover several embedded protostars that have developed complex organic chemistry in the disk-forming region. Recent observations also show potential signs of planet formation in these young disks, hinting at a stronger chemical link between the protostellar cores and planetary systems. While observations start to find rich spectra of COMs in embedded protostars, only a few observations attempt to statistically constrain the abundances of COMs at embedded protostars and their relationships to star formation processes. With the PEACHES survey, an unbiased chemistry survey of embedded protostars in the Perseus molecular cloud, we have begun to systematically characterize the COMs in the disk-forming regions[1] in addition to simple molecules, such as SO and SO_2[2]. The majority of young protostars in Perseus have COMs. For the COM-rich protostars, their column densities of COMs correlate between species, hinting at similar chemistry for the protostars in Perseus. Particularly, the abundance of CH_3OH tightly correlates with that of CH_3CN (Figure 1 left); however, a direct chemical link between these two molecules has not been firmly established. Protostellar properties, such as bolometric luminosity and bolometric temperature, have little impact on the occurrence of COMs. While emission of COMs concentrates on the embedded disk or the inner envelope, the emission of SO and SO_2 appears asymmetric in a few sources. I will discuss the origin of these asymmetry which serendipitously corresponds to major changes of polarization near the edge of disks (Figure 1 right). I will also discuss our plan to understand the origin of COMs using JWST, which is accepted to the Cycle 1 GO program.

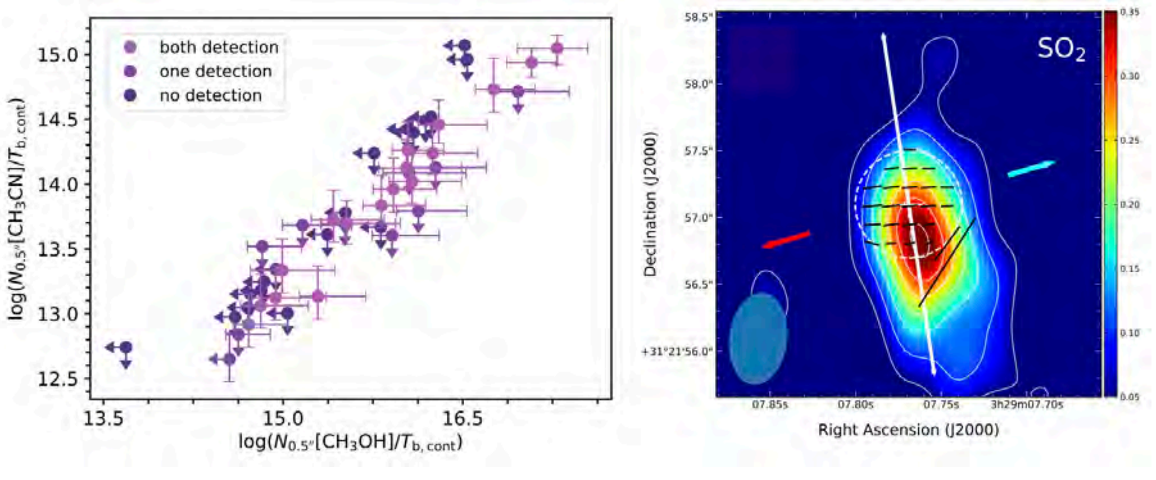

Figure 1: Left: The normalized column density correlation between CH_3OH and CH_3CN in the PEACHES sample. Right: The SO_2 emission of Per-ebb 50 compared to the linear polarization fraction. The white line indicates the disk direction, while the red and blue arrows show the outflow direction.

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Formation, Abundance Distribution and Evolution of Complex Organic Molecules in Starless/Pre-stellar Cores

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Observations carried out toward starless and pre-stellar cores have revealed that complex organic molecules (COMs) are prevalent in these objects (Vastel et al. 2014; Jimenez-Serra et al. 2019; Scibelli et al. 2020). However, it remains unclear what chemical processes are involved in COM formation and at what stage in dense core evolution complex organics form. In this contribution, we will present high-sensitivity observations carried out toward the L1517B and L1498 starless cores. These cores are believed to be at earlier evolutionary stages than the well-known L1544 pre-stellar core, also studied in COM emission by our group. Similarly to what we found in L1544, small O-bearing molecules and N-bearing species are enhanced by factors ~4-14 toward the outer shells of L1498 and L1517B. However, unlike L1544, large O-bearing COMs such as CH3CHO, CH3OCH3 or CH3OCHO are not detected within our sensitivity limits - comparable to the ones obtained for L1544. Surprisingly, N-bearing organics are more abundant toward the outer shells of L1498 and L1517B than in L1544. We have carried out a detailed modelling of the formation of O-bearing and N-bearing COMs in L1498 and L1517B following the model of Vasyunin et al. (2017), which considers both the chemical reactive desorption of COM precursors and their subsequent gas-phase chemistry yielding COMs. The distribution of the COM abundances predicted for L1498 and L1517B nicely matches our observations for both O-bearing and N-bearing COMs in these cores, and reveal that the differences observed between the complex organic content in L1498, L1517B and L1544 are due to the different physical structure of these cores, which in turn is a consequence of their evolution. From our results we conclude that while N-bearing COMs form early in dense core evolution, O-bearing COMs form at a later stage when enough CO has catastrophically depleted onto the surface of dust grains. These results have been published recently in Jimenez-Serra et al. (2021).

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Formation of phosphorus monoxide (PO) in the interstellar medium: insights from quantum-chemical and kinetic calculations

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In recent years, phosphorus monoxide (PO) –an important molecule for prebiotic chemistry– has been detected in star-forming regions and in the comet 67P/Churyumov-Gerasimenko [1]. These studies have revealed that, in the interstellar medium, PO is systematically the most abundant P-bearing species, with abundances that are ∼1-3 times greater than those derived for phosphorus nitride (PN), the second most abundant P-containing molecule. The reason why PO is more abundant than PN remains still unclear. Experimental studies with phosphorus in the gas phase are not available. Therefore, the reactivity of atomic phosphorus needs to be investigated using reliable computational tools. To this end, state-of-the-art quantum-chemical computations have been employed to evaluate accurate reaction rates and branching ratios for the P + OH → PO + H and P + H_2O → PO + H_2 reactions in the framework of a master equation approach based on ab-initio transition state theory. While the reaction of atomic phosphorus in its ground state with water is not a relevant source of PO because of emerged energy barriers, the P + OH reaction represents an important formation route of PO in the interstellar medium[2].

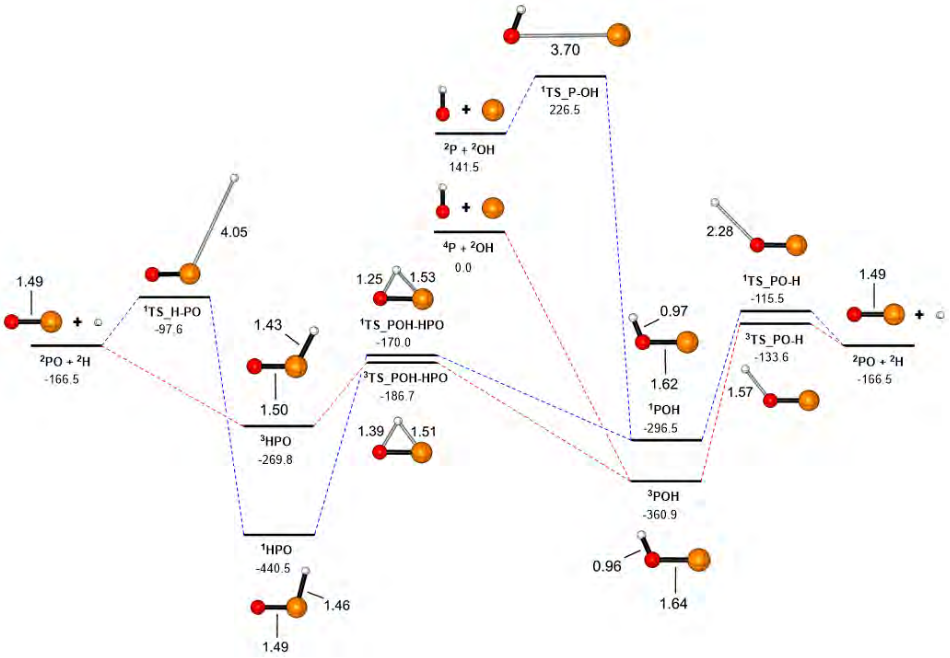

Figure 1. Singlet (blue profile) and triplet (red profile) potential energy surfaces (ZPE-corrected energies) for the formation of PO from OH + P

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A systematic computational study of radical—radical reactions on interstellar ice surfaces

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Understanding how insterstellar complex organic molecules (iCOMs) are formed and destroyed is of high importance to predict the ultimate organic complexity reached in the interstellar medium (ISM) ([1], [2]). Two paradigms are invoked in the literature. Both argue that simple molecules and atoms are hydrogenated on the interstellar grain surfaces during the cold prestellar phase. Following this first step, one paradigm assumes that iCOMs appear as a result of gas-phase chemical processes, whereas the other predicts that radical-radical reactivity on the grain surfaces is the major responsible for the observed chemical complexity. The latter has profited of much popularity among astrochemical models in the last years, even though some basic assumptions of the paradigm are still a topic of debate. Among them, the radical-radical reactivity assumption, which is extremely difficult to quantify experimentally. We propose a complementary and, sometimes, alternative method: theoretical quantum chemical calculations, which can provide a precious atomistic perspective from which to study such processes (e.g. [3], [4], [5]).

In this contribution, we present our recent systematic quantum chemical study on the surface reactivity of several radical pairs. Some of the studied systems are CH3 + X and HCO + X (X = CH3, HCO, NH2, CH2OH and CH3O). According to observational evidences, the icy mantles that cover interstellar dust grains are dominated by water ([6]). We, therefore, use two cluster-like ice models consisting on 18 and 33 water molecules to simulate the grain surface where the radical-radical reaction occurs. We then study the reactivity of the above biradical systems by means of static quantum chemical calculations to obtain the potential energy surfaces of several complex species and the approximate efficiency of the different reaction product channels. We found that many reactions leading to iCOMs have non negligible activation barriers and that the transfer of a hydrogen atom from a radical acting as a donnor to its partner, acting as an acceptor are important competitive processes. The occurrence of one process or the other could entirely depend on the relative orientation of the radicals upon encounter, namely on the water ice structure and interaction with the two radicals. These results indicate that the fraction of iCOMs generated in the current astrochemical models is certainly overestimated since (i) it is assumed that reactions always occur and (ii) the competitive reactions are not included.

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The thickness and UV absorption effect on UV photolysis of CH_4 ice

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The secondary UV light induced by cosmic rays has been seen as a dominant energetic source impinging on the ice mantles in the region of cold dense clouds and interstellar medium (ISM), contributing to the photodesorption of solid molecules. Among the ice mantle, CH_4 is one of the most abundant ice observed, and the UV irradiation of CH_4 ice is widely interesting. The UV emission spectra of microwave-discharged hydrogen-flow lamp (MDHL) generated in the laboratory has an analogous profile as the simulated one[1, 2]. In addition, the configuration of MDHL is influential on the photodepletion and photodesorption[3, 4], and this effect is molecule dependent since the absorption cross-section should be considered. The Ly-α (121.6 nm) photon plays a vital role in MDHL spectra, and the CH_4 ice also has a largest absorption around at Ly-α in the range of 114-170 nm. As long as the ice thickness becomes thicker, the absorption ratio increases but saturates at a certain thickness.

In this study, we investigate the photodepletion as well as photodesorption in three characteristic topics: thickness effect, light effect, and deposition temperature effect. We performed three different configurations of MDHL to investigate the destruction cross-section of CH_4 as a function of thickness from 50 to 400 ML (1 ML = 10^{15} molecules cm^{-2}), and the contribution from Ly-α line and H_2 emission band are defined. The depletion seems to be thickness dependent, but if we calculate the absorbed photons rather than incident photons, the destruction cross-section in different MDHL configurations have a great similarity. The photodesorption is also independent of the ice thickness, confirming that the process happens in the top layers.

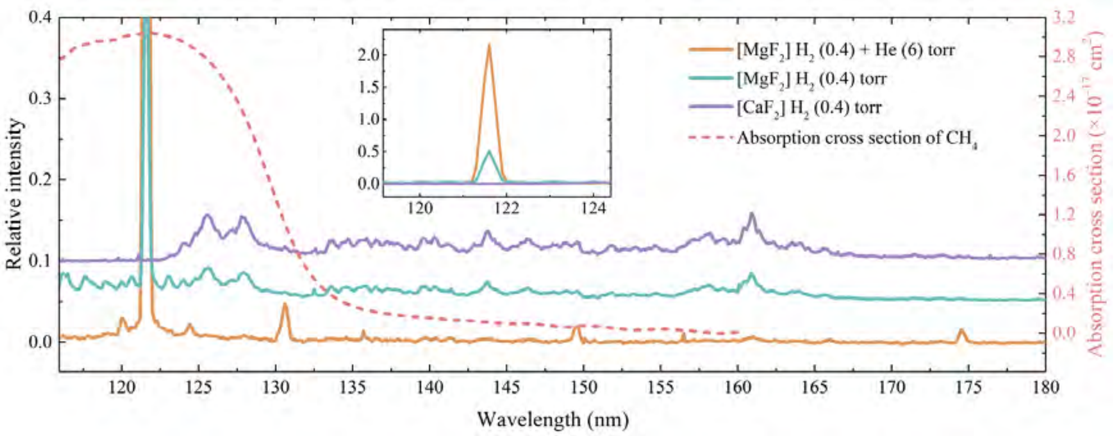

Figure 1: The MDHL spectra of 3 configurations and the absorption cross-section of solid CH_4.

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Theoretical study of adsorption energies of molecules on interstellar ice surfaces

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The adsorption of a series of atoms and small molecules and radicals (H, C, N, O, NH, OH, H_2O, CH_3, NH_3) on hexagonal crystalline and amorphous ice clusters were obtained via classical molecular dynamics and electronic structure methods. The geometry and binding energies were calculated using a QMHigh:QMLow hybrid method on model clusters. More accurate binding energies were also refined via single point Coupled Cluster calculations. Most species, except carbon atom, physisorb on the surface, leading to rather small binding energies. Amorphous ices are characterized by slightly stronger binding energies than the crystalline phase. A major result of this work is to also access the dispersion of the binding energies since a variety of adsorption sites is explored. The interaction energies thus obtained may serve to feed or refine astrochemical model. The present methodology could be easily extended to other types of surfaces and larger adsorbates.

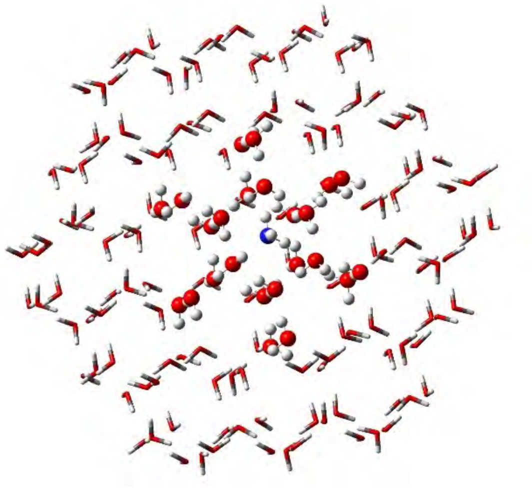

Figure 1 : NH_3 adsorption optimized geometry on ice surface

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Carbon atom addition reactions in interstellar ices: How to marry laboratory and computational chemistry

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I will focus on surface reactions of carbon atoms on amorphous solid water (ASW) ices, mimicking the icy mantle covering the micron-sized dust grains in the interstellar medium. In the translucent stage of a molecular cloud, carbon is predominantly present in its atomic form $C(^3P_0)$ [1] and even in dense regions it is likely more abundant than typically thought [2,3]. Moreover, already in 2001 carbon atoms additions have been proposed to lead to the formation of complex organics [4]. Therefore, a carbon atom beam source was installed at the Leiden Laboratory for Astrophysics [5], successfully demonstrating that methane can be formed from experiments of C + H on ASW [6]. In this talk I will discuss three new projects:

1. The interaction of atomic carbon with water has been extensively studied, both experimentally and theoretically [e.g., 7, 8], but particularly puzzling is the different chemical behaviour in the gas phase versus in condensed phases. I will provide a detailed explanation of the formation of **formaldehyde** from carbon atoms with amorphous solid water within a theoretical framework, supported by tailored experiments [9].
2. I will touch upon the reactions of carbon atoms with molecular hydrogen and show that an intricate interplay of reactions can lead to the formation of **methane**, even when H atoms are not present. I will discuss this both from an experimental and computational point-of-view and link the various intermediates to other recent studies [10].
3. Finally, I will show that the reactivity with H_2 and H_2O does not restrict the formation of complex organics, and in fact the reaction between C and CO occurs so rapidly that **ketene** and **acetaldehyde** can be formed in the presence of H atoms [11].

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Application of the Tight Binding GFN2-xTB Method to Model Large Interstellar Amorphous Icy Grains

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Interstellar grains are made of a silicate core covered by a mantle of several layers of amorphous ice. In the gas-phase of dense molecular clouds chemical species freeze onto the grain and can diffuse on its surface, react to give interstellar more complex molecules and ultimately desorb back to the gas-phase. Hence, the study of interstellar grains is an important part for understanding the chemical evolution in time of the Interstellar Medium (ISM). There is still no consensus in the Astrochemistry community on how to model these icy grains at atomistic level with the requisite of treating the hydrogen bond interaction and other important components accurately. Furthermore, the grain should be large enough to be representative of the variability present in the ISM, which renders impractical the adoption of plain DFT methods. Also, the adopted method should, not only be relatively fast, but also applicable to study the interaction of large interstellar molecules with the grain itself. Force fields are not the proper solution, due to the parametrization specific for each considered species, breaking the universality of the approach. To fill in the above requested, we resort to a newly developed semi-empirical quantum mechanical method based on the tight binding DFT approach called GFN2-xTB[1] and a universal force field method called GFN-FF[2], both developed by the Grimme's group at the Bonn University. We present the methodology to build a water cluster model up to 1000 H2O molecules and to characterize its structural and electrostatic potential surface (EPS) as a free grain (Fig. 1). Then, NH3 was chosen as relevant interstellar molecule to compute its binding energy (BE) at more than 150 different grain sites to characterize the BE distribution which revealed a bimodal distribution.

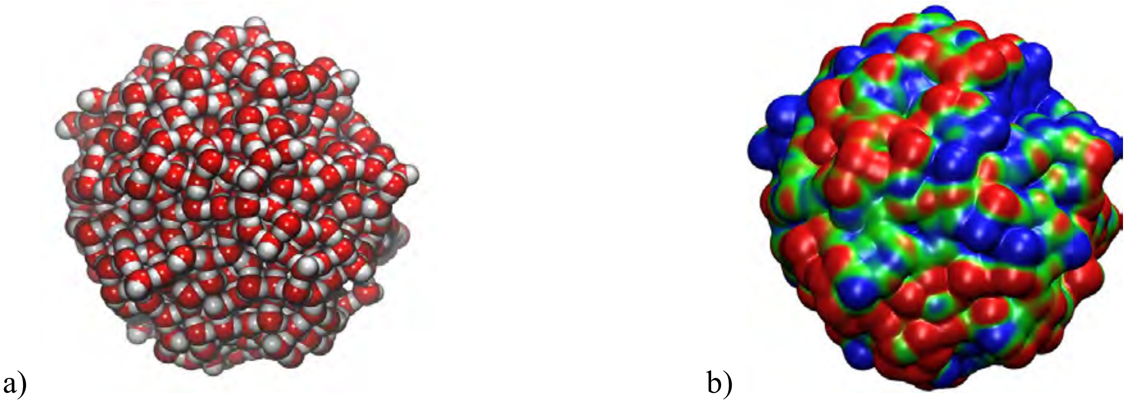

Figure 1: a) Structure and b) EPS of the GFN2-xTB water cluster model (1000 H2O)

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

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

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

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

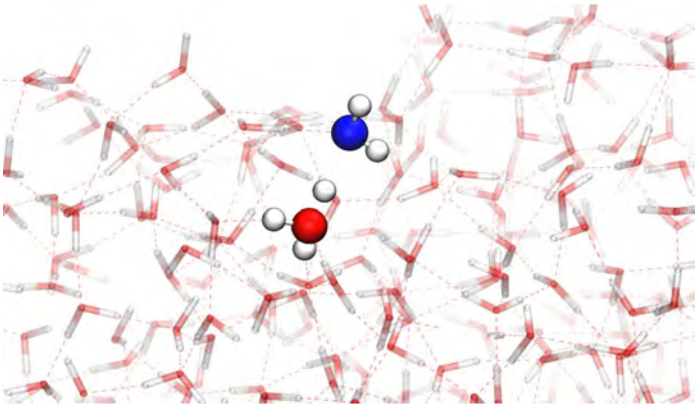

Figure 1: H3O(+) NH2(-) complex formation on an amorphous ice surface.

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Photon Stimulated Desorption from interstellar ice analogs: recent results using synchrotron radiation.

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Photon Stimulated Desorption (PSD) processes play a key role in the exchanges between the gas and solid phases of cold regions of the interstellar medium, where a lot of molecules are expected to freeze out on dust grains with the temperature forbidding their thermal escape. These processes have been used to explained otherwise puzzling gas phase observations of simple molecules like CO in dense cores or cold H_2O in outer parts of protoplanetary disks. They are also invoked as ways to get complex organic molecules (COMs) presumably formed on grains into the gas phase. Second, photon-induced desorption of residual molecules adsorbed on the cryogenic parts of accelerators such as the LHC can be a limiting factor for their vacuum performances. Desorption rates and mechanisms, especially in the sub-monolayer regime, can therefore be of particular interest in this case.

I will present an approach to study PSD of condensed films of molecules of astrophysical interest at cryogenic temperatures, using synchrotron radiation. Recent results obtained in the VUV and soft X-ray ranges will be presented. In the VUV, we will focus on the PSD from Amorphous Solid Water (ASW) and discuss experimental results evidencing two major desorption mechanisms [1], [2]. Quantitative desorption yields from acetonitrile CH_3CN in pure and mixed samples will be also presented [3]. In the soft X-ray range, results obtained at the K-edge of Oxygen atoms will be discussed in the context of protoplanetary disks, first in the case of pure H_2O [4], CO [5], CH_3OH [6] samples and secondly in the case H_2O-rich and CO-rich samples containing CH_3OH [7].

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Non-thermal desorption of ice mantles: cosmic rays desorption of complex organic molecules

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Determining experimentally the magnitude of interstellar grain mantles accretion and desorption mechanisms is mandatory for astrophysical models to constrain and predict gas and solid phase chemical evolutions. Irradiation by cosmic rays have been simulated experimentally using high energy ions. The ice mantles phase transformation and sputtering yields for released species were monitored simultaneously by infrared spectroscopy and mass spectrometry. The dominant ice mantle species, can be effciently sputtered by cosmic rays. In this talk, the sputtering yield and its evolution as a function of ice mantle thickness for high-energy ions will be discussed in the context of astrophysical environments. Cosmic rays penetrating deep into dense clouds provide a major sputtering mechanism to desorb the observed complex organic molecules (COMs) built over the lifetime of dense clouds, when many other mechanisms fail at releasing them effciently from cold grains. We focused our study on the sputtering effciency of two complex organic molecules that are observed either in interstellar dense clouds ice mantles directly by infrared spectroscopy (CH3OH), or observed in the gas phase by millimetre telescopes (CH3COOCH3). The sputtering was measured for different ice matrices dominated by water ice or carbon dioxide ices.

A large fraction of COMs desorbs as intact molecules with a proportion corresponding to the time dependent bulk composition of the ice mantles, the latter evolving with time due to the secondary photons VUV photolysis and CR ice mantle radiolysis. The astrophysical cases in relation with these experiments will be discussed.

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Quantifying the chemical desorption of H_2S and PH_3 from water ice surface

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Non-thermal desorption of molecules from icy grain surfaces is required to explain molecular line observations in the cold gas of star-forming regions [1]. Chemical desorption is one of the non-thermal desorption processes, and is caused by the energy released by chemical reactions; after an exothermic surface reaction, the part of excess energy goes into products' translational energy in perpendicular direction to the surface, leading to desorption. The desorption probability of product species, especially from water ice surfaces, is not well determined. This limits our understanding of the interplay between gas-phase and ice surface chemistry.

In this work, we constrained the desorption probability of H_2S and PH_3 per reaction event on porous amorphous solid water (ASW) by numerically simulating previous laboratory experiments of chemical desorption [2,3]. Adopting the microscopic kinetic Monte-Carlo method, we found that the desorption probability of H_2S and PH_3 from porous ASW per hydrogen addition event of the precursor species are 3 ± 1.5 % and 4 ± 2 %, respectively. These probabilities are consistent with a theoretical model of chemical desorption in the literature, if around 7 % of energy released by the reactions goes into the translational excitation of the products. As a bi-product, we also found that around 70 % (40 %) of adsorption sites for atomic H on porous ASW should have the binding energy lower than ~300 K (~200 K).

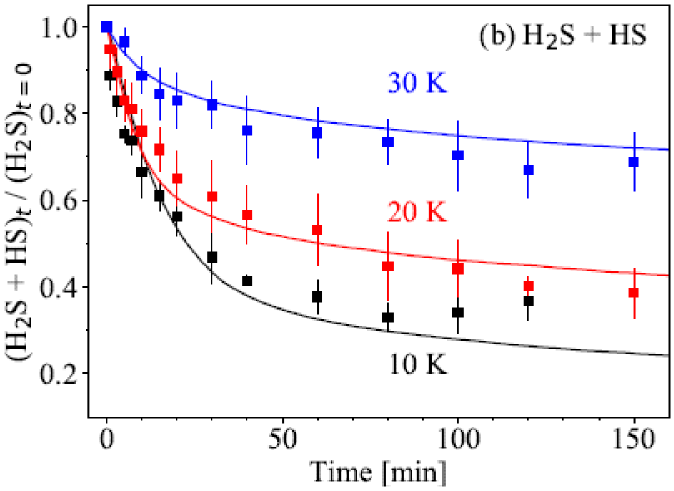

Figure 1: Total abundance of H_2S and HS on porous ASW normalized by the initial H_2S abundance as functions of the H atom exposure time in our best-fit model. Square symbols indicate the experiments by [2] and [3].

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The role of UV photolysis and thermal processing in interstellar ice chemistry

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It has been shown through both laboratory and observational studies that direct and cosmic-ray induced UV photodissociation drives a complex network of chemistry in interstellar ices. Astrochemical models have demonstrated that gradual heating of these UV-processed ices during star formation can lead to a wide variety of complex organic molecules. Additional modeling and observational studies have shown that these molecules are likely incorporated into protoplanetary disks and participate in the chemistry of planet formation. These processes could therefore serve as molecular starting points for prebiotic chemistry in the universe. Our observations of the chemistry of star-forming regions have shown that there is wide variation in the chemical compositions of hot cores, and that methanol photodissociation on icy grains may be the key process feeding the formation of larger prebiotic molecules. To test possible chemical routes in interstellar ices, we have built a novel laboratory experiment that couples the traditional tools of ice studies – FTIR spectroscopy and mass spectrometry – with the structure specificity of rotational spectroscopy. Such measurements can provide the "ground truth" to guide observations of star- and planet-forming zones. In this talk I will present both the observational and laboratory studies and discuss these results in the context of prebiotic astrochemistry.

Water-promoted formation of methyl formate from methanol via methoxymethanol on ice

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Methyl formate (MF; $HCOOCH_3$) is abundantly found in various astronomical objects, including cold molecular clouds [1]. Because of a good correlation with MF in observations, methanol, which is a primordial organic molecule on interstellar dust, is thought to be parent molecule. However, the results of laboratory experiments on the photolysis of pure methanol solid did not to explain the MF abundances astronomically observed [2, 3]. Recently, laboratory observation of ice dust analogue indicated that methanol would contact water ice at the dust surface rather than being as pure solid [4]. Therefore, the effect of H_2O on the MF formation should be considered as well as the photolysis of methanol. To study the details of the MF formation mechanism, small amounts of products and those radical precursors on the ice surface need to be monitored, which is difficult with conventional methods, such as FT-IR. Therefore, we newly developed highly sensitive nondestructive detection method, so-called Cs^+ ion pickup method [5], to monitor products and radicals, and performed the experiments for the photolysis of methanol (0.3 ML) on ice [6].

Analysis of the reaction products from the photolysis showed the formation of methoxymethanol (MM; CH_3OCH_2OH) and MF as the main components. This result was different from the UV photolysis of pure methanol solids, in which CH_2OH-derived molecules such as ethylene glycol (EG; $HOCH_2CH_2OH$) and ethanol were mainly produced. This MF generation is well consistent with cosmic MF observations. To clarify the reaction process of MM and MF, the irradiation time dependence of the signal intensities of trace reaction products such as CH_3O and/or CH_2OH, MM, MF, and OH was measured (Figure 1). A sequential behavior such as $CH_3OH \rightarrow CH_3O$ and/or $CH_2OH \rightarrow$ MM → MF was observed, indicating found that MF was efficiently generated by photodissociation of MM. In addition, from the fact that MM is the main product on ice among the $C_2H_6O_2$ isomers, it is considered that the formation of CH_3O was promoted by the abstraction reaction from methanol by the OH radical generated by the photolysis of H_2O.

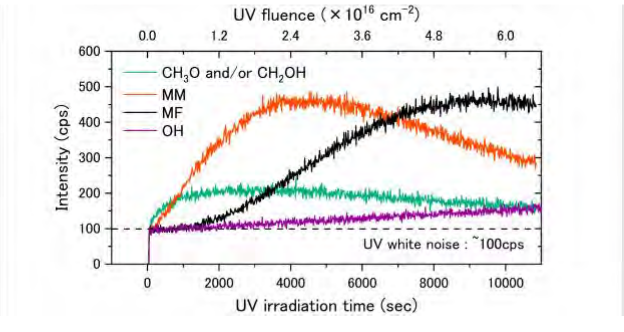

Figure 1: Variations in the signal intensities of surface species generated during UV irradiation to the sample of CH_3OH (0.3 ML) on ASW (10 ML) at 10 K. Pickup signals of MF, MM, CH_3O and/or CH_2OH, and OH which are photoproducts.

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Calculation of the ortho-para conversion rate of gaseous methanol by the internal axis method

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In astrophysics and astrochemistry, the ortho-para conversion rate is an important parameter which is related to the ortho-to-para population ratio (OPR) and the nuclear-spin temperature of nuclear-spin isomers of molecules in the interstellar medium (ISM) [1]. The methanol (CH_3OH) molecule is a major source of interstellar organic species due to its abundance in the ISM. Although conversion rate of nuclear-spin isomers in gaseous methanol has been experimentally measured recently [2], the quantum calculation of the ortho-para conversion rate of methanol molecules in the gas phase, the conversion mechanism in the nuclear-spin isomers conversion of methanol, and the most probable gateways of spin conversion in methanol have not yet theoretically studied by the internal axis method (IAM) that is a classical method commonly used by many researchers.

In molecular physics, methanol is one of the simplest asymmetric-top molecules with hindered internal rotation (*i.e.* torsion) [3]. Methanol does not rotate around the overall rotational symmetry axis but the methyl (CH_3) group axis. In the IAM, the CH_3-group and the OH-group in methanol relatively rotate in the opposite directions with each other, and the coupling of the angular momenta between torsion and overall rotation in the Hamiltonian of methanol can therefore be completely separated from each other. In accordance with Pauli's principle in quantum mechanics, the identical nuclei in the methyl group produce a specific type of nuclear spin isomers of the ortho-CH_3OH and para-CH_3OH in methanol. In this study, we have developed a theoretical model by the IAM for the description of isomer conversions by molecular collisions in gaseous methanol. The model is based on the quantum-relaxation theory confirmed to be valid for the standard nuclear-spin isomers based on the molecular rotational states [4]. The expressions of the ortho-para state-mixing strengths induced by intramolecular nuclear-spin–nuclear-spin and nuclear-spin–rotation interactions in methanol have been analytically deduced and numerically calculated. We found that the ortho-para states-mixings and ortho-para conversion can be induced by both of these two intramolecular hyperfine interactions whereas the nuclear-spin–rotation interaction plays a major role. The conversion rates at room temperature low pressures over eight ortho-para level pairs have been calculated to be closely to the measured values and the most probable gateways of spin conversion in methanol by collision-induced population transfers are found.

Acknowledgements

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An Aromatic Universe - Low Temperature Molecular Mass Growth Processes to Polycyclic Aromatic Hydrocarbons (PAHs)

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Polycyclic aromatic hydrocarbons (PAHs) represent key molecular building blocks leading to carbonaceous nanoparticles identified in combustion systems and extraterrestrial environments. However, the understanding of their formation and growth has remained elusive. Here, we present evidence based on laboratory data combined with electronic structure calculations on fundamental mass growth processes of PAHs in the gas phase via ring expansion and ring annulation. Key reaction pathways operate at ultralow temperatures such as at 10 K as present in cold molecular clods like TMC-1 synthesizing PAHs at least from two to five six membered rings such as naphthalene, anthracene, phenanthrene, triphenylene, [4]-helicene, and [5]-helicene. These elementary reactions are rapid, have no entrance barriers, and synthesize PAHs via van-der-Waals complexes and submerged barriers. This facile route to complex PAHs signifies a critical shift in the perception that PAHs can be only formed at high-temperature combustion and circumstellar conditions providing a detailed understanding of the low temperature chemistry through untangling elementary reactions on the most fundamental level. An outlook is also presented on the synthesis of PAHs in low temperature, hydrocarbon-dominated ices in deep space and in the outer Solar System upon interaction with (non)-ionizing radiation; these processes are driven by non-adiabatic reaction dynamics and low lying triplet states of acetylene leading to PAHs as complex as coronene. Overall, these mechanisms eventually lead to graphene-type PAHs and two dimensional nanostructures providing an exciting view about the transformation of carbon in our universe.

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Hayabusa2 returned samples from C-type near-Earth asteroid (162173) Ryugu: Preliminary report of initial analysis

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JAXA's Hayabusa2 spacecraft returned the sample from C-type (carbonaceous) near-Earth asteroid (162173) Ryugu in December 2020. The total weight of samples collected from two surface locations of the asteroid exceeds 5 grams, which is the largest ever from deep space. The Hayabusa2 project has begun a year-long analysis of returned samples on a priority basis (initial analysis). In order to unravel the nature of C-type asteroid and the origin and evolution of Solar System, the Hayabusa2 initial analysis team consists of six sub-teams focusing on 1) chemistry (elements and isotopes), 2) petrology and mineralogy of coarse grains (mm-sized grains referred as 'Stone'), 3) petrology and mineralogy of fine grains (<100 μm-sized grains referred as 'Sand'), 4) volatiles, 5) insoluble organic matter (macromolecular organics), and 6) soluble organic matter (organic molecules).

After six-month initial description inside clean chambers at Institute of Space and Astronautical Science (ISAS), JAXA, ~6 % of the samples (0.3 g out of total 5 g) was allocated to the initial analysis team and has been investigated since June 2021. Twenty-two particles were individually photographed, weighed, and spectroscopically described without exposure to air at ISAS in advance of allocation to the team. Most of individual particles are one to a few millimeter in size except for a centimeter-sized grain obtained during the second landing at Ryugu. Along with the individual particles, ten sets of aggregate samples, consisting of grains with <1 mm diameter, were allocated to the team. The aggregate samples range from 0.3 to 38.8 mg.

We will present current status of initial analysis and discuss some preliminary results at the workshop.

Poster Presentations

HCO$^+$ and ionization structure observed by ALMA

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We observed HCO$^+$(J=1−0) and H^{13}CO$^+$ (J=1−0) emission towards the five protoplanetary disks around IM Lup, GM Aur, AS 209, HD 163296, and MWC 480 as part of the MAPS project[1][2]. HCO$^+$ is detected and mapped at 0.3” resolution in all five disks, while H^{13}CO$^+$ is detected (SNR $>6\sigma$) towards GM Aur and HD 163296 and tentatively detected (SNR $>3\sigma$) towards the other disks by a matched filter analysis. Inside a radius of R~100 au, the HCO$^+$ column density is flat or shows a central dip. At outer radii ($\gtrsim 100$ au), the HCO$^+$ column density decreases outwards, while the column density ratio of HCO$^+$/CO is mostly in the range of $\sim 10^{-5}$–10^{-4} . We derived the HCO$^+$ abundance in the warm CO-rich layer, where HCO$^+$ is expected to be the dominant molecular ion. At $R \gtrsim 100$ au, the HCO$^+$ abundance is ~ 3×10^{-11}–3×10^{-10} , which is consistent with a template disk model with X-ray ionization. At the smaller radii, the abundance decreases inwards, which indicates that the ionization degree is lower in denser gas, especially inside the CO snow line, where the CO-rich layer is in the midplane. Comparison of template disk models with the column densities of HCO$^+$, N$_2$H$^+$, and N$_2$D$^+$ indicates that the midplane ionization rate is $\gtrsim 10^{-18}$ s^{-1} for the disks around IM Lup, AS 209, and HD 163296. We also find hints of an increased HCO$^+$ abundance around the location of dust continuum gaps in AS 209, HD 163296, and MWC 480.

We also plan to show the summary of molecular column densities obtained in MAPS project and some model results for discussions in the poster session.

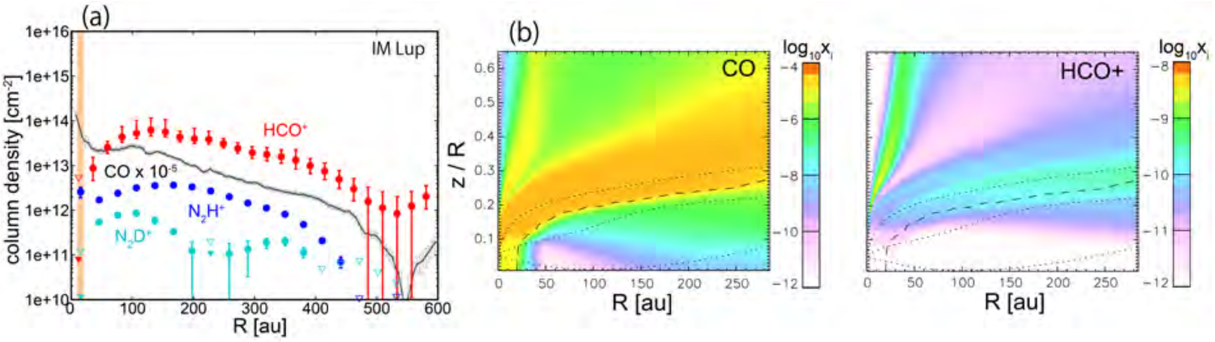

Figure: (a)Radial distributions of column densities of CO, HCO+, N2H+, and N2D+ in IM Lup derived from MAPS project. (b) Distributions of CO and HCO+ in a tempate disk model.

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Testing Dust-Surface Formation Model of Prebiotic Molecule CH_3NCO in Star-Forming Cores Sagittarius B2 (M) and (N)

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Origin of organic molecules on Earth is discussed to be interstellar clouds, because comets carried molecules produced in clouds. Methyl isocyanate CH_3NCO is presumably one of the delivered organic molecules at the primitive earth. This molecule was firstly detected in the the (N) core of the Galactic Center star-forming region Sagittarius (Sgr) B2 [1]. Recently, the theoretical studies have suggested that this molecule is formed on dust surface in molecular cloud [2]. If that is the case, CH_3NCO abundantly desorbs from dust surface as hot gas in a central region of a star-forming core and slightly exists in an outer region as cold gas.

To examine an outer region of a star-forming core, we observed the (M) core in Sgr B2 with the 45-m telescope of Nobeyama Radio Observatory. Rotational transitions of CH_3NCO were firstly detected in this region. The abundance ratio and the rotational temperature are derived to be $[CH_3NCO]/[HNCO] = 0.03 \pm 0.01$ and $T_{rot} = 28 \pm 6$ K, respectively.

To examine temperature and distribution of CH_3NCO, the archival data toward the (N1) core of Sgr B2 observed by ALMA were investigated in the 94–113 GHz region. Considering intensity maps and velocity structures, a compact distribution having a clumpy toroidal structure was firstly imaged by CH_3NCO showing high temperature of ~60 K, as shown in Fig. 1. These results suggest a hot and abundant condition of this molecule in the central region of the core. Hence, CH_3NCO and/or its precursors are likely to be produced on dust surface.

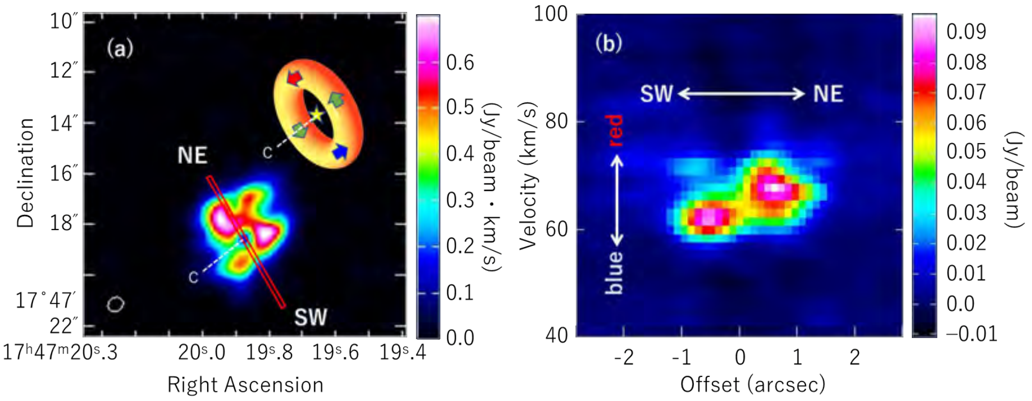

Figure 1: The integrated intensity map of the $J_{Ka,Kc} = 11_{1,10}$–$10_{1,9}$ line of CH_3NCO (a) and its position velocity map (b). The illustration in (a) shows an expected toroidal structure. The map (b) is sampled in the red square of (a).

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Can grain-surface chemistry explain the surprisingly low C/CO ratio in the HD 32297 debris disk?

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Debris disks are analogues of the solar system's asteroid and Kuiper belt. They consist of kilometer-sized rocky or icy bodies ("exocomets") that continuously collide and produce dust. However, in recent years observations of CO emission have shown that some of these objects also contain substantial amounts of gas [e.g. 1]. Like the dust, this gas is probably produced by collisions of cometary bodies. It is important to understand the nature of this gas for a number of reasons. For example, the gas allows us to study the composition of the exocomets [e.g. 2]. Furthermore, the gas might be accreted by planets, thereby changing their atmospheric composition [3].

The A-type main sequence star HD 32297 (age of 15-30 Myr) hosts a debris disk with a high CO mass. Since CO is quickly photo-dissociated by the interstellar radiation field, it has been suggested that CO is shielded by neutral carbon atoms that are produced by the photo-dissociation [4]. This would allow a large CO mass to accumulate from the collisional destruction of icy exocomets. In order to test this scenario, we observed neutral C emission with ALMA towards HD 32297 [5].

In order to interpret our observations, we set up a simple model where CO is produced from cometary bodies and destroyed by the interstellar field, taking into account CO self-shielding and shielding by neutral C. We find that the observed C/CO ratio can only be explained if 1) the CO production rate is uncomfortably high and 2) C is removed from the system on a short time scale by an unknown process. We hypothesize that grain surface chemistry might solve this puzzle: C and O atoms might accrete onto dust grains and re-form CO, which is than re-released to the gas phase. This would provide an additional CO source and a C sink, therefore explaining the surprisingly low C/CO ratio. However, a more detailed examination with the help of grain surface chemistry experts is needed in order to assess whether this is a realistic scenario.

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Nitrogen inclusion in organic dust in novae revealed by laboratory synthesis of Quenched Nitrogen-included Carbonaceous Composite (QNCC)

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The unidentified infrared (UIR) bands have been widely observed in various astrophysical environments. They consist of a series of emission features arising from aromatic and/or aliphatic C-C and C-H bonds in the near- to mid-infrared wavelength range[1] and therefore, their carriers are thought to be related to organics. Although the carriers must be a major constituent of the Galaxy, our knowledge of their properties is still limited. Dusty classical novae are valuable to investigate the formation process of dust because of their high occurrence. Past studies have shown that the UIR bands in novae are characterized by the presence of a broad 8μm feature [2,3].

We have succeeded to synthesize Quenched Nitrogen-included Carbonaceous Composite, laboratory organics whose infrared properties cane reproduce the UIR bands in novae. QNCC is synthesized by quenching plasma produced from nitrogen gas and hydrocarbon solids. This synthesis method qualitatively mimic a possible formation process of organics in the circumstellar environment of novae, where nitrogen-rich novae wind react with pre-existing carbonaceous dust. Based on the infrared and X-ray analyses of QNCC, we found that QNCC show the presence of amine structure, which can contribute to the broad 8μm feature characterizing the UIR bands in novae. QNCC is at present the best laboratory analog of organic dust formed in circumstellar environments of dusty classical novae[4].

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Development of Cavity Enhanced Absorption Spectrometer Aiming to Measure Optical Absorption Bands of Interstellar Molecules

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Diffuse Interstellar Bands (DIBs) are mysterious unidentified absorption bands detected optically in diffuse clouds. DIBs are presumed to be electronic transitions of large organic molecules. Identification of their origins allows us to unveil a wide variety of chemical composition of space, because approximately 600 DIBs have been found so far [1]. However, at present only the five bands were assigned to the fullerene cation C_{60}^{+} [2] and the other bands are not identified yet.

To reveal DIB carriers, comparative studies of astronomically observed bands with laboratory spectra are required. However, a covering range of a high-resolution laboratory spectrometer is generally narrow, although DIBs disperse over a wide range. A wide-band spectrometer can be a powerful tool to identify these bands.

Cavity enhanced absorption spectroscopy is possible to widely measure a high-resolution spectrum [3]. This method enables us to achieve a very long optical path length, because white light introduced in between two high reflectivity mirrors reciprocates more than ten thousand times. Based on these advantages, this spectrometer is suitable to measure DIB-candidate molecules produced in laboratory. In this study, we developed this spectrometer that simultaneously covers the 60-nm range by using the 1200 lines/mm grating. As a demonstration of sensitivity, the fifth CH stretching overtones ($v' = 6$) of methyl acetate (a) and ethyl acetate (b) were detected for the first time, as shown in Fig. 1. Additionally, we also detected methanol produced via saponification of methyl acetate by sodium hydroxide (c3). As a next step, we plan to install a hollow-cathode discharge system to produce DIB-candidate ion and radical of large organic molecule.

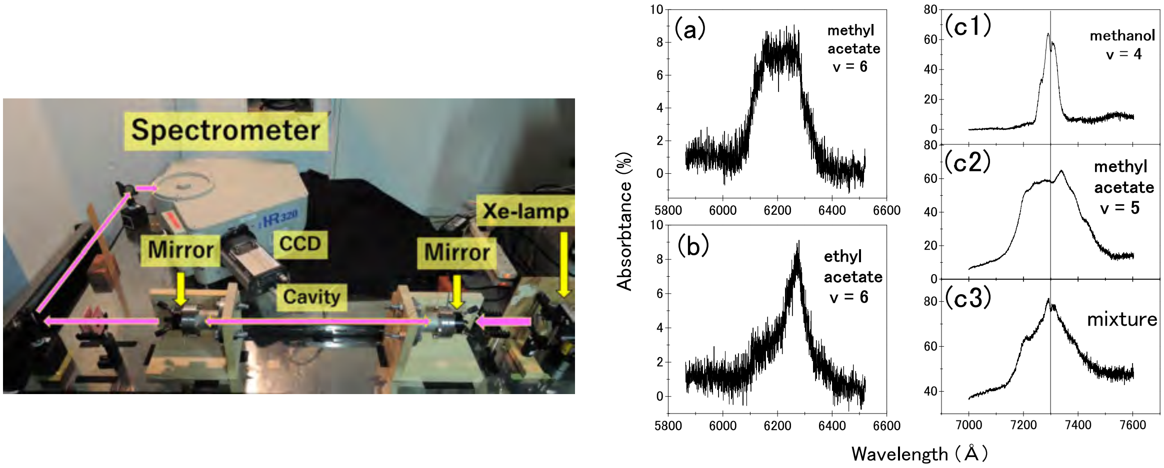

Figure 1: Cavity-enhanced absorption spectrometer (left) and the observed spectra. (a) $v' = 6$ of methyl acetate. (b) $v' = 6$ of ethyl acetate. (c1) $v' = 4$ of pure methanol. (c2) $v' = 5$ of pure methyl acetate. (c3) mixture of methyl acetate with methanol produced by saponification of methyl acetate. The sample pressure was adjusted in the range of 0.020 – 156 Torr depending on the peak intensities.

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Experimental measurement of the absorption cross section of dangling OH bonds in water ice

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Recent astronomical observations have revealed water (H_2O) ice to be ubiquitous in space. For example, it is the most abundant solid component in interstellar molecular clouds and the outer cold part of protoplanetary disks. Its ubiquity makes it essential to clarify the physics and chemistry of ice to further our understanding of the formation of stars and planetary systems, including our solar system [1].

Key infrared (IR) features related to interstellar ice are signals at 3720 and 3696 cm^{-1} from dangling OH bonds, which have respectively been assigned to the free OH stretch modes of two- and three-coordinated H_2O molecules at the surface of ice [2, 3]. Because dangling OH bonds reflect the porosity of ice and serve as catalytic sites for adsorption and chemical reactions, they have been intensely studied in many fields including interstellar chemistry [4, 5]. Despite much active research, the absorption cross section, a fundamental optical constant, of dangling OH bonds remains unknown. This hampers the quantification of dangling OH bonds from IR spectra of ice.

Recently, we developed an experimental setup for in situ infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) in low-temperature, ultrahigh-vacuum conditions [6]. IR-MAIRS is a spectroscopic method combining oblique incidence transmission measurements and multivariate analysis to retrieve both pure in-plane (IP) and out-of-plane (OP) vibration spectra for a thin sample, which was originally developed for quantitative molecular orientation analysis of organic thin films without the use of optical parameters [6, 7]. In this study, we report our recent challenge to measure the absorption cross section of dangling OH bonds of water ice using IR-MAIRS [8].

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Cloudlet capture model for the origin of asymmetry in the molecular emission in TMC-1A

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Protostars are associated with protoplanetary disks and are surrounded by infalling envelopes. The gas accretion from the envelope is thought to be more or less symmetric around the rotation axis of the disk. However, some young protostars show highly asymmetric features in the molecular emission lines. Blue-shifted component is much stronger than red-shited one in the CS emission line in TMC-1A harboringIRAS 04365+2535, Class I protostar in Taurus. The asymmetry may indicate that we are observing the capture of a cloudlet. We examine this possibility based on hydrodynamical simulations in which a cloudlet accretes and collides the pre-existing disk. The orbital plane of the cloudlet is inclined to the disk. This model explains several features such as (1) the asymmetry in the infalling gas, (2) a partial lack in the disk, and (3) apparently slow infall velocity. We discuss the implications of our hypothesis that the gas accretion onto protostar may be successive but sporadic captures of cloudlets rather than continuous flow.

Submillimeter H_2O masers in high-mass star-forming regions

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Molecular masers have been employed to investigate dynamical structures of circumstellar disks and outflows in young stellar objects (YSOs). In particular, some representative centimeter radio lines such as the 1.6 GHz OH, 6.7 GHz CH_3OH, and 22 GHz H_2O masers are widely used for high resolution interferometric observations. In contrast, higher frequency masers have not been well studied until recent developments with ALMA (Atacama Large Millimeter/submillimeter Array).

Here we will present observational results of submillimeter H_2O masers toward high-mass star-forming regions. We will review recent progress of our ALMA observations of submillimeter H_2O lines toward the nearest high-mass YSO, Source I in Orion KL [e.g. 1,2], which shows a rotating outflow driven from the Keplerian disk. We will also show tentative results from ALMA observations of the 321 GHz H_2O masers toward high-mass YSO samples associated with the 22 GHz H_2O masers observed with VERA (VLBI Exploration of Radio Astrometry) [e.g. 3]. We find that the higher excitation 321 GHz H_2O masers are in general co-located with those of the 22 GHz H_2O masers while in some sources they are emitted from inner part of the outflows traced by the 22 GHz masers. The results suggest that multiple maser lines at different excitation conditions can be unique probes of physical and chemical properties of high density and temperature regions in the close vicinity to high-mass YSOs associated with disk/outflow systems.

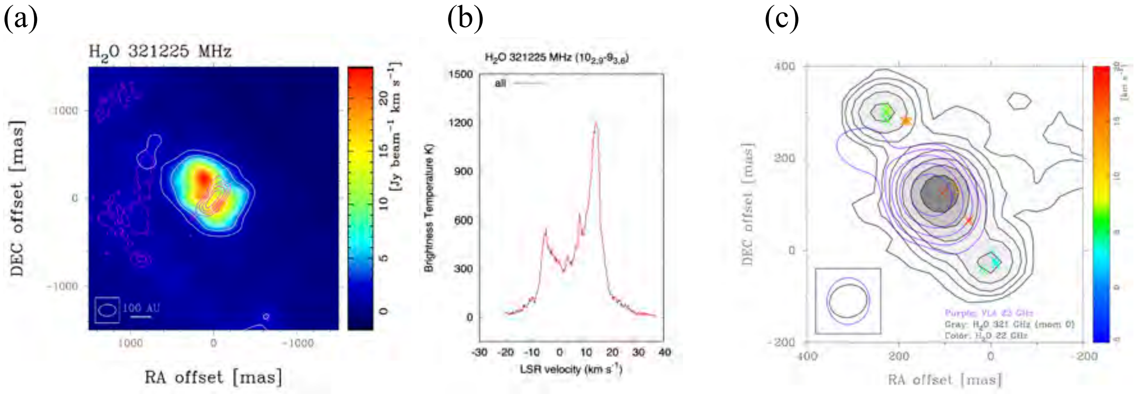

Figure 1: (a) Moment 0 map of the 321 GHz ($10_{2,9}$ - $9_{3,6}$) H_2O maser (color) and ALMA Band 10 continuum emission (contour) toward a high-mass YSO Orion Source I [1,2]. (b) Spectrum of the 321 GHz H_2O maser toward Source I [1,2]. (c) Moment 0 map of the 321 GHz H_2O maser (gray), VLA 22 GHz continuum (contour), and positions of the 22 GHz ($6_{1,6}$ - $5_{2,3}$) H_2O maser (cross) toward a high-mass YSO S255 NIRS3 [3].

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Microwave Spectroscopy of Isothiazole

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Five-membered ring structure are found in some amino acids. In addition, five-membered ring cyanocyclopentadiene has been identified toward TMC-1 [1]. Therefore isothiazole (C_3H_3NS) is a potential interstellar molecule of five-membered ring with two adjacent hetero atoms, nitrogen and sulfur. Previous studies of microwave spectroscopy have been conducted below 35 GHz including information on the dipole moment, isotopologues, and the Zeeman effect [2-4]. The *a*-axis and *b*-axis components of the dipole moment are doubled by 1.1 D and 2.2 D, respectively. Information on higher frequency range is essential for future detection.

In this study, microwave spectroscopy of isothiazole was performed in the 40-360 GHz region at room temperature at the University of Toyama and University of Wisconsin–Madison. The assignment was based on the frequency prediction using molecular constants from previous high-resolution infrared studies [5,6]. The spectra were analyzed by using AABS package.[7] Figure 1 shows an example. Over 2000 lines were assigned and analyzed using Watson's *A*-reduced Hamiltonian.

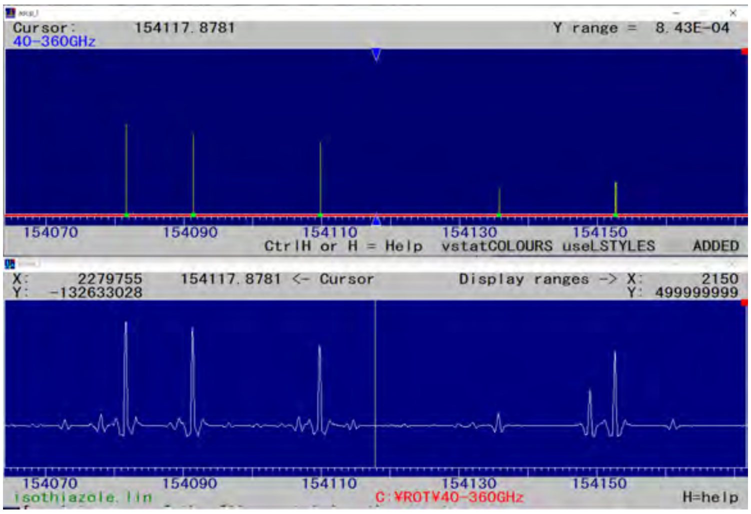

Figure 1: The spectrum and the frequency prediction of isothiazole.

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Energetic processes caused by sub-keV electrons impacting on H_2O+CO ice mixtures

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The irradiation of molecules in condensed water is an important process in the chemistry of a wide variety of astronomical environments. An important component of interstellar ices is carbon monoxide, and consequently, a number of experiments have been performed in mixtures of such species with water [1, 2].

In this work, we use middle-range electrons (200-1000 eV) to study the radiation induced chemistry in H_2O + CO ice mixtures. We derive destruction and production cross-sections of parent molecules and products, and for the case of CO being the desorption cross-section. We label the products observed after irradiation with energetic electrons from IR spectra (Figure 1) to understand the mechanisms and kinetics associated with the relevant reactions. A comparison is made with the results of experiments performed using different processing sources, such as X-ray, UV and hydrogenation. Finally, we discuss the difference of desorption relevant depths [3] between in the present case and that of a pure CO ice.

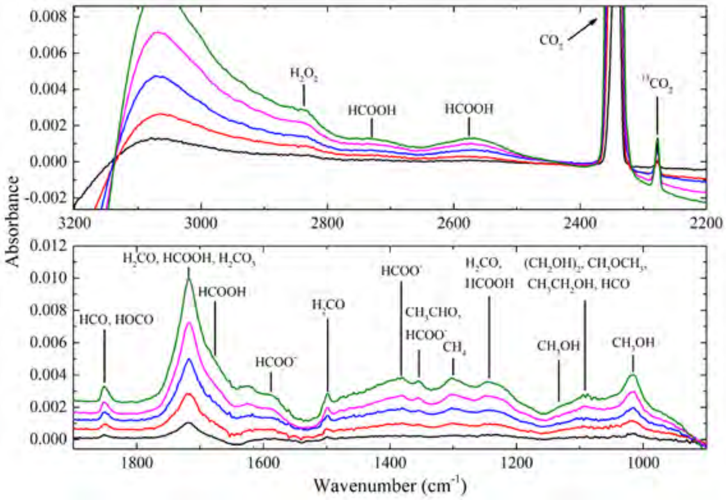

Figure 1: Assignment of products in irradiated H_2O:CO ice mixture. From bottom to top are spectrum in 200, 400, 600, 800, and 1000 eV experiments.

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Anomalous Properties of Condensed Hydrogen Molecules under Extreme Thermodynamic Conditions Revealed by the Non-Empirical Quantum Molecular Dynamic Simulation Method

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The nuclear and electron wave packet molecular dynamics (NEWPMD) method describes floating and thawed Gaussian nuclear wave packets (NWPs) via the time-dependent Hartree method, and electron wave packets (EWPs) through the perfect-pairing valence bond theory that treats the Pauli exclusion energy. [1,2] The non-empirical ab initio intramolecular and intermolecular interactions were explicitly derived with which the equations of motion (EOMs) for a time-dependent wave function composed of the NWPs and EWPs are time-evolved. The simple EOMs ensure a stable long-time solution, that is, the time-dependent wave function even for condensed hydrogen molecules. In addition, the NEWPMD approach reproduces a long-range intermolecular dispersion force between H_2 molecules which the conventional density functional theory cannot provide.

The NEWPMD method has successfully reproduced various experimental observations without any model potential and empirical parameter such as (1) the radial distribution functions, diffusion coefficients, viscosity and shifts of the H-H vibrational frequency in liquid hydrogens [2,3], (2) the stable crystal lattice structure below the freezing temperature(13.8 K), vibrational displacement and reasonable lattice phonon frequency in solid hydrogens [4], (3) the discrete jump of the H-H vibrational frequency at the liquid-solid phase transition [4,5], (4) the thermal conductivity of non-equilibrium liquid hydrogens under a temperature gradient[6], (5) the isotope-dependent bond length and diffusion coefficient in liquid deuterium[7], (6) the decelerated diffusive dynamics at an optimal mixing rate for the H_2-D_2 mixture[8], and (7) the Widom line to divide liquid-like and gas-like regions hidden in supercritical hydrogens [9]. The temperature and density were never adjusted or scaled in any of these simulations. All the above-mentioned successful agreements with the experimental results in the far-different various phases and thermodynamic states demonstrate that the NEWPMD method not only reflects the real thermodynamic states of hydrogen systems at the same temperature and densities as the experimental values but also successfully reproduces the appropriate intermolecular interaction potential which essentially influences the thermodynamic properties.

In this presentation, we will report our computational results especially focusing on the latest computational findings on the two extreme thermodynamic conditions: (1) the decelerated liquid dynamics induced by component-dependent supercooling in hydrogen and deuterium quantum mixtures at low temperature, and (2) the distinct molecular dynamics dividing liquid like and gas-like supercritical hydrogens at higher temperature than the critical temperature (33K). In the former, we computationally found that the dynamics of the quantum H_2-D_2 mixtures significantly slows down at a specific mixing ratio, which is directly connected to the experimentally observed anomalous slowdown of crystallization in quantum H_2-D_2 mixtures at extremely low temperature. The latter proposes a new index to monitor the supercriticality and especially to distinguish liquid-like and gas-like supercritical regions which are different from normal liquid and gas. Both of the computationally predicted properties and obtained insights will help future experimental searching and understanding anomalous and unknown hydrogen molecular dynamics which could play an important role in interstellar space.

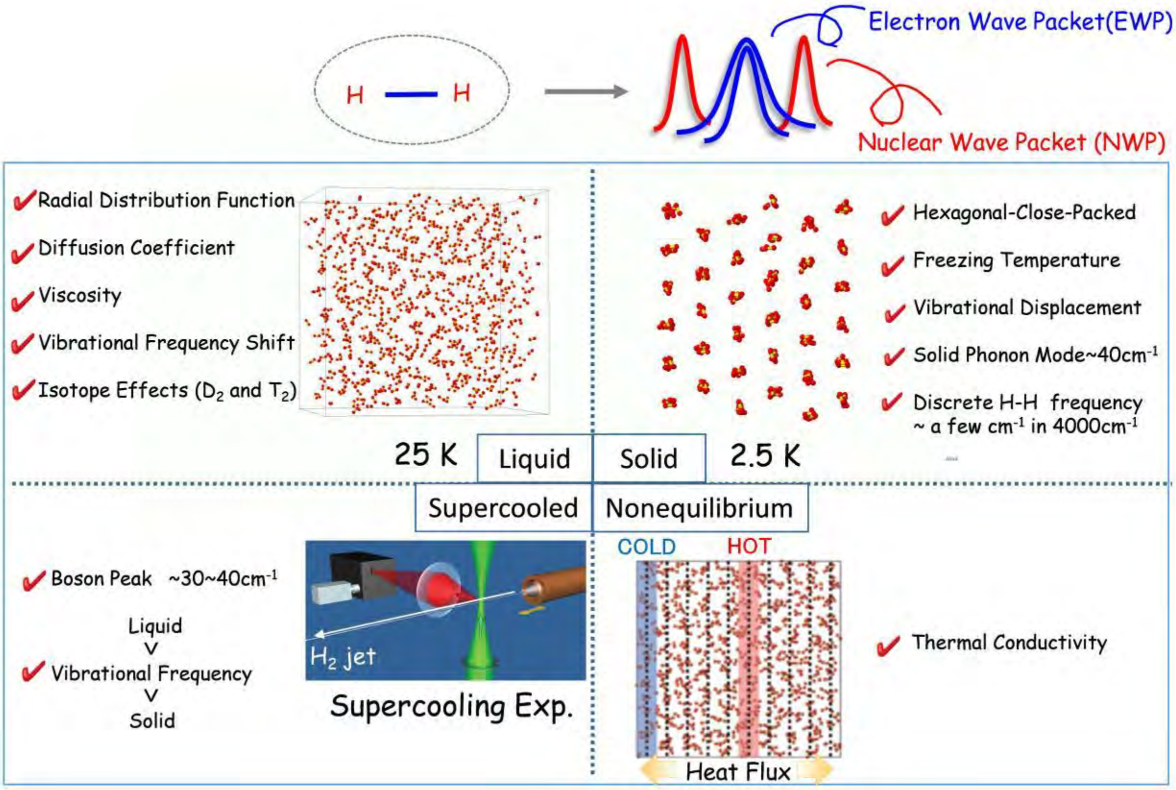

Figure 1: Far-different various phases and thermodynamic states of hydrogen molecules calculated by the NEWPMD method. The left-bottom figure was taken from Kuhnel et al., 2014, Phys. Rev. B 89, 180201.

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A new electrochemical property of ice: negative charge transport triggered by reactions of surface OH radicals with electrons

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The electrochemical behavior of water ice is of particular interest in astrophysical chemistry and atmospheric chemistry. Much research has shown that the ice can be a p-type semiconductor due to the conduction of excess protons along the hydrogen bonds. In contrast to positive charges, the conductivity of negative charges due to the relay of hydroxide ions (OH^-) in ice has not been verified. We have recently observed the negative charge conductivity of ice simultaneously exposed to UV and electrons at temperatures below 50 K [1]. The phenomenon can be explained by the following processes: (1) production of OH radicals on ice surface by UV irradiation, (2) electron attachment to OH radicals, and (3) the produced OH^- induce the sequence of proton abstraction from surrounding H_2O. To confirm the above processes, we additionally measured the density of surface OH radicals using a novel technique, a combination of photostimulated desorption and resonance-enhanced multiphoton ionization [2].

Figure 1(a) shows the temporal variation of the negative currents through H_2O ice at 10 K. One can see the increase in negative currents during simultaneous exposure to UV and electrons. A transient peak initially formed by electron irradiation may be attributed to the leakage of electrons through pores or cracks in ice. Meanwhile, as shown in Figure 1(b), the density of surface OH radicals decrease upon electron exposure. The results suggest that the surface OH radicals are consumed via electron attachment to the radicals to produce OH^-. We consider that the negative currents are subsequently induced by the relay of OH^- in ice at low temperatures.

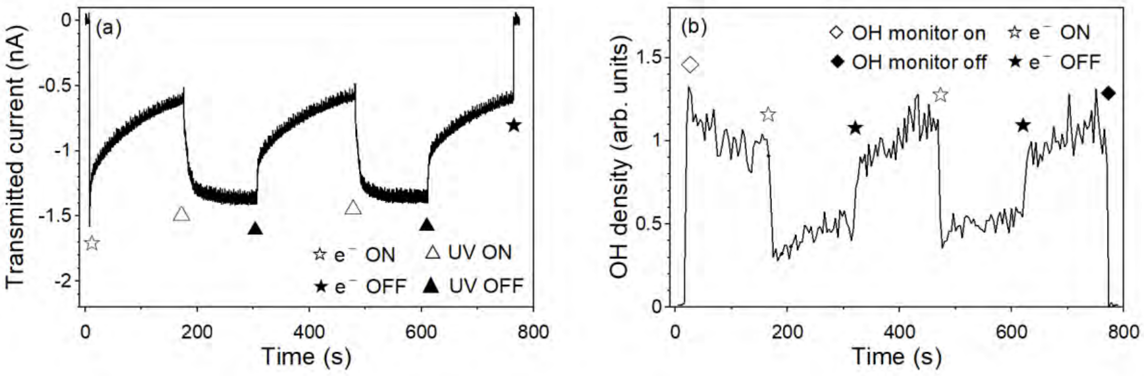

Figure 1 (a) Temporal variation in negative currents through H_2O ice at 10 K upon repetitive UV irradiation with continuous exposure to electrons. (b) Temporal variation in OH radical densities on ice at 10 K upon repetitive electron irradiation with continuous exposure to UV.

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Mono-deuterated methanol in prestellar cores

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Mono-deuterated methanol is thought to form during the prestellar core stage of star formation. Variations in the CH_2DOH/CH_3OD ratio suggest that its formation is strongly dependent on the surrounding cloud conditions. Thus it is a potential tracer of the physical conditions before the onset of star formation.

A single-point physical model descriptive of a prestellar core is coupled to chemical models to investigate potential formation pathways towards deuterated methanol at the prestellar stage and discussed in context with observational findings [1]. The implementation of an abstraction scheme [2] leads to the efficient formation of methyl-deuterated methanol, but lacks sufficient formation of hydroxyl-deuterated methanol.

This leads to the conclusion that CH_3OD is most likely formed at a later evolutionary stage, potentially from H/D exchange in warm ices between D_2O (or HDO) and CH_3OH.
Our results suggest that the ratio of CH_2DOH/CH_3OD is therefore not an appropriate tracer of the physical conditions during the prestellar stage, but might be better suited as a tracer of ice heating.

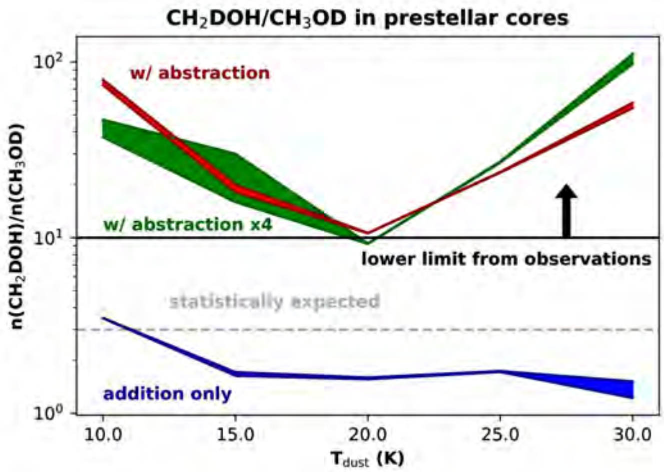

Figure 1: Ratio of CH_2DOH/CH_3OD over a grid of core ages and dust temperatures descriptive of the prestellar phase as obtained with three different chemical networks [1]. The gray, dashed line indicates the statistically expected value of 3, the solid, black line indicates the lower limit derived from observations [3].

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Early stages of water cluster growth observed with low-temperature scanning tunnelling microscopy

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Water ice is known to form on carbonaceous dust grains in the interstellar medium [1], but the structural morphology of icy grains including their chemical activity is still under investigation.

It has recently been shown that water molecules are mobile at temperatures down to 25 K on highly-oriented pyrolytic graphite (HOPG), suggesting that ice may grow via clustering rather than layer-by-layer [2]. However, realistic interstellar grains are not pristine and are likely terminated by various functional groups, which may further affect ice formation [3].

We have studied the initial stages of ice formation on HOPG and O-terminated HOPG, as dust grain analogues, using low-temperature scanning tunneling microscopy (LT-STM). Data reveal that step-edges and O-functional groups act as nucleation sites for ice formation. The size, fractal structure, and porosity of nanometer size water clusters are found to be strongly dependent on the sample temperature.

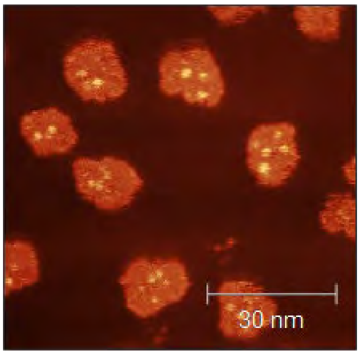

Figure 1: LT-STM image of water ice clusters on O-HOPG. It: 4 pA, Vt: 4.5 V.

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Computational Investigation on the Potential Energy Surface of the Formation Route of Formamide from Reaction between NH_2 and H_2CO on Interstellar Water Ice Surface

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Formamide has a key role in prebiotic chemistry as it is the simplest molecule containing the four most important atoms from a biological point of view: hydrogen, carbon, nitrogen and oxygen. But also, because it is the simplest molecule containing the amide bond O-C-NH, the group that join amino acids forming peptides [1]–[3]. Since it was first detected and due to its importance, different pathways leading to its interstellar formation has been studied considering both the gas-phase scenario and on ices of dust grains[2]–[4]. In the present contribution, computational simulations based on quantum chemical calculations are presented, focusing on the energetics of the NH_2CHO formation from reaction of NH_2 with H_2CO (a channel proposed to occur in the gas phase [3]) on water ice surfaces. To model the water ice surfaces, a periodic approach has been adopted, in which both a crystalline and an amorphous model has been used. Different DFT functionals have been employed to obtain accurate energy values for the mechanistic steps involved in the reaction.

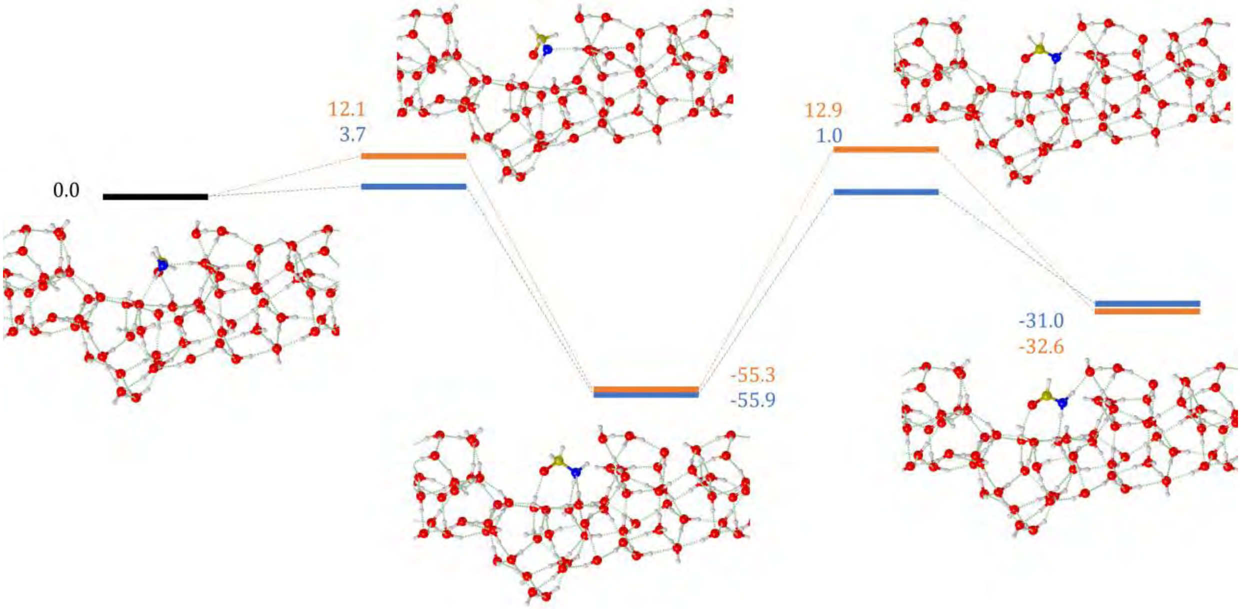

Figure 1: Potential Energy Surface and optimized structures of the stationary points of the studied reaction on the amorphous slab model. Values are in kJ/mol. Bare values correspond to those at B3LYP-D3(BJ), in brackets to those at PBE-D3(BJ) and in square brackets to those at M06-2X-D3. Atom color legend: red, O; blue, N; green, C white, H.

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Detection of photodesorption OH radicals from H_2O ice surface by visible light

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[3] *Komaba Institute for Science, The University of Tokyo, Japan*

There are various molecules including complex organic molecules in interstellar molecular clouds. Surface reactions involving radicals on interstellar ice-dust grain play an important role in chemical evolution because they are indispensable for the formation of complex interstellar molecules [1,2]. In order to understand the details of the molecular formation on the surface of dust, it is necessary to clarify the behavior of radicals on the surface. However, the detection of radicals on ice surface has intrinsic experimental difficulties.

In this study, we investigated behavior of OH radicals on the ice surface. Because they can be easily produced by photolysis of ice and would greatly contribute to the formation of complex molecules or those precursors. Using the combination of photo-stimulated desorption and resonance-enhanced multiphoton ionization, we have first succeeded in monitoring OH radicals on ice [3]. The results of the experiments indicate that photodesorption of OH radicals are induced by one photon absorption at 532 nm, which is transparent for gaseous OH radical as well as for water ice. I present the details on the behavior of OH radicals and adsorption sites on water ice [4,5].

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An infrared spectroscopic approach towards understanding the orientation of dangling OH bonds on amorphous solid water

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The surface reaction on amorphous solid water (ASW) is the key to figuring out the chemical processes in interstellar molecular clouds, where stars and planets are being born [1]. Macroscopic properties of ASW such as heat transfer coefficient [2], surface potential [3] have progressively become understood through intensive research. By contrast, our understanding about the microscopic structure of ASW is still at an early stage. For example, there is almost no experimental study about the molecular orientation in ASW, which is a key factor to control the physicochemical properties of organic thin films [4], due to the lack of direct measurement technique. Recently, we built an experimental apparatus for low temperature ultrahigh vacuum infrared multiple-angle incidence resolution spectrometry (IR-MAIRS [4][5]. IR–MAIRS is a spectroscopic method combining oblique incidence transmission measurements and multivariate analysis to retrieve both pure (in-plane; IP) IP and (out-of-plane; OP) OP vibration spectra for a thin sample. The method has the unique advantage that the average molecular orientation is determined by comparing the IP to OP band intensity ratio spectra on the absorbance scale. In this research, we report our recent IR-MAIRS results for dangling OH bands in ASW at 10 to 90 K. It is found that the average orientation angle of dangling OH bonds exhibit a drastic ice temperature dependence in the range of 10 to 90 K. The detailed results are presented in the poster.

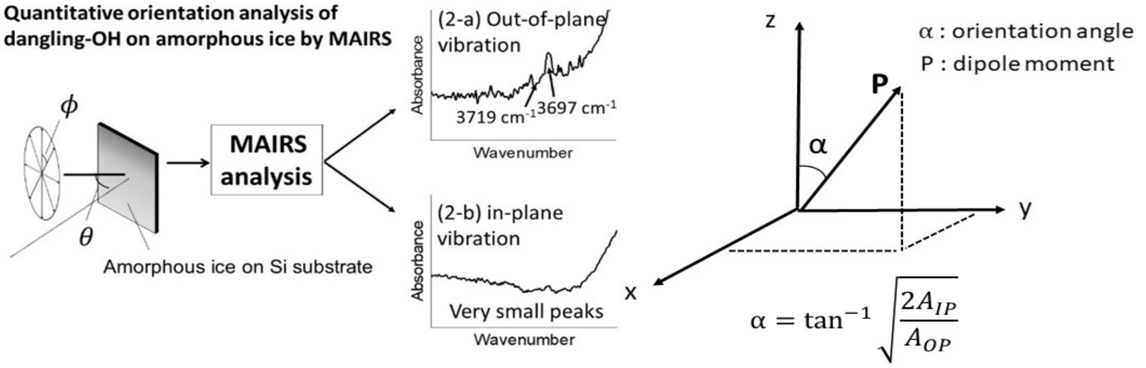

Figure: (left) Schematic illustration of IR-MAIRS. IR–MAIRS: Typical single-beam spectra measured at an angle of incidence of 45° at various polarization angles from 0° to 90° in 15° steps, and then extracting the IP and OP spectra by multivariate analysis.
(right) Molecular orientation analysis based on IR-MAIRS. The average orientation angle of molecules is determined by comparing the ratio of absorbance both IP and OP spectra.

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Methanol production via interactions of low-energy CH_3^+ ions with ASW surface: experimental investigation of ion-surface reactions

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Various neutral and ion species have been observed in molecular clouds, despite their very low temperatures. To understand how molecules evoluve, many chemical processes have been proposed. In gas phase, ion-molecule reactions have been always considered to play an important role. However, the abundances of some molecules such as water and methanol molecules cannot be explained only by the gas-phase reactions. Consequently, reactions between neutral radicals and neutral species on an icy grain surface have been proposed as the other essential pathways and it has been experimentally confirmed that reactions of hydrogen atoms adsorbed on an ice surface are essential for productions of hydrogen, water, methanol, and so on [1, 2]. Besides pure gas-phase and surface reactions, it is reasonably inferred that processes triggered by interactions of gas-phase ions with an ice mantle play some role in molecular evolution. In this context, the experiments of energetic ion bombardment to an ice containing other primordial molecules have been performed for a long time. In contrast, little is known about the interactions between low-energy ions and an ice surface, while molecular cations have been simply considered to recombine with negative charge (electrons) on an ice surface in theoretical models [3, 4]. However, it is not clear how electrons exist on icy grains, and thus it is also unclear if cation-electron recombination immediately occurs or not.

In fact, the reactions of very-low-energy ions with an icy surface have been theoretically proposed as new non-energetic reaction pathways [5, 6]. Since an icy grain can be regarded as a huge molecular cluster, reactions of ions with an icy grain surface would occur without reaction barriers as ion-molecule reactions. For example, the quantum chemical calculation predicted that the reaction of a CH_3^+ ion with a water ice surface spontaneously produces a methanol molecule [5]. Despite recent theoretical progress, no experimental study for low-energy ion reactions with ice surface have been performed due to experimental difficulties in obtaining enough reaction products for their detection using conventional methods such as infrared absorption spectroscopy. Accordingly, we have newly developed an experimental setup to enable us detecting trace amounts of reaction products. Using this setup, we have performed the experiments for production of methanol through the reaction of low-energy CH_3^+ ions with a water ice surface. The CH_3^+ ions with their energies as low as or lower than ~10 eV impinged on an amorphous solid water (ASW) prepared on an Al substrate around 10 K. Reaction products by CH_3^+ irradiation were monitored through pick-up reaction method by Cs^+ ions at several tens eV [7, 8]. After CH_3^+ irradiation, methanol molecules on the ASW were observed as the theoretical study suggested.

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Experimental and computational studies on the physicochemical behavior of phosphine induced by reactions with H and D atoms on interstellar ice grains

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Phosphine (PH_3) is an important molecule for the chemistry of phosphorus (P-) bearing species in the interstellar medium (ISM). Interstellar PH_3 is thought to primarily form on icy grains, where several surface processes may occur during and after its formation. To better understand the physicochemical behavior of PH_3 on ice grains in dense molecular clouds, we performed experimental and computational studies on the reactions of phosphine with H and D atoms at low temperatures. We found that phosphine and its deuterated isotopologue PD_3 are released into the gas phase from ice surfaces via chemical desorption. We confirmed that H-D substitution reactions of PH_3 and D-H substitution reactions of PD_3 occurred following reactions with D and H atoms, respectively, at 10 K on icy surface. Because the activation barrier for the abstraction of H and D atoms from phosphine is ~1500 K, quantum tunneling should play a role at low temperatures. On the other hand, the D-H substitution reactions of PD_3 was slightly faster than the H-D substitution reactions of PH_3, meaning that the rates of the H-D and D-H substitution reactions are not constrained by tunneling reactions but rather by other elementary processes such as atoms diffusion on ice.

X-ray-induced chemistry of water and related molecules in low-mass protostellar envelopes

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Water is a key molecule in star and planet forming regions. Recent water line observations toward several low-mass protostars suggest low water gas fractional abundances (<10^-6) in the inner warm envelopes (r<100 au). Water destruction by X-ray radiation has been proposed to influence the water abundances in these regions, but the detailed chemistry, including the nature of alternative oxygen carriers, is not yet understood. In our study [1], we calculated the chemical composition of low-mass Class 0 protostar envelopes using a detailed gas-grain chemical reaction network including X-ray induced chemical reactions. We aimed to understand the impact of X-ray radiation on the composition of low-mass protostar envelopes, focusing specifically on water the related oxygen bearing species.

On the basis of our calculations [1], the protostar X-ray luminosity has a strong effect on the water gas abundances, both within and outside the water snowline (T<100K, r<100 au). Outside the water snowline, the water gas abundance increases with X-ray luminosities, due to X-ray-induced photodesorption of water ice. Inside the water snowline, water maintains a high abundance of 10^-4 for low X-ray luminosities, with water and CO dominant oxygen carriers. For high X-ray luminosities (>10^30 erg/s), the water gas abundances significantly decrease just inside the water snowline (down to ~10^-8–10^-7) and in the innermost regions with T >250K (~10^-6). For these cases, the fractional abundances of molecular and atomic oxygen gas reach <10^-4 within the water snowline, and they become the dominant oxygen carriers. In the presence of strong X-ray fields, gas-phase water molecules within the water snowline are mainly destroyed with ion-molecule reactions and X-ray-induced photo-dissociation. In addition, the fractional abundances of HCO+ and CH3OH, which have been considered to be tracers of the water snowline, significantly increase and decrease within the water snowline, respectively, as the X-ray fluxes become larger. These X-ray effects are larger in envelope models with lower number densities. Future molecular line observations for protostars (using e.g., ALMA, ngVLA) will access the regions around protostars where such X-ray induced chemistry is effective.

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First direct detection of OH radicals photodesorbed from liquid organic surface by using laser-induced fluorescence technique

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The 5th assessment report of the Intergovernmental Panel on Climate Change provides that aerosols contribute the largest uncertainty of the Earth's changing energy budget and this should be evaluated in order to understand climate change [1]. Especially, interfacial reactions at atmospheric aerosols and sea surface are of increasing importance because these interfaces occupy a great deal of reaction fields on the Earth. Recently, photochemical reactions of surfactant organic compounds such as fatty acids that cover the top surfaces of aerosols and sea have attracted much attention. For example, it had been believed that gaseous and liquid nonanoic acids (NA) do not absorb ultraviolet – visible radiation (> 295 nm). However, Rossignol *et al*. found that NA at the air-water interface absorbs the ultraviolet, and then complex organic compounds were produced, which eventually act as aerosol precursors [2]. Although the photochemical reaction mechanism of NA is still poorly understood, it has been suggested that OH radicals are a primary photoproduct in the ultraviolet photolysis of NA at the interface [2, 3].

$$CH_3(CH_2)_7COOH + h\nu(> 295\text{ nm}) \rightarrow CH_3(CH_2)_7CO + OH?$$

OH radical is one of the most important chemical species in atmospheric chemistry and quantum yields of OH radical formation are needed to incorporate the interfacial reactions into atmospheric models. However, even direct measurements of desorption of OH radicals in photolysis of liquid NA have not been achieved yet.

We have developed an instrument for direct detection of photodesorbed OH radicals in the ultraviolet photolysis of liquid NA by using laser-induced fluorescence (LIF) technique. Liquid NA was put on a silicon substrate in a low vacuum chamber (1 – 100 Pa) and irradiated with a pulsed 213 nm Nd:YAG laser. OH radicals desorbed from the NA surface were excited by a second harmonic 282 nm dye laser, and OH-LIF at 315 nm was detected by a photomultiplier tube.

$$OH\ (X^2\Pi, v = 0) + h\nu(282\text{ nm}) \rightarrow OH\ (A^2\Sigma, v = 1) \rightarrow OH\ (X^2\Pi, v = 1) + h\nu(315\text{ nm})$$

In order to verify that the detected OH radicals were desorbed from liquid NA surface not formed from gaseous NA, we measured OH-LIF intensities as a function of the delay time between the two lasers, changing a distance between the dye laser and the Si substrate. Moreover, we performed single shot experiments to clarify that OH radicals were originated from parent NA molecules on the liquid surface not from photoproducts.

In the workshop, we will show our new experimental setup for the photolysis of liquid organics and detection of photodesorbed OH radicals using the LIF technique.

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FAUST III. Misaligned rotations of the envelope, outflow, and disks in the multiple protostellar system of VLA 1623$-$2417

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We report a study of the low-mass Class-0 multiple system VLA 1623AB in the Ophiuchus star-forming region, using H^{13}CO$^+$ ($J=3-2$), CS ($J=5-4$), and CCH ($N=3-2$) lines as part of the ALMA Large Program FAUST. The analysis of the velocity fields revealed the rotation motions on a wide range of scales in the envelope and the outflows (about 2000 au down to 50 au). We further investigated the rotation of the circum-binary VLA 1623A disk as well as the VLA 1623B disk.

We found that the minor axis of the circum-binary disk of VLA 1623A is misaligned by about 12 degrees with respect to the rotation axis of the large-scale outflow and the envelope. In contrast, the minor axis of the circum-binary disk is parallel to the large-scale magnetic field according to previous dust polarization observations, suggesting that the misalignment may be caused by the different directions of the envelope rotation and the magnetic field.

The outflow rotation shows a constant angular momentum with a mean specific angular momentum of about 100 au km s^{-1}$.

The launching radius is estimated to be $5-16$ au, suggesting that the outflow is launched from the VLA 1623A1 disk rather than the circum-binary disk.

Furthermore, we detected for the first time a velocity gradient associated with rotation toward the VLA 16293B disk. The velocity gradient is opposite to the one from the large-scale envelope, outflow, and circum-binary disk. The origin of its opposite velocity gradient is also discussed.

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Experimental study toward the measurements of rotational state dependence of interstellar ion-polar molecule reactions at low temperatures

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Recent astronomical observations have revealed the details of chemical composition in star-forming regions and molecular clouds. However, the chemical processes in those regions have not been fully understood using the existing chemical models with available data on relevant reaction rate constants [1]. This is because the temperature dependence of the gas-phase ion-molecule reactions in the range of low to intermediate temperatures (10 - 200 K) and their reaction branching ratio remain unknown. Thus, we have been developing a new experimental apparatus to measure the reaction temperature dependence of ion-polar molecule reactions at low temperatures [2, 3].

We report on an experimental study of the rotational cooling effect on the reaction rate constant of $Ca^+ + CH_3F \rightarrow CaF^+ + CH_3$ at low translational temperatures as a performance test of a new experimental apparatus. Combining a cold helium buffer gas cell with a wavy Stark velocity filter provides us with rotationally and translationally cooled polar molecules, we could compare the reaction rate constants measured at two different gas cell temperatures, namely the room temperature and about 30 K. The translational temperatures of the velocity-selected molecules were set in the range of approximately 10 to 40 K. The rotational level distribution of the velocity-selected CH_3F molecules was determined by numerical simulations of the velocity filtering and was used to calculate the rotationally-averaged capture rate constants with the Perturbed Rotational State (PRS) theory [2]. Comparing to the results obtained under the condition of room temperature gas cell, we observed a notable increase in the reaction rate constant at low buffer-gas temperatures. This clearly shows a strong rotational state dependence of the rate constant at low translational temperatures.

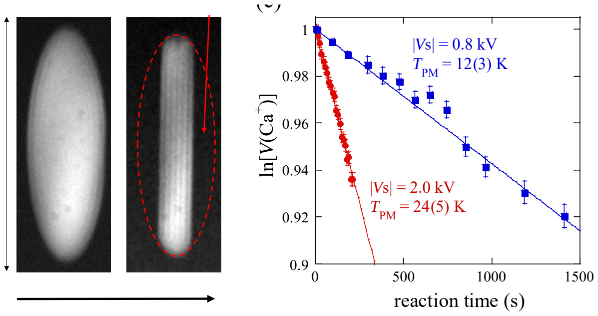

Figure 1 Fluorescence images of Ca^+ Coulomb crystals before (a) and after (b) the $Ca^+ + CH_3F \rightarrow CaF^+ + CH_3$ reactions. (c) A decay curve of the relative number of Ca^+ ions due to the reactions between Ca^+ and the velocity-selected CH_3F measured at two different translational temperatures of CH_3F extracted from the helium buffer gas cell at about 30 K (He pressure 80 Pa, UV laser detuning –40 MHz).

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Chemical Differentiation and its Relation with the Physical Structures in Disk-Forming Regions of Young Low-Mass Protostellar Sources

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To understand the chemical origin of the Solar system, the chemical evolution along the star/planet formation is a key issue. Extensive observational studies have so for demonstrated a chemical diversity in young low-mass protostellar sources [e.g. 1, 2, 3]. Furthermore, chemical differentiations in the vicinity of the protostars have recently been reported (Figure 1). This suggests that molecular distribution is sensitive to a change in the physical conditions associated with disk formation. Some kinds of molecular lines are therefore prospected to work as molecular markers to highlight particular structures of disk forming regions. Sulfur-bearing species, for instance OCS and H_2CS, especially seem good tracers.

Conversely, detailed physical characterization is essential for elucidating the chemical evolution occurring there. It has recently been recognized that some molecular lines tend to trace the mid-plane of a disk/envelope system and others its surface [e.g. 4]. The traced kinematic structure may differ among these molecular emissions, and thus, their careful analyses are essential for further observational studies in disk forming regions. Machine learnings may help us to disentangle the observed structures.

In this presentation, we would like to report recent progresses in delineating the chemical differentiation and the physical structures in disk forming regions of young protostellar sources (IRAS 16293-2422 A, L483, B335, etc.) with ALMA.

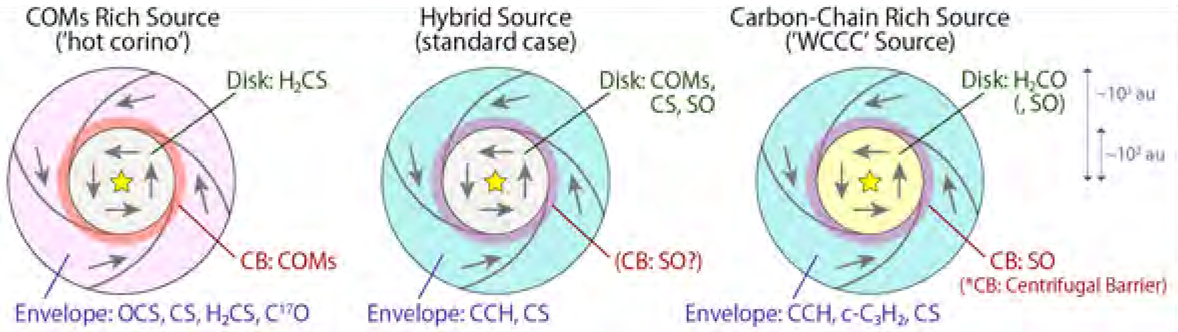

Figure 1: Chemical differentiation in disk forming regions of young low-mass protostellar sources with different chemical characteristics.

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Formation of 3-Pyrolline in Interstellar Space: A Computational Study

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Complex organic molecules (COMs) are thought to form on icy dust grains in the earliest phase of star formation. Interstellar detection of the straight-chain (n-propyl cyanide, $n-C_3H_7CN$) and branched-chain (i-propyl cyanide, $i-C_3H_7CN$) molecules toward the star-forming region, Sgr B2(N2) has attracted attention to study the formation mechanism of COMs [1]. The first detection of COM strongly hints the existence of other linear and ring-shaped molecules, which are prebiotic and building block of proteins.

Through computational methods, we suggest new possible formation and destruction pathways of branched aliphatic molecule to aromatic compounds in space. We computed binding energy, enthalpies of formation of several species. We also calculate the kinetic data of reactions and other spectroscopic information in order to understand the chemical evolution and formation of aromatic compounds to be present in the Interstellar medium (ISM).

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H and D diffusion on interstellar water ices

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Studies of surface diffusion of atoms on interstellar ices are a popular topic in the field of Astrochemistry. These chemical processes occur at very low temperatures (e.g., around 10K). At low temperatures, quantum tunneling becomes a dominant factor deciding the diffusion through barriers [1]. Therefore, quantum tunneling must be taken into account in calculating rate constants. Here, I discuss the single H and D atom diffusion on crystalline (I_h) and amorphous ice surfaces (ASW). The harmonic transition state theory was used to calculate the rate constants, and the Wigner tunneling correction was employed as well as a tunneling correction based on the Eckart potential to address the tunneling effect. The adaptive kinetic Monte Carlo method was applied to analyze the random walk trajectories [2]. A range of diffusion coefficients were found at low temperatures [3].

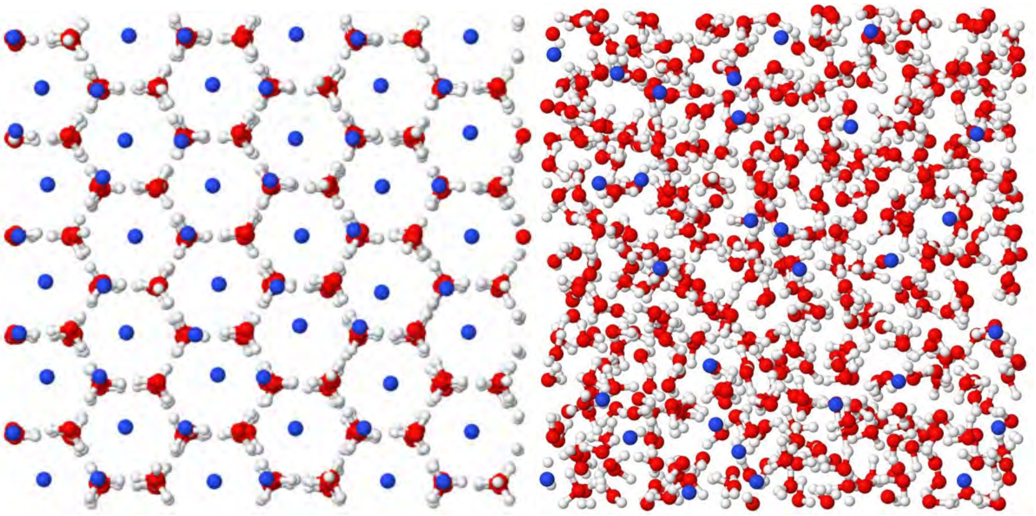

Figure 1: A map of local minima on a crystalline ice surface (left) and on an ASW surface (right). The blue dots are the local minima and the red and blue are O and H atoms of the water molecules. There are 59 local minima on the I_h surface and 30 local minima on the ASW surface.

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DFT study on hydrogenated and deuterated derivatives of interstellar fullerenes

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The credible detection of C_{60}, C_{70} and C_{60}^{+} in astronomical environments enables the search for other fullerene molecules and their derivatives (Zhang et al. 2017). The high reaction rates of fullerenes with atomic H, the most abundant element in the universe, suggest the dominance of their hydrogeneted forms (García-Hernández et al. 2010), which can go through deuterium enrichment as well (Cataldo et al. 2009c).

Here, we present theoretical infrared (IR) spectra and standard enthalpy of formation for neutral and singly ionized $C_{60}H_m$, $C_{60}D_m$, $C_{70}H_n$ and $C_{70}D_n$ using Density Functional Theory (DFT). The calculated IR spectra is then compared with observations.

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Formation of acetaldehyde on mixed-ice grain surfaces

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Interstellar complex organic molecules (iCOMs) are defined as compounds with ≥6 atoms, in which at least one is carbon. [1] Since their discovery in star-forming regions, they have been gaining increasing interest, as they can be considered the precursors of more complex molecules, which can have biological relevance. [2] However, understanding how iCOMs are formed is still a matter of debate, as it is supposed that both gas-phase and on-grain chemistry are needed for their synthesis. [3], [4] Acetaldehyde is one of the most detected species, therefore its formation routes are of paramount interest in astrochemical models. [5]

In the gas phase, CH_3CHO appears to be efficiently synthesized from ethanol and from ethyl radical. [5], [6] On the surface, radical-radical recombinations are preferred, for being barrierless, even though the orientation of the fragments has a crucial role and side reactions like H-abstraction may take place. [7], [8] We investigated a new reaction pathway for the formation of acetaldehyde, namely $CH_3 + CO_{(ice)}$, where the CO is a component of the ice surface. Our H_2O:CO amorphous model contains 25% of carbon monoxide and was chosen to avoid H-abstraction reactions. We found that the reaction, in the case to follow a Langmuir-Hinshelwood mechanism, exhibits a high energy barrier to be surmountable in interstellar conditions, but when adopting a Eley-Rideal mechanism it is barrierless. Subsequent hydrogenation step is found to be barrierless depending on the orientation of the two radicals. Thus, we suggest this pathway to form acetaldehyde to be likely when a CH_3 radical coming from the gas phase lands on a CO-rich region in icy surfaces.

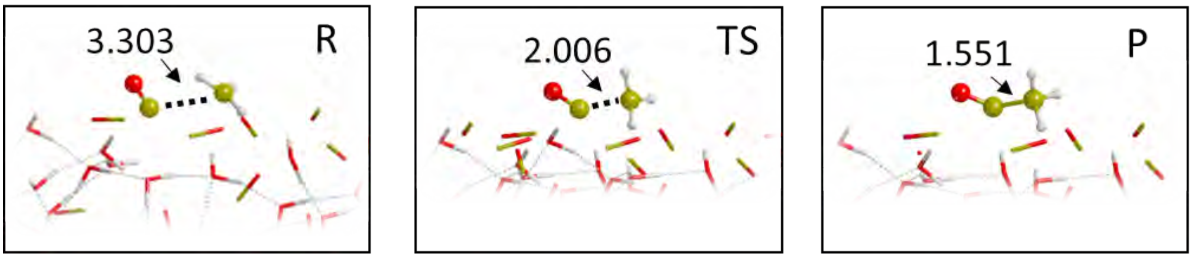

Figure 1: Reactant (R), transition state (TS), and product (P) of the reaction of CH_3 with a CO molecule of the (001) surface cut from our H_2O:CO amorphous ice model. Fragments involved in the reaction are represented as balls and sticks. Colour code: gray, H; brown, C; red, O. Distances are in Å.

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PyQMMM for modelling chemical processes in the interstellar medium

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We have developed PyQMMM; [1] a Python-based interfacing software for subtractive quantum mechanics/molecular mechanics (QM/MM) calculations with the AMOEBA09 polarizable force field. PyQMMM enables calculating large molecular systems, such as interstellar ices, using the ONIOM(QM:MM) [2-7] method at a low computational cost. We have used PyQMMM, employing the ONIOM(QM:AMOEBA09) method, to calculate the binding energy of SH and OH radicals on amorphous solid water (ASW). A range of binding energies was obtained for SH radical (0.10-0.36 eV) and OH radical (0.21-0.52 eV) on ASW. Computed average binding energies, 0.22 eV of SH and 0.36 eV of OH, suggested that the SH radical binding on ASW is weak compared to that of OH. We have also rationalized the mechanism for the reaction between OH anion and CO_2 in ice using the ONIOM(wB97X-D:AMOEBA09) calculations. The computed reaction mechanism showed a very low energy path, giving rise to HO-C(O)-OH and OH anion is recovered during the reaction. Thus, for implications in astrochemistry, we propose that OH anions in interstellar ices can react with the molecules trapped in ices to synthesize organic molecules. These examples evidence that the PyQMMM is a user-friendly strategy to study chemical processes in the interstellar medium.

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Star Formation Feedback to a Parent Cloud: The Elias 29 Case

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Elias 29 is a low-mass Class I protostar in the ϱ-Ophiuchi molecular cloud complex. According to the recent ALMA observation, a compact component (~50 au) associated to the protostar is abundant in SO and SO_2, while deficient in CS and organic molecules such as CCH and CH_3OH [1]. On the other hand, a southern ridge component apart from the protostar by 500 au is mainly traced by CS and $H^{13}CO^+$. For these interesting features, this source is selected in the ALMA large program FAUST (Fifty AU STudy of the chemistry in the disk/ envelope system of Solar-like protostars).

To further characterize this source, we have studied an outflow/jet around the protostar and the star formation feedback to a parent cloud by using the chemical diagnostic power of FAUST. Main results are as follows. (1) We have detected the $C^{18}O$ (2-1) and SO (6_5-5_4) emission at a spatial resolution of 70 au, and found that they trace an outflow cavity on a 2000 au scale for the first time. (2) We have detected a compact component in the SO emission at the eastern side of the protostar. Since the SO emission is often recognized as a shock tracer, this component is likely attributed to a bow shock caused by a protostellar jet. (3) We have found a relatively low DCO^+/HCO^+ ratio in the southern ridge. In particular, the ratio is as low as 0.0029 at the interaction position between the outflow and the ridge. Thus, this low ratio would originate from the outflow interaction. (4) We have evaluated the rotation temperature around Elias 29 by using the SO (6_5-5_4) and SO (6_6-5_5) emission and identified the relatively high temperature at the position of the bow shock and the interaction region.

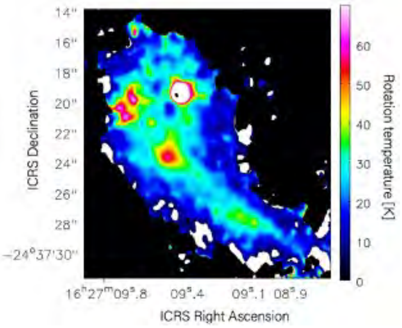

Figure 1: The rotation temperature around the protostar. The highest temperature is observed at the protostar position. The high temperature at the eastern side of the protostar is attributed to the bow shock and that at the southern side to the interaction between the outflow and the ridge.

This study reveals a chemical change associated to a small-scale (~100 au scale) dynamic interaction between the Class I outflow/jet structure and the surrounding cloud material, i.e., the southern ridge.

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Measurements of Microwave Spectra of Methanol Isotopologues in ALMA Band 6 Frequency Range

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In radio astronomy, accurate rest frequencies of molecular transitions are indispensable for secure identification of molecular species and accurate analyses of Doppler shifts caused by motions of the target sources. In observations, we have seriously realized the importance of the accurate rest frequencies of molecular transitions [cf; 1-4]. By strong lines, we can discuss gas motions in detail, and can set the velocity of the target system to the Solar system. As demonstrated in many sources, velocity analysis not only tells us kinematics of the system but also excitation condition of the gas on the corresponding position [cf; 5]. Accurate rest-frequencies of lines are therefore indispensable for such astronomical studies.

Methanol is a fundamental saturated-organic molecule and known to be abundant in star forming regions. It is thought to be formed on grain surface through hydrogenation reactions of adsorbed CO molecule. Since methanol can be a parent of more complex organic molecules (COMs), tracing it's abundance along protoplanetary-disk formation is important to understand origin of the chemical complexity in the Solar system. Especially isotopic ratios of molecules tell us critical information about their formation pathways. With these in mind, we have measured rotation spectra of methanol isotopologues by using SUMIRE (Emission type microwave spectrometer developed in RIKEN, [6]) in the frequency range corresponding to ALMA Band 6 (215-265 GHz). A portion of the results will be presented.

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Development of the RHEED apparatus for *in situ* structural analysis of water ices in low-temperature and ultrahigh vacuum conditions

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Water (H_2O) ice is a ubiquitous material for all of us, which has been also found to exist in cold regions of the Universe. In interstellar molecular clouds, the birth places for stars and planets, water ice is the dominant solid component, and chemical reactions occurring on the ice surface are expected to contribute greatly to the evolution of interstellar molecules [1].

Due to its cryogenic environment in interstellar molecular clouds, it has been regarded that interstellar water ice is mostly in amorphous forms. However, Hama et al. recently reported for the first time that ice with a long-range ordered crystalline structure can be formed even at cryogenic temperatures by preparing a H_2O/Ne matrix at 6 K in a vacuum environment and heating it to 11~12 K to sublimate Ne [2]. They determined the crystallinity only by infrared (IR) spectroscopy, whereas IR spectroscopy has a problem that Ice Ic (cubic) and Ice Ih (hexagonal) cannot be distinguished. Therefore, further structural analysis by diffraction is crucial.

In this research, we report on the development of the experimental apparatus necessary to identify the crystal structure of ice surfaces. Specifically, an Al vacuum chamber is evacuated at the base pressure of 10^{-7} Pa. An Al substrate is mounted on the cold head of a closed-cycle He refrigerator, which is cooled down to 6 K for water vapor deposition. The structure of vapor-deposited ice is then analyzed by RHEED (Reflection High Energy Electron Diffraction). The RHEED patterns are projected onto a fluorescent screen. Figure 1 shows the present view of the RHEED apparatus in the laboratory. We will report more details of the experimental setup and present some preliminary RHEED data.

Figure 1: The present view of the RHEED apparatus

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A Theoretical, Neural-Network Assisted Study of Methane Formation under Astrophysical Conditions

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Dense molecular clouds are cold regions (~10-20 K) in the interstellar medium (ISM) that accommodate dust grains coated with ice, usually amorphous. The chemical components of those ices are H_2O, CO, CO_2, CH_3OH, etc. with strongly fluctuating compositions. These surfaces play a central role in the chemistry of the ISM and therefore in the evolution of molecular clouds, acting as templates of atoms, radicals and molecules, to meet on top of them [1]. Additionally these ices help to dissipate the energy of the reactions occurring on them. Hence, these surfaces enable the synthesis of a variety of chemical compounds that would not be accessible by gas phase reactions alone. In this work, we studied the formation of CH_4 by investigating the reaction of a CH_3 radical with H on the surface of amorphous solid water (ASW). Among the things we analyzed is the energy redistribution vs chemical desorption [2, 3]. A periodic model of ASW was used to mimic the reaction. As a first step, we have obtained the binding energy (BE) distribution of CH_3 on the surface with values between -500 and -4000 K. The reaction was modeled by placing CH_3 on binding sites with high, medium and low BEs for both axial and planar orientation of the CH_3 radical on the surface. Later, hydrogen atoms have been placed spherically around the CH_3 radical to sample many possible trajectories. Subsequently, molecular dynamics simulations for the reaction were carried out at a temperature of 10 K. The potential driving the dynamics is a neural network potential trained on DFT energies and forces [4, 5]. We have found that the initial orientation of the CH_3 radical hardly plays any role on the reaction. On the contrary, we found huge differences in the evolution of the reaction as a function of the CH_3 binding site and the initial orientation of the H with respect to the methyl radical.

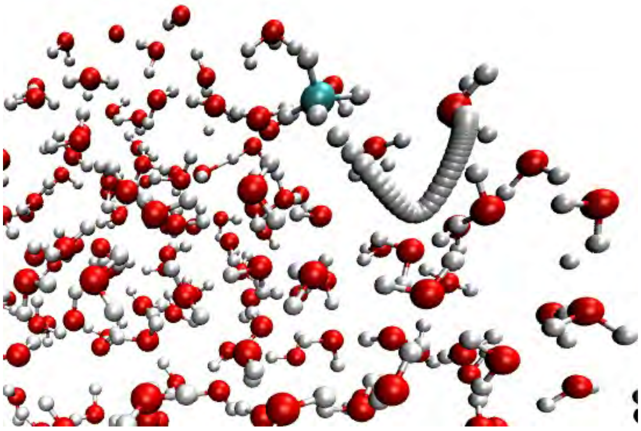

Figure 1: Trajectory of the hydrogen atom approaching the methyl radical to form methane during the MD simulation in increments of 2 fs per hydrogen frame.

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H and D diffusion on interstellar water ices

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Studies of surface diffusion of atoms on interstellar ices are a popular topic in the field of Astrochemistry. These chemical processes occur at very low temperatures (e.g., around 10K). At low temperatures, quantum tunneling becomes a dominant factor deciding the diffusion through barriers [1]. Therefore, quantum tunneling must be taken into account in calculating rate constants. Here, I discuss the single H and D atom diffusion on crystalline (I_h) and amorphous ice surfaces (ASW). The harmonic transition state theory was used to calculate the rate constants, and the Wigner tunneling correction was employed as well as a tunneling correction based on the Eckart potential to address the tunneling effect. The adaptive kinetic Monte Carlo method was applied to analyze the random walk trajectories [2]. A range of diffusion coefficients were found at low temperatures [3].

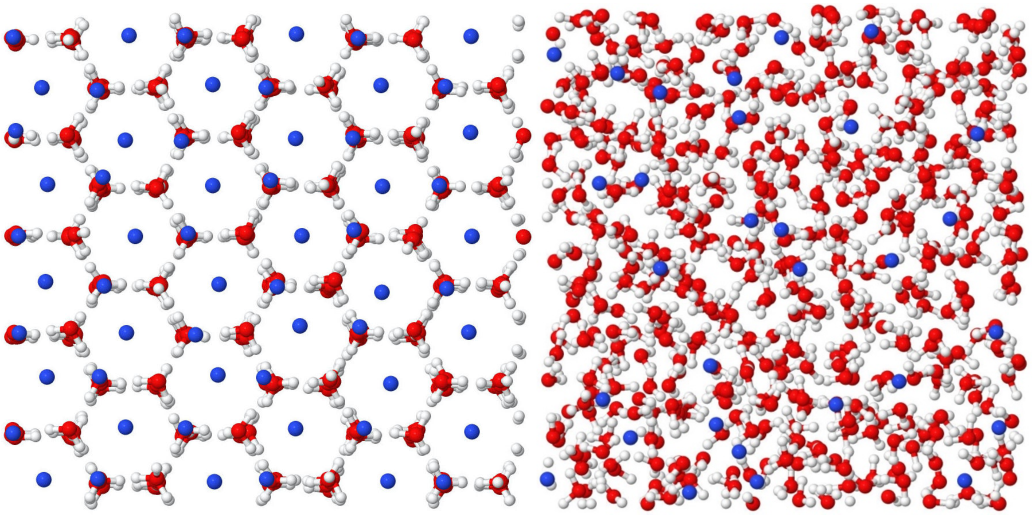

Figure 1: A map of local minima on a crystalline ice surface (left) and on an ASW surface (right). The blue dots are the local minima and the red and blue are O and H atoms of the water molecules. There are 59 local minima on the I_h surface and 30 local minima on the ASW surface.

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Development of a high-sensitivity and non-destructive detection system for trace amounts of adsorbates on ice

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Molecular evolution on the surface of interstellar ice dust is important. In particular, the information of radical is crucial for understanding the formation process of complex organic molecule. Although many experiments have been performed [1], the detection of trace adsorbates like radicals is still difficult with conventional experimental methods due to the lack of sensitivity and thus little is known about behavior of such species on the ice surfaces.

Recently, we newly developed highly-sensitivity and non-destructive mass analysis apparatus for trace amounts of adsorbates on the amorphous solid water (ASW) surface. Based on a design in literature [2], we constructed an apparatus composed of a Cs^+ ion gun and Quadrupole Mass Spectrometer (QMS) in an ultra-high vacuum chamber. Using that, adsorbed species X (Mass: M) on ASW substrate were picked up with Cs^+ ion and mass-analyzed by the QMS as $Cs\text{-}X^+$ (Mass: 133 + M). As a result of various improvements, we have succeeded in detecting the trace of radicals adsorbates on ASW surface. As shown in Figure 1, we can monitor the behavior of OH radical on ASW upon the photolysis of H_2O.

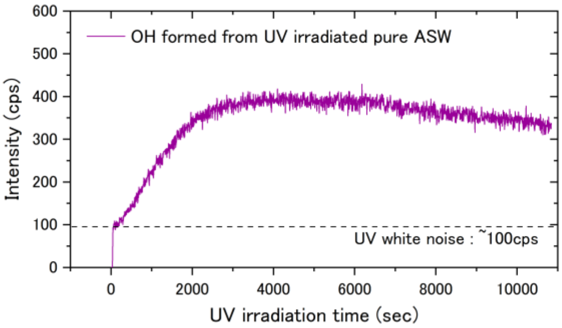

Figure 1: Variations in the pickup signal intensity of OH radical generated by ASW (10 ML) during UV irradiation at 10 K.

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Branched Chain Molecules in Interstellar Medium

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Interstellar detection of the straight-chain (n-propyl cyanide, n−C_3H_7CN) and branched-chain (i-propyl cyanide, i−C_3H_7CN) molecules toward the star-forming region, Sgr B2(N2) has attracted attention to study the formation mechanism and chemical evolution of branched carbon-chain molecules. These moleules are the precursors of biologically relevant prebiotic molecules, i.e., amino acids. In this light, we consider n-butyl cyanide and higher-order branched chain molecule, t-butyl cyanide from the C_5H_9N isomeric group. We employ gas-grain chemical model to study the chemical evolution of these species. We predict new formation and destruction pathways which could lead to more insight into the formation and destruction schemes of complex organic branched chain molecules in space. Quantum chemical calculations such as binding energy, enthalpy of formation, reaction enthalpies, activation barrier, dipole moments, and other spectroscopic information assist to study the chemical evolution and examine the possibility of detecting higher-order branched-chain molecules in high-mass star-forming regions.

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Nitrile chemistry in a disk structure around the G24.78+0.08 hyper-compact H_{II} region

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Complex nitrile species, such as CH_3CN and HC_3N, have been usually detected in disks around T Tauri stars and Herbig Ae stars (e.g., [1]). The Molecules with ALMA at Planet-forming Scale (MAPS) [2] Large Program reveals that CH_3CN and HC_3N trace different layers of these disks; HC_3N traces upper and warmer layers compared to CH_3CN [3]. Thus, it is useful for investigating physical conditions of disks to observe different nitrile species. However, only CH_3CN lines have been used as typical disk tracers around massive stars ($M > 8$ M_{sun}) so far, and the nitrile chemistry in disks around such massive stars is still unrevealed yet.

We have analyzed Atacama Large Millimeter/submillimeter Array (ALMA) Cycle 6 Band 6 data toward the hyper-compact H_{II} region G24.78+0.08 A1 (hereafter G24 HC H_{II} region). A current protostellar mass is derived to be ~20 M_{sun} by the SED fitting. Two vibrationally-excited lines of HC_3N ($v_7=2$, J=24-23, l=0 and l=2e) have been detected from this HC H_{II} region. The spatial distribution and position-velocity (P-V) diagram of the HC_3N line (l=2e) are similar to those of the vibrationally-excited CH_3CN line ($v_8=1$, $J_{K,l}=12_{6,1}-11_{6,1}$). The CH_3CN lines were confirmed to trace the molecular disk in the G24 HC H_{II} region [4]. These results suggest that the HC_3N emission traces the molecular disk around the G24 HC H_{II} region previously identified by CH_3CN.

Using the $^{13}CH_3CN$ ($J=13_K-12_K$, K=0-6) and $HC^{13}CCN$ (J=26-25) lines, we have derived the $N(^{13}CH_3CN)/N(HC^{13}CCN)$ column density ratios at the two positions around the G24 HC H_{II} region, which we name "HC H_{II} region" and "Molecular Peak", respectively. The $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios are derived to be ~3.0-3.5. If there are no effects of the ^{13}C isotopic fractionation in each molecule (e.g., [5]) and the selective photodissociation of $^{13}CH_3CN$ and $HC^{13}CCN$, the $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratio is expected to reflect the CH_3CN/HC_3N abundance ratio. We compare these $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios to the CH_3CN/HC_3N abundance ratio in disks around T Tauri stars and Herbig Ae stars [3], as shown in Figure 1. The $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios around the G24 HC H_{II} region are more than an order of magnitude higher than the CH_3CN/HC_3N abundance ratios in the other disks (~0.03-0.11). The higher $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios around G24 suggest that the CH_3CN/HC_3N abundance ratios in the disk around the massive star are higher than those around the other disks.

Another possible interpretation of the much high $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios around the G24 HC H_{II} region is that the column density ratios do not reflect the CH_3CN/HC_3N abundance ratios. In fact, the integrated-intensity ratios of the vibrationally-excited lines of CH_3CN and HC_3N, which have almost same upper-state energies (~770 K), are derived to be ~ 0.5-1.5 around the G24 HC $\mathrm{H_{II}}$ region. These integrated-intensity ratios are still higher than the abundance ratios in disks around T Tauri stars and Herbig Ae stars. Thus, it is most likely that the CH_3CN/HC_3N abundance ratios around the G24 HC $\mathrm{H_{II}}$ region are higher than those in the other disks around the lower-mass stars.

The high CH_3CN/HC_3N ratios around the G24 HC $\mathrm{H_{II}}$ region imply the thermal desorption of CH_3CN in the hot dense region, and efficient destruction of HC_3N by the UV radiation and reactions with ions (e.g., H_3^+) in the ionized region. The former is supported by the fact that the derived excitation temperatures of CH_3CN (~ 330 K) around the G24 HC $\mathrm{H_{II}}$ region are much higher than its sublimation temperature. This is different from a suggestion that the photo-evaporation is important in disks around T Tauri stars and Herbig Ae stars. The higher UV photodissociation rate of HC_3N compared to CH_3CN [6] can destroy both HC_3N and $HC^{13}CCN$ efficiently, which should increase the CH_3CN/HC_3N abundance ratios and the $N(^{13}CH_3CN)/N(HC^{13}CCN)$ ratios. In summary, the nitrile chemistry around the massive star is likely different from that in the disks around T Tauri stars and Herbig Ae stars.

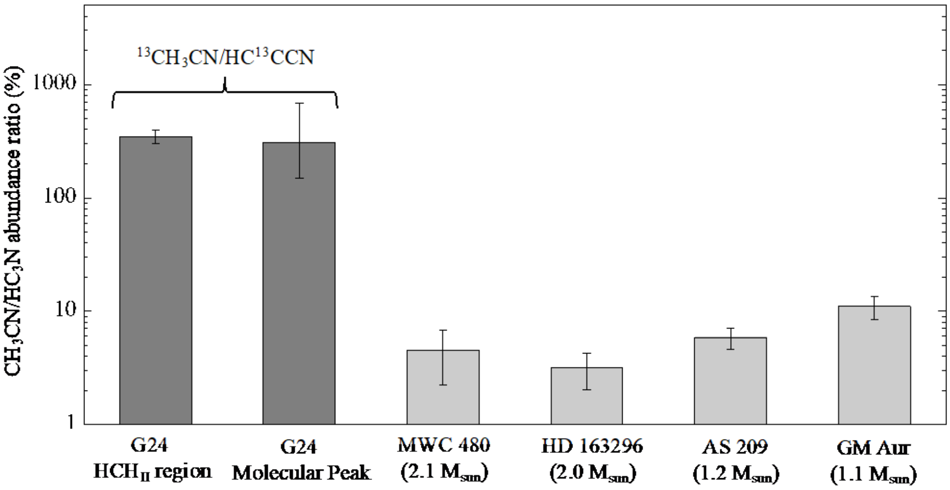

Figure 1: Comparisons of the CH_3CN/HC_3N abundance ratio among disks with different stellar masses.

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A New Approach to Compute the Accurate Binding Energy Distribution of Molecules at Ice Interstellar Grain Models: the Case of NH_3

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In the denser ($\geq 10^4$ cm^{-3}) and colder ($\leq$20 K) regions of the interstellar medium (ISM), sub-micron sized dust grains are covered by several layers of H_2O-dominated ices [1]. The composition and thickness of these ices is governed by whether molecules and atoms remain glued to the grain surfaces or not and whether they can move on the surfaces and scan them, so to meet other species and react. On the other hand, in warmer regions, these interstellar ices can (partially) sublimate and enriched the gas of its components. The ice-gas interaction is, therefore, a hugely important process that determines the chemical composition of the ISM. The basic quantity that rules all these processes is the binding energy (BE) of the species to the interstellar ice surface. It is thus not an exaggeration to affirm that the BE of interstellar atoms and molecules is a small quantity with a huge impact. So far, with very few exceptions, astrochemical models have assumed single values for each species BE. In this work, we present a new and robust computational strategy to evaluate BEs by theoretical computations on a novel amorphous solid water (ASW) cluster [2]. This cluster exhibits a large number of adsorption sites where NH_3 (our test molecules) can be adsorbed. The BEs are computed through the ONIOM [3] approach using a QM:QM layer envisaging xTB-GFN2 [4] as the low method and DLNPO-CCSD(T) [5] as the high level method. The generality of xTB-GFN2 as a low-level method allows to treat a large variety of interstellar species, at variance with the adoption of *ad hoc* force fields as currently done in the literature. As a first study and astrochemically important case, we applied this new methodology, to derive the BE distribution of ammonia, computed on about 160 different adsorptions shown in the right figure. Machine learning clustering analysis is performed and further the two clusters found were fitted by Maxwell-Boltzmann distributions, which reflect the different nature of the possible bonds of NH_3 on ASW. Particularly important is the low-energy end of the BE distribution, which has an unexpected impact on some astrochemical situations, like protoplanetary disks.

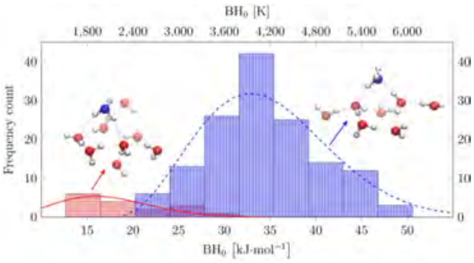

Figure 1: *NH_3 ZPE corrected BE Distribution*

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STM and Non-Contact-AFM observation of Si(111) by a self-made qPlus sensor at low temperatures

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In recent years, many laboratory experiments have been performed to simulate chemical reactions on the surfaces of interstellar ice dust. In those experiments, amorphous ices were formed by water vapor deposition onto the low-temperature substrate under an ultra-high vacuum condition as an analogue of ice dust. The morphology of such amorphous ices strongly depends on the various experimental conditions like deposition angle, growth rate, and the deposition temperature when ices were formed. Because the morphology would affect chemical processes occurring on the surface, direct observation of ice morphology is essentially important to understand the simulation experiments appropriately. Therefore, to observe the surface morphology of amorphous ice under various formation conditions, we are developing a new device. To perform nondestructive real-space measurements of the nanoscale structure of the amorphous ice surface, an ultra-high vacuum low-temperature scanning probe microscope (SPM: INFINITY, Scienta Omicron) with a non-contact atomic force microscope (nc-AFM) mode is used. Although this device is powerful tool for our purpose, the probe generally used in this type of SPM, named qPlus sensor, is not sufficiently sharp for measuring the fine surface structure of amorphous ice. Therefore, the ultra-sharp qPlus sensor (the tip curvature radius of ~ 1 nm) is required. In this presentation, we introduce the present status of the production of the ultra-sharp qPlus sensor.

For a Si cantilever, which is conventional type of the SPM probe, many commercial products with the ultra-sharp shape are available because the manufacturing technology with a tip curvature radius of ~ 1 nm is well established. Therefore, we tried to construct the ultra-sharp qPlus sensor by using the tip of an ultra-sharp Si cantilever instead of the conventional tungsten wire tip. As the tentative production, the qPlus sensor using the tip of an inexpensive Si cantilever (the tip curvature radius of ~ 10 nm) was produced. To test the self-made qPlus sensor, STM (scanning tunneling microscope) and nc-AFM measurements of Si(111)-7×7 were conducted. Figure 1 shows the results of observations at 10 K using (a) Pt/Ir tip for STM and (b) the self-made qPlus sensor for STM and nc-AFM. We confirmed that the self-made qPlus sensor could obtain the Si(111)-7×7 structure in STM and AFM.

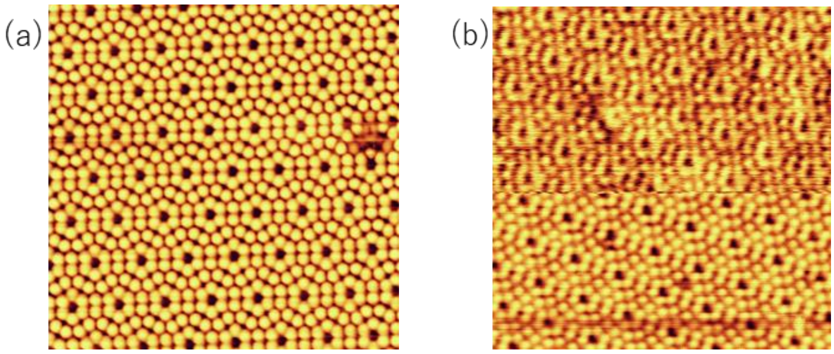

Figure.1 (a)STM image scanned by Pt/Ir tip at 10 K. (b) Image scanned by the self-made qPlus sensor at 10 K. The upper and lower sides are nc-AFM and STM images, respectively. Scan areas of both images are 20 nm×20 nm.

Diffusive hydrogenation of CO embedded in amorphous solid water at temperature up to 70 K

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Surface processes on interstellar dust grains have an important role in the chemical evolution in molecular clouds. Hydrogenation reactions on ice surfaces have been extensively studied and are known to occur at low temperatures mostly below 20 K [1,2]. In contrast, information about the chemical processes of molecules within an ice mantle is lacking. In this work, we investigated diffusive hydrogenation reactions of carbon monoxide (CO) embedded in amorphous solid water (ASW) as a model case and discovered that the hydrogenation of CO efficiently proceeds to yield H_2CO and CH_3OH even above 20 K when CO is buried beneath ASW [3].

In our experiments, layered ice samples were prepared by depositing water molecules over solid CO (~5 monolayers, MLs), in which the thickness of ASW layer was varied from 1 to 80 MLs. The temperature of layered ice sample was set within the range 10–70 K for H-atom irradiation. Depletion of CO and formation of H_2CO and CH_3OH were monitored by the reflection absorption infrared spectrometry.

Figure 1 shows the experimental result for a layered ice at 20 K; in the IR spectrum (left panel), depletion of CO and formation of H_2CO and CH_3OH are clearly seen, and time variation of column densities are plotted on the right panel. For the ASW layer with 20 MLs, temperature dependence was investigated, and it was found that CO hydrogenation efficiency is enhanced by elevating temperatures from 10 to 20 K and that CO hydrogenation occurred even at temperatures up to ~70 K. Another series of experiments performed by varying the thickness of the ASW layer (at 20 K) revealed that hydrogenation of CO occurs when CO is fully buried under the ASW layer. The experimental results suggest that H atoms diffuse through the cracks of ASW and have a sufficient residence time to react with embedded CO. Cracks collapse at elevated temperatures but the occurrence of hydrogenation reactions means that the cracks would not completely disappear and remain large enough for penetration by hydrogen atoms. Considering the H-atom fluence in the laboratory and molecular clouds, we suggest that the penetration of H atom and its reactions within the ice mantle occur in astrophysical environments.

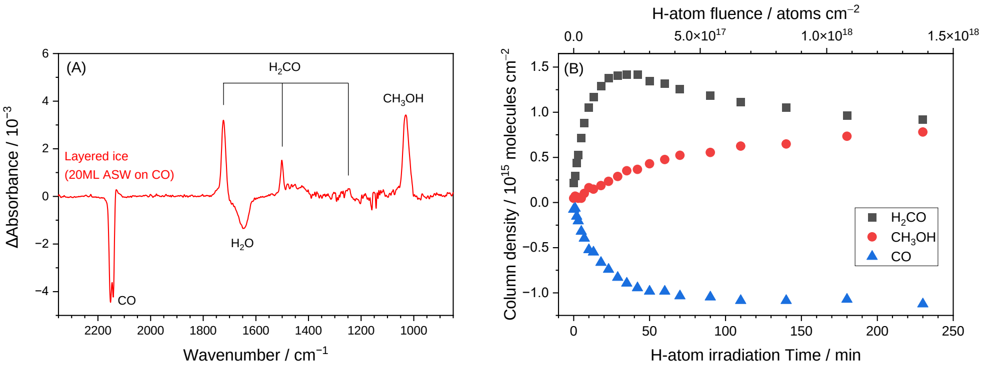

Figure 1: (A) Infrared difference spectrum after 180 min H-atom irradiation on a layered sample with 20 MLs ASW on 5 MLs CO. (B) Variations in column densities with H-atom irradiation time.

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Ortho-to-para nuclear spin conversion of H_2 on interstellar bare grain analogues

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The H_2 molecule has two nuclear spin isomers: ortho and para isomers. The energy difference between ortho and para state is as large as 14.7 meV (~170 K), and the nuclear spin conversion between these states is forbidden in the gaseous phase. Therefore, these isomers are often considered different species. The ortho-to-para ratio (OPR) is known to affect chemical evolution as well as gas dynamics in space. To understand the meaning of H_2 OPR determined from astronomical observations, the mechanisms that change the OPR should be clarified. In contrast to the gaseous phase mechanisms, in which spin exchange reactions with protons and hydrogen atoms alter OPR, little has been known about H_2 nuclear spin conversion (NSC) on astrophysically relevant surfaces. In this work, we investigated the H_2 NSC on interstellar bare grain analogues: silicate and carbonaceous materials [1,2].

In our experiments, time evolution of H_2 OPR on the surfaces was traced by using a combination of temperature-programmed desorption (TPD) and resonance-enhanced multiphoton ionization (REMPI) methods. H_2 with OPR = 3 was deposited onto amorphous-Mg_2SiO_4 or amorphous diamond-like carbon film kept at 10–18 K, TPD was initiated after certain waiting times after deposition, and desorbing ortho and para isomers were selectively ionized by the REMPI method and detected by a time-of-flight mass spectrometer.

The NSC time constants obtained for the surfaces of astronomical grain analogues [1–3] are plotted as a function of temperature in Figure 1. In each case, the NSC time constants became smaller as temperature increases. This temperature dependence indicates that surface phonons play an important role in the energy dissipation process associated with the H_2 NSC. Using a simple model considering collision rate of gaseous H_2 with grain surfaces, sticking probability, NSC time constant, and sublimation timescale of adsorbed H_2, we found that the H_2 NSC process especially on bare silicate grain surface is efficient to reduce the gaseous H_2 OPR within astronomically meaningful timescale.

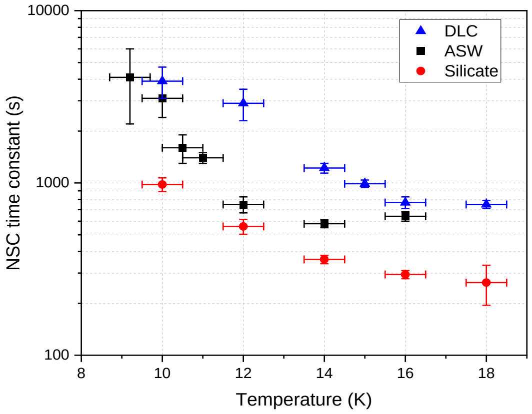

Figure 1: The plot of temperature dependence of the NSC time constants for amorphous diamond-like carbon (DLC, blue triangle) [1], amorphous solid water (ASW, black square) [3], and amorphous-Mg_2SiO_4 (silicate, red circle) [2].

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Development of Spectrometer Using Superconductor Mixer Receiver (SUMIRE)

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Thanks to the high sensitivity and high spatial resolution of ALMA, many unidentified molecular lines have been detected in various sources [*e.g.*, 1-3]. In order to identify these lines, it is essential to measure the rest frequencies of the molecular transition lines accurately. For the molecular spectroscopy in the submillimeter wavelength in a laboratory, we have been developing an emission-type molecular spectrometer by using state-of-art radio astronomical technics (Figure 1) [4]. The spectrometer is equipped with a 200 cm glass cylinder cell, an ALMA-type cartridge heterodyne receiver with 2SB SIS mixers in the 230 GHz band corresponding to ALMA Band 6, and wide-band digital autocorrelation spectrometer XFFTS. By using the four 2.5 GHz digital spectrometers, a total instantaneous bandwidth of the 2SB SIS receiver of 8GHz can be covered with a frequency resolution of 88.5 kHz. Recently, we applied anti-reflection grooves on the surface of the gas cell windows and receiver window to reduce reflection. As a result, the standing wave seen on the measured spectra is greatly improved, and the system noise temperature is decreased from 300-400 K to 90-300 K. In addition, we are now fabricating a new cartridge receiver that covers the radio frequency from 275 – 500 GHz corresponding to the ALMA Band 7 and 8 receivers. With this receiver, we plan to measure higher-*J* transition lines of methanol, and its isotopologues, including D, ^{13}C, ^{17}O, and ^{18}O.

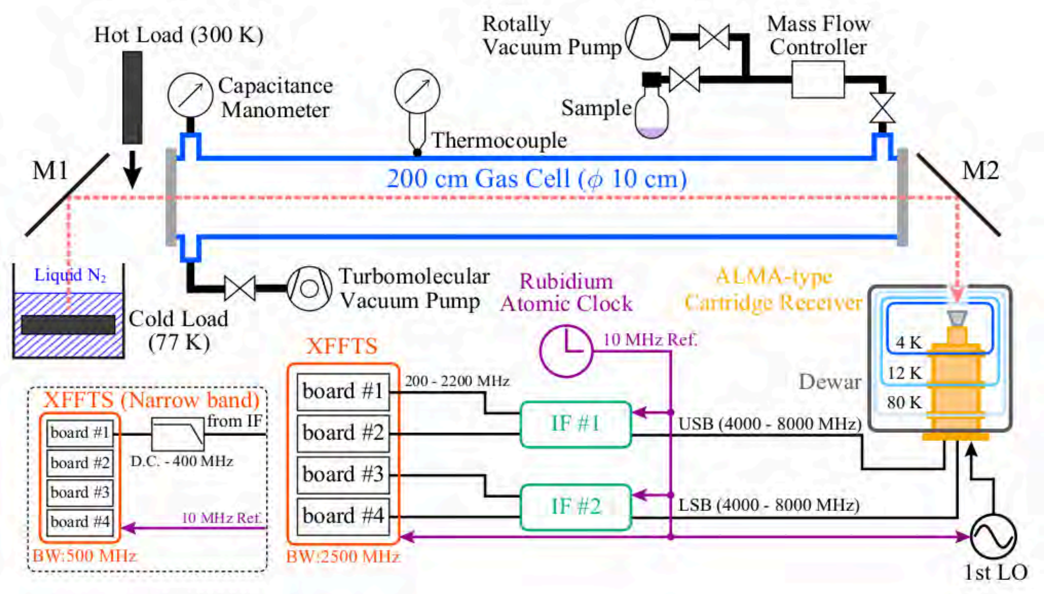

Figure 1: A block diagram of the SUMIRE system.

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A new measurement method of isotopologue ratios in protoplanetary disks: a case study of the ^{12}CO/^{13}CO ratio in the TW Hya disk

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Isotope ratio is a powerful tool to investigate the material origin and evolution from molecular clouds to planetary systems. For instance, the ratio of deuterium to hydrogen can be used as a tracer of material formed in a low-temperature environment, permitting us to study the origin of water on the Earth. The oxygen isotope ratios have an anomaly in the solar system, which is considered to reflect mass-independent fractionation of the carbon monoxide (CO) molecule in the pre/early stage of the solar system formation [1]. To explain the isotopic compositions in planetary systems, physicochemical models of molecular clouds and protoplanetary disks have been proposed.

Despite its importance, however, the observational constraint is difficult especially in protoplanetary disks. The molecular gas in protoplanetary disks is observed in emission lines. Since isotopologue ratios often reach tens and handreds, it is common that rarer isotopologue emission becomes too weak to be detected. In contrast, when the rarer isotopologue line is bright enough, the main isotopologue line (center) becomes optically thick, which makes column density measurement impossible. However, the lines broaden due to thermal motion in general, which makes line wings optically thin. Therefore, we have a chance to measure the isotopologue ratios by observing the multiple isotopologue line wings.

We present that the isotopologue ratios in protoplanetary disks can be practically measured using the line wings, assuming high velocity resolution observations with Atacama Large Millimeter/submillimeter Array (ALMA). Detailed disk models are used for proof of the method. Moreover, we analyzed archival ALMA observations of the ^{12}CO 3-2 and ^{13}CO 3-2 lines toward a protoplanetary disk around a T Tauri star, TW Hya. The ^{12}CO/^{13}CO ratio in the outer disk (R~60-100 au) was estimated to be 23±6, which is extremely smaller than the canonical interstellar value of 69±6 [2]. This could imply that a volatile C/O ratio larger than unity promotes an isotope exchange reaction between the carbon ions and the CO molecules, making ^{13}CO richer. Indeed, such a high C/O ratio has been suggested in previous observations of hydrocarbon species [3]. In addition, it is also suggested that the ^{12}CO/^{13}CO ratio is enhanced beyond a radius of 120 au with a lower limit of ~100, although the origin is unclear.

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Multi-tracer Observations for Multi-scale Accretion Structures in Massive Star Formation

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How massive forming stars accrete material from their surrounding dense clouds are still unclear. Growing observational evidences have shown disk-mediated accretion is a viable mechanism to form massive stars. However, disks in massive star formation, as it contains material in drastically different physical and chemical conditions, cannot be effectively traced by any single type of tracers.

Our recent high-resolution ALMA observations have shown that, in addition to typical hot-core molecular lines, a group of "hot-disk" line can exclusively trace the disks around massive forming stars, including gaseous refractory molecules such as SiO, NaCl, and high upper state energy transitions of a few simple molecules such as H2O [1,2]. Furthermore, recombination lines are important in tracing the innermost disk which has been ionized by the forming massive star, supplementary to the molecular tracers for the neutral disk [3,4].

Here we report another case study using ALMA observations to reveal the complex multi-scale accretion structures around massive young star G35.20-0.74 (Zhang et al. in prep.). The molecular line emissions such as SO2, H2CO, and CH3OH show rotational structures around the main sources, with SO2 emission further traces two spiral arm structures in the fragmented disk perturbed by a forming binary system, as well as the inner and faster-rotating materials around the primary. The innermost region is photoionized with its kinematics revealed by the hydrogen recombination lines. This study agains shows the importance of using different molecular lines and recombination lines to trace different components of the accretion structures, in order to obtain the full picture of the accretion process in massive star formation.

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Inventory of Nitrogen-bearing organics towards G+0.693-0.027

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Among over 250 molecules discovered in the ISM, nitrogen-bearing (N-bearing) species are of interest as many likely play a crucial role in prebiotic chemistry and thus essential for the emergence of life. In the last two decades, a great effort has been put in order to explore the level of molecular complexity of N-bearing species and the corresponding chemical processes. With sensitive unbiased spectral surveys towards the quiescent Galactic Centre molecular cloud G+0.693-0.027, we present in this talk the temporary (still evolving) census of N-bearing species[1], including the first detection of vinylamine ($C_2H_3NH_2$) [2] and ethyl isocyanate (C_2H_5NCO)[3] in the ISM. We compared the derived abundance with respect to H2 to those obtained towards other interstellar sources. We also discussed the possible chemical routes, in gas-phase and/or on the grain surface, of the interstellar synthesis of these N-bearing molecules along with their prebiotic relevance. This study have allowed us to better understand the chemical complexity and diversity of N-bearing species in extreme environments and provided observational constraints for chemical models and laboratory studies in terms of investigating the chemical processes at work in space.

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Experimental Molecular Emission Spectroscopy of Ethylene Oxide in ALMA Band 6

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New discoveries related to astrochemistry in mm and sub-mm frequency ranges have provided us fruitful information on valuable chemical properties of organic compounds. Thanks to the highly sensitive ALMA telescope, it has become possible to detect very complex interstellar organic molecules than ever before [1-4]. Emission and absorption lines from each molecule obtained from observations give us a clue to understand the chemical pathways from simple molecules to complex molecules including the essential molecules of life.

Either or both of theoretically calculated and experimentally measured emission spectra are applied for interpretation of observed molecular lines in general. One of major problems concerning molecular survey is that an insufficient supply of experimentally measured data sets for both organic and inorganic compounds in millimeter and submillimeter frequency ranges. To solve this problem, we have set up the emission type molecular spectroscope for astronomically relevant materials in the frequency range between 216 GHz and 264 GHz (ALMA Band 6). Superconductor-Insulator-Superconductor (SIS) mixer for ~230 GHz band mounted on the ALMA-type cartridge receiver as a heterodyne apparatus (SUMIRE) is applied in this measurement (details in [3]).

In here, we introduce our experimental broadband and high-resolution spectroscopic apparatus as well as a measured ethylene oxide (C_2H_4O) which has been detected in high-mass star forming regions such as the galactic center source Sgr B2 (N) [5], hot molecular clouds DR21 (OH), NGC7538 [6] and low-mass protostar IRAS 16293-2422 [7]. In consequence, 677 peaks due to rotational transitions have been detected. Molecular parameters including predicted transition frequencies, rotational constants, and centrifugal distortion constants were derived by making use of a least-squares analysis and self-developed SUMIRE data analysis code, Aqualious for both C_2H_4O and $^{13}C_2H_4O$. 256 peaks and 108 peaks were assigned as contributions from C_2H_4O and $^{13}C_2H_4O$ rotational transitions, respectively. In addition, we compared our experimental outcomes with the data sets in Cologne Database for Molecular Spectroscopy (CDMS) [8] and previous works [9-10]. Thereby our results are in good agreement with previously obtained data. This also demonstrates the reliability of our experimental results.

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