The evolution of ice mantles during the star formation process: an IceAge JWST study of Chamaeleon I

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Icy grain mantles are the main reservoir for volatile elements in star-forming regions. The IceAge Early Release Science program [1,2] on the James Webb Space Telescope proposes to observe infrared spectra of objects at various stages of star formation, from dense cloud to protoplanetary disk. By observing Chamaeleon I – a representative low-mass star-forming region containing objects at each of these stages – we aim to trace the evolution of pristine and complex ice chemistry that accompanies the physical evolution of the objects. The dense cloud was observed using the NIRCam, NIRSpec and MIRI instruments in summer 2022, providing high spectral resolution (R~1500-3000) and sensitivity (S/N>100) infrared spectra from 2.5 to 13 µm of two highly extincted background stars (Av < 100) and additional L and M band spectra towards hundreds more field stars. In this talk, we will present the first results of the IceAge program: a complete ice inventory towards observed lines of sight, including derived column densities for expected ice species as well as the first detection of several species along lines of sight in a quiescent cold core [3]. We will also present some more recent advances and give perspectives for the rest of the IceAge program, with a particular focus on the NIRCam observations that permit mapping the spatial distribution of ices down to ~20-50 au with the aim of identifying the onset of ice formation.

Figure 1: Star-forming region Chamaeleon I, imaged by the JWST NIRCam instrument.[4]

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Icy Origin of Complex Molecules in Embedded Protostars

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In recent years, the increasing detection of gas-phase complex organic molecules (COMs) in Class 0/I protostars highlights the extensive chemical evolution at the onset of star and planet formation. Recent ALMA surveys found ~40% protostars without detectable gaseous COMs [1]. It is thus unclear whether most protostars undergo the similar chemical evolution, resulting in formation of COMs. Most COMs are thought to form in the ice mantles covering dust grains. Therefore, constraining the ice composition in embedded protostars would provide the smoking gun evidence to answer the origin of chemical diversity in gas-phase measurements. Ice measurements had been limited by low-resolution and limited sensitivity until JWST, which can probe ices at a spatial scale comparable to that by ALMA with unprecedented sensitivity. In this talk, I will present the results of the CORINOS program, which aims to map the ice distribution toward a sample of protostars chosen to represent ranges of complex chemistry and thermal structure using JWST/MIRI. I will share the ice analysis toward a Class 0 protostar, IRAS 15398-3359 [2], where we detect ice absorption of H2O, CO2, CH3OH, CH4, and NH3 as well as signatures of organic ice, including HCOOH, H2CO, C2H5OH, CH3CHO, CH3COOH, and HCOOCH3. The ice abundance will be compared with the abundance of gas-phase COMs surveyed by ALMA, compiling a complete chemical budget of ice and gas. I will also present preliminary results of the observations of the remaining sources. The data of the CORINOS program show striking details on the ice absorption as well as the protostellar structure, demonstrating the prospect of understanding organic chemical evolution from protostars to planets.

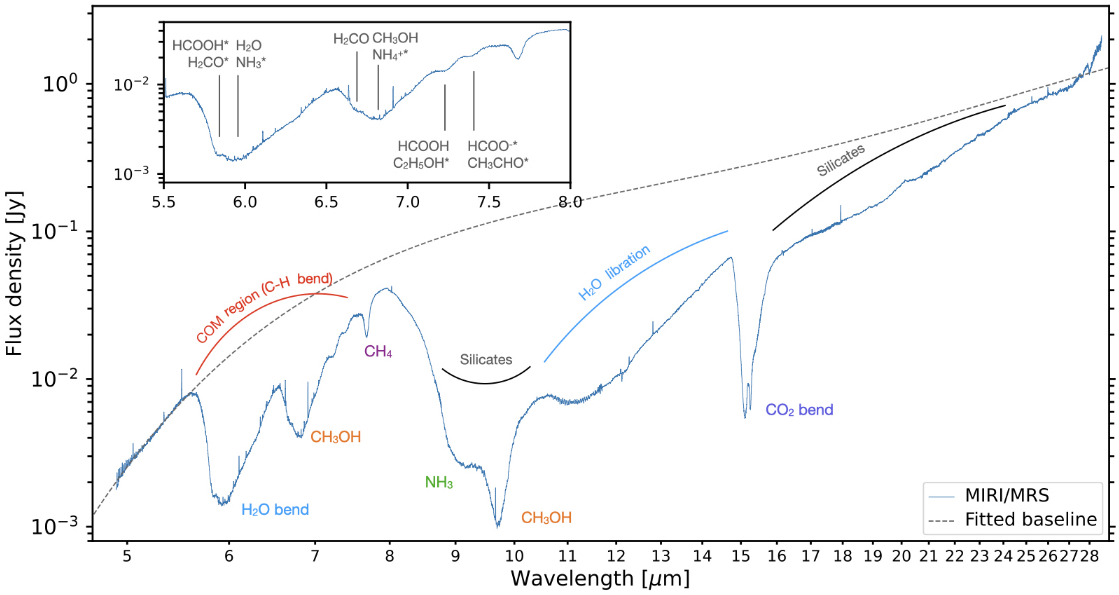

Figure 1: MIRI MRS spectrum of IRAS 15398-3359, showing various ice absorption features detected at the highest fidelity achieved to date.

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Molecules in Outflow Shocked Regions: JWST meets ALMA

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How low-mass protostars at the earliest stage grow has still been veiled. As one approach to this problem, we study shock regions in the outflow structure of IRAS 15398-3359 by using some molecular lines observed with JWST (James Webb Space Telescope) and ALMA (Atacama Large Millimeter/submillimeter Array).

IRAS 15398-3359 is a Class 0 protostellar source (T_{bol} = 44 K) in the Lupus 1 molecular cloud (d= 156 pc). In the previous studies (e.g., [1][2][3][4]), some molecular lines, such as H_2CO, CS, and ^{12}CO etc, were found to trace the outflow structure extending from the northeast to southwest axis, which is almost parallel to the plane of the sky. The rotationally supported disk was detected in the SO emission, which is perpendicular to the outflow direction. The protostellar mass was estimated to be 0.007 solar mass on the assumption of a Keplerian rotation [5]. Based on the dust continuum data, the envelope mass was reported to be much larger, 0.5-1.2 solar mass[6][7], and hence, IRAS 15398-3359 should be a very young source.

CORINOS have conducted the JWST observation toward this source, and have detected the southern part of the outflow structure with the mid-infrared instrument (MIRI) [8]. The MIRI image shows the three shell structures and the front shock (Fig.1a). We compare the structure to molecular-line distributions observed with ALMA. The H_2CO and CS lines show the shell structures corresponding to those in the MIRI image, and the ^{12}CO line traces the whole structure including the front shock. We determine the outflow direction of P.A 235 degree, based on the structure in the MIRI image, which is slightly different from the outflow direction near the protostar (P.A 220 [5] and 230 degrees [1]). Furthermore, we detect eight lines of H_2 with JWST, mainly tracing the southern part of the outflow near the protostar (Fig. 1b). Assuming the LTE condition, we derive the temperature and the column density map to be ~700-800 K and ~10^{19} cm^{-2}, respectively. Comparing between the distributions of H_2 and those of the molecular lines (H_2CO, CS, and ^{12}CO), we find that the three molecular lines show a weak emission where the H_2 lines are enhanced with the high temperature. In the shock regions of the outflow cavity, the temperature is estimated to be 46-126 K when the H_2 density is assumed to be 10^6 cm^{-2}, by using the three H_2CO lines observed with ALMA. Our results suggest an episodic outflow ejecting with precession.

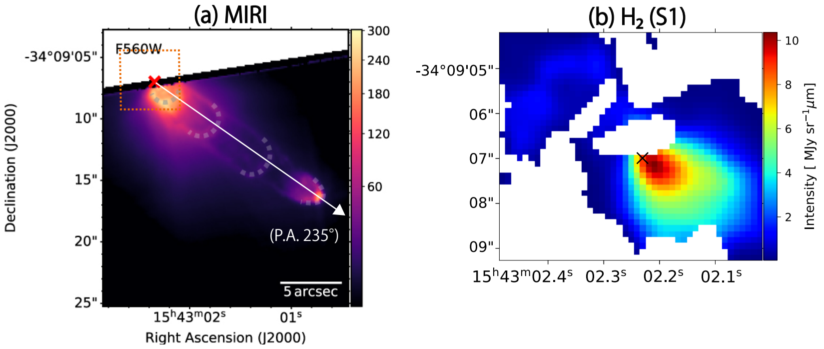

Figure 1: (a) MIRI image with JWST. Red cross mark shows the continuum peak. Dotted lines represent the shell structures and the front shock. The box with orange dotted lines corresponds to the area in the panel (b). (b) Integrated intensity map of H_2 (S1). Black cross mark shows the continuum peak.

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Exploiting Molecular Beams and Surface Science Studies to Untangle the Formation of Complex Organics in Deep Space - From Nanoparticles to Interstellar Ices

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Ice coated interstellar nanoparticles have emerged as molecular factories in the synthesis of (aromatic) hydrocarbons and of complex, biorelevant organics in cold molecular clouds and in star forming regions. An detailed understanding of the fundamental reaction mechanisms leading to these organics in deep space requires new knowledge not only on the formation of these nanoparticles (carbonaceous, silicates, sulfides) from the bottom up via elementary gas phase reactions, but also on the processing of low temperature ices by (non)ionizing radiation present even deep inside cold molecular clods. Extensive gas phase and condensed phase (ices) physical chemistry laboratory experiments have been at the center of attention in providing this knowledge. This talk provides an overview on recent molecular beams experiments (gas phase) and surface science studies (ice chemistry) of particular importance in deciphering the underlying reaction dynamics and kinetics leading to fundamental molecular building blocks of interstellar nanoparticles and to complex organics of astrobiological significance and concludes with new developments in this field. The gas-phase studies have culminated in the preparation of planar (2D) and bent (3D) polycyclic aromatic hydrocarbons (corannulene [1], coronene [2], C40 nanobowls [3], helicenes [4-6]) involving multifaceted reaction mechanisms [7] as fundamental molecular building blocks of graphenes, fullerenes, and nanotubes; surface science experiments advanced to an understanding of the non-equilibrium chemistry leading to C1-C6 complex organics (alcohols, aldehydes/ketones, carboxylic acids, sugars) connected to the *Origin of Life* theme [8-15]

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Electronic Spectroscopy of Polycyclic Aromatic Hydrocarbons in solid *para*-Hydrogen

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Polycyclic aromatic hydrocarbons (PAH) and their heteroatom-substituted, protonated, hydrogenated, and cationic derivatives are commonly considered as the carriers of the unidentified infrared (UIR) bands and as promising candidates for the carriers of the diffuse interstellar bands (DIB), [1] absorption bands in the UV/VIS to near-IR region. However, despite the large number of known DIB (well over 200 up to today), only the buckminsterfullerene cation C_{60}^{+} has been confirmed as the carrier of two DIB at 9577.5 and 9632.7 Å on the basis of its laboratory spectrum. [2,3]

Para-hydrogen (p-H_2) has frequently been employed as a matrix host for IR spectroscopy of PAH, PANH, and their protonated and hydrogenated derivatives; the IR absorption spectra exhibit only small shifts relative to the gas-phase, in line with the “softness” of solid p-H_2. Over the past years, we have recorded the dispersed fluorescence and fluorescence excitation spectra of various PAH with 10 to 42 carbon atoms as well as a small number of protonated and hydrogenated PAH and PANH, to assess the properties of p-H_2 as a matrix host for electronic spectroscopy and its potential to provide laboratory reference spectra for comparison to observations. We find a generally good agreement with previously literature data, indicating a rather small but consistent redshift of $<100\ \text{cm}^{-1}$ relative to the gas phase due to the matrix environment.

In our contribution, we discuss advantages and disadvantages of p-H_2 as a matrix host for electronic spectroscopy by providing experimental data and spectra simulated based on quantum-chemical calculations for three examples: the 1-hydronaphthyl radical (1-$C_{10}H_9$), which has been extensively studied in the gas phase and in solid Ne, and the two large PAH *peri*-hexabenzocoronene (*peri*-HBC, $C_{42}H_{18}$) and ovalene ($C_{32}H_{14}$). Our work on 1-$C_{10}H_9$ demonstrates the good agreement of the p-H_2 data with previous work and the comparably easy accessibility of hydrogenated (and protonated) PAH in p-H_2, but also shows the stronger influence of p-H_2 on spectral line positions compared to Ne. We observed the D_1–D_0 origin at 18881 cm^{-1} giving a matrix shift of 68 cm^{-1}; for Ne, a blue shift of ~13 cm^{-1} can be inferred from the work of Garkusha et al. [4] *Peri*-HBC has rarely been studied before. We provide a first full assignment of the vibrational structure of the fluorescence emission and excitation spectra centered around the S_1–S_0 origin band located ~22075 cm^{-1} in solid p-H_2. Ovalene has been discussed as potential DIB carrier and a system exhibiting anomalous fluorescence from higher excited singlet states. Combining experiment and theory, we found, however, that the lowest excited singlet state (S_1) was previously assigned erroneously; we report the fluorescence emission and excitation spectra as well as fluorescence lifetimes of the true S_1 state.

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Experimental measurement for absorption cross section of two-coordinated dangling OH bonds on the surface of amorphous ice at 20 K

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In cold and dense interstellar clouds, amorphous water (H_2O) is abundant and forms icy dust grains [1]. Infrared (IR) spectra of amorphous water prepared at low temperatures show two weak absorption peaks at 3696 cm^{-1} and 3720 cm^{-1} in laboratory experiments. These are assigned to "dangling OH bonds", which are the free OH stretching modes of 3-coordinated (one H doner and two H acceptors; 3dOH) and 2-coordinated (one H donor and one H acceptor; 2dOH) H_2O on the ice surface, respectively [2]. Dangling OH bonds reflect the surface structure of ice and act as a chemical reaction site on the ice surface. Recently, the James Webb Space Telescope, a high sensitivity infrared telescope in space launched in 2021, detected possible dangling OH feature for amorphous icy dust grains in an interstellar cloud, where stars and planets will form [3]. With the absorption cross section for dangling OH bonds, the number density can be calculated from the observed absorbance, which leads us to understanding the surface structure of interstellar ices [4]. In this study, we measured the number densities of 2dOH and 3dOH on amorphous ice at 20 K using infrared multiple-angle incidence resolution spectrometry (IR-MAIRS). IR-MAIRS is a technique combining oblique incidence transmit measurements and multiple variation analysis to obtain pure out-of-plane (OP) and in-plane (IP) spectra. Figure 1 shows the OP and IP spectra of amorphous water at 20 K before and after the deposition of carbon monoxide (CO). Both 2dOH and 3dOH features appeared and quenched after CO exposure at 20 K. At the same time new peaks appeared at around 2152 and 2139 cm^{-1}, which are assigned to the CO stretching vibration bands for CO molecules adsorbed at dangling OH bonds and hydrogen-bonded OH bonds [5]. Assuming that the amount of the CO molecules adsorbed at dangling OH bonds to fully quench the two peaks corresponds to the column densities of 3dOH and 2dOH, the absorption cross section for 2dOH is estimated much smaller than that for 3dOH.

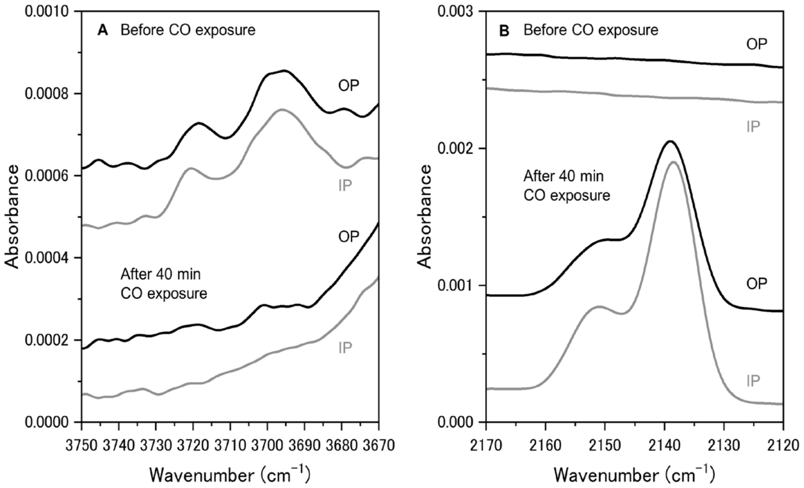

Figure 1. OP and IP spectra of amorphous ice vapor deposited at 20 K before (A) and after (B) CO exposure.

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Exploring the Mysteries of CO Ices: Weak Interactions and Vibrational Energy Relaxation

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One of the largest fractions of interstellar ice and gas, carbon monoxide, still remains shrouded in mystery. In particular, models still fail to accurately reproduce the observed ice-to-gas ratio of CO without adding unrealistic tweaks to the models. We previously investigated the binding energy of CO on CO ices, where we found a rather large number of weak binding sites [1]. These weak sites, if incorporated within models, could reduce the discrepancy between observations and models [2]. Additionally, non-thermal desorption mechanisms are being scrutinized to understand their role in non-destructively desorbing molecules. One such novel mechanism speculated by experiments is vibrationally-induced desorption.

Recently, infrared-induced desorption of interstellar CO ice analogs was experimentally performed [3]. However, for it to explain the gas-phase CO abundance, we need to understand the mechanism behind the desorption. We studied the vibrational energy relaxation (VER) of CO ices, with a particular aim of unraveling how desorption could be induced. We find that CO has an extremely slow classical VER timescale and that vibrational to translational energy conversion is extremely inefficient. Furthermore, we do not observe any desorption within the 4700 simulations that we carried out. These results suggest that possible explanations for the desorption seen experimentally are: (i) quantum effects that are not captured by the classical simulations, or (ii) surface or local heating.

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Heterogeneous catalysis in space: CH_3OH formation via Fischer-Tropsch reactions. A computational approach.

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Gas-phase chemistry under extreme conditions, characterized by low densities and temperatures, poses significant challenges. The presence of interstellar grains plays a crucial role in facilitating the formation of molecules that cannot naturally emerge in the gaseous phase. Interstellar grains are believed to enhance the interaction between reactive species, promoting reactions on their surfaces, and mitigate the energy excess of highly exothermic reactions. However, their function as chemical catalysts, offering low activation energy pathways to accelerate reaction rates, remains less explored.

Nevertheless, various materials with catalytic properties can be found in interstellar environments, including refractory grains containing transition metals abundant in space. In this study, we present novel mechanistic insights into the synthesis of methanol (CH_3OH) via the Fischer-Tropsch process under astrophysical conditions. We employ single-atom iron (Fe)-containing silica surfaces as heterogeneous catalysts in an interstellar context. Our approach involves quantum chemical calculations considering extended periodic surfaces to identify stationary points and transition states, ultimately constructing reaction potential energy surfaces. Additionally, we conduct binding energy and kinetic calculations based on the Rice–Ramsperger–Kassel–Marcus (RRKM) scheme to assess the catalytic capability of these grains and place these reaction processes within the framework of astrochemistry.

Our mechanistic investigations demonstrate the feasibility of astrocatalysis in astrophysical environments. While the proposed process is thermodynamically highly exergonic, it exhibits kinetic barriers necessitating an activation energy to proceed. Furthermore, our kinetic calculations underscore the strong temperature dependence of this reaction process, with tunnelling effects being insignificant across the involved energetic barriers. These findings shed light on the presence of CH_3OH in various regions where current models struggle to explain its observed abundance. Moreover, the revelation of astrocatalysis introduces an entirely new spectrum of synthetic pathways, sparking chemical evolution in space.

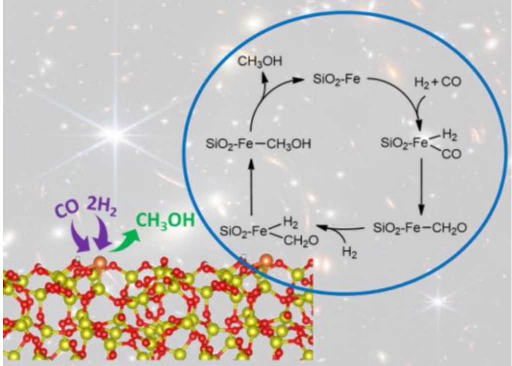

Figure 1. Representation of the surface model and the catalytic cycle under study.

Atomistic insight into molecular processes on interstellar ice analogs

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The darkness observed between the stars on a clear night sky is far from empty, in fact a hidden chemical world thrives. The focus of my group is primarily on the cold, dense molecular medium where surface reactions orchestrate the build-up of 'dirty' ices, forming a molecular mantle covering the micron-sized dust grains.

Species accrete, diffuse, and react on the surface after which they can evaporate back into the gas phase. The interplay between these processes dictates the composition of icy mantles, along with where and whether or not they are astronomically observable, either in the solid or gas phase. With the use of computational chemistry, we aim to contribute to an atomistic understanding of the relevant surface processes and untangle the web of reactions within realistic, amorphous ices.

In this presentation specifically I will shine light on the creation, structure, and accompanying spectroscopy of H_2O:CO_2 ice mixtures, on the types of bonding the CN radical can undergo on H_2O and CO ices, and on the potential implications thereof for interstellar surface chemistry.

Next-generation cosmic ice models for the JWST Era

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The key role of grain-surface processes for accurately simulating interstellar chemistry has long been known [1]; however, the importance of modelling processes occurring within dust grain ice mantles has only been fully realized in the last decade or so [2,3]. This new appreciation for solid-phase chemistry has been largely motivated by an extensive body of laboratory astrochemical studies, which have conclusively demonstrated the rich array of complex molecules that can form at very low temperatures [4-6]. More recently, data from the newly-launched James Webb Space Telescope has already revealed that even in regions previously thought to have been COM-poor, there exists a hidden reservoir of COMs within cosmic ice, which are unlikely to have been formed primarily via gas-phase reactions [7]. Substantial progress in treating cosmic ice chemistry is likely needed before simulations will be able to reliably replicate such observational results, and in this talk, I review some of our recent work along these lines, as well as present preliminary results from two projects that represent promising breakthroughs in how grain-surface chemistry is simulated in astrochemical models.

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A framework for incorporating binding energy distributions in astrochemical models

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One of the most severe limitations of the current astrochemical models is that only a single type of binding site is considered, although laboratory and quantum chemical studies have found that there are multiple types of binding sites with different potential energy depths [e.g., 1, 2]. On a surface with multiple types of binding sites, adsorbed species can be trapped in sites with a deep potential, increasing the resident time of the adsorbed species. On the other hand, species can be populated in shallow potential sites, activating thermal hopping and thus two-body reactions even at low temperatures, where thermal hopping from deeper sites is not activated. Such behavior cannot be described by the conventional rate equation method [3, 4].

I present a framework for incorporating binding energy distributions in gas-ice astrochemical models as a natural extension of the conventional rate equation method. I developed a simple method to estimate the probability distribution function for the occupation of binding sites with different potential energy depths, assuming a quasi-steady state. By using hopping and desorption rates weighted by the probability distribution functions, the effect of binding energy distribution is incorporated into the rate equation method without increasing the number of ordinary differential equations to be solved. This method was found to be accurate and computationally efficient and enables us to consider binding energy distributions even for a large gas-ice chemical network, which contains hundreds of different icy species. The impact of the binding energy distribution on the interstellar chemistry will be discussed quantitatively.

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HCN adsorption and reactivity on cosmic silicates

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Hydrogen cyanide (HCN) has been receiving an increasing attention as a possible precursor of life since when J. Orò synthesized adenine from a solution of HCN and ammonia. [1] Since HCN molecules are widespread in the interstellar medium and the products of their polymerization (including purines) have been detected on meteoritic fragments, [2] the scientific community is now investigating the possible pathways for the oligomerization of HCN in cosmic environments to form molecules of prebiotic interest. In this sense, the gas phase oligomerization of HCN is hindered by high energetic barriers which cannot be overcome at the conditions of a molecular cloud. [3] In the condensed phase, instead, more promising results were obtained, thanks to a more feasible acid-base chemistry. [4]

For these reasons, the surfaces of cosmic silicates in interstellar and interplanetary dust grains, cometary nuclei, asteroids and planetary systems, may play a fundamental role in this type of chemistry. Moreover, it has been recently demonstrated that the surfaces of silicates, among the primary components of dust grains cores, are able to catalyze the oligomerization of HCN to adenine. [5]

In this work, we studied by mean of atomistic simulations the adsorption and the reactivity of HCN molecules on different model surfaces of the crystalline pure Mg-silicate (forsterite). We computed the structures and relative adsorption energies of 16 adsorption complexes, together with the energetic barriers for 5 cases of dimerization of two adsorbed molecules to form the dimer iminoacetonitrile ($H_2C_2N_2$). We observed that, thanks to the acid-base properties of its surfaces, [6] forsterite is able to efficiently deprotonate HCN molecules, hence triggering the polymerization process, and to stabilize the transition states of iminoacetonitrile formation. Most cases show favorable energetic barriers and, according to a kinetic analysis, the reaction is likely to take place at the conditions proper of proto-planetary disks and planetesimals formation, while it results to be hindered in molecular clouds.

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Surface chemical properties of interstellar grains. Insights from quantum chemical simulations

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There is clear evidence that dust grain particles are central players contributing to the chemical inventory of the Universe. However, the exact role played by the grains is still not well understood and hard to unveil in a "rule-of-thumb" fashion: with the research progress made, the role of grains appears to be case-dependent. Grains are usually referred to as catalysts, a concept attributed in a generic sense, meaning that their presence allows the reactions to evolve, which is not the case in their absence. However, by dissecting this general idea of catalysis, for the case of ices, one can realize that, rather than being actual chemical catalysts (i.e., bodies that activate the reactants and provide alternative routes with lower energy requirements) they are more like reactant concentrators/suppliers [1,2,3,4] and/or third bodies that absorb the large extra energies released in chemical reactions (hence stabilizing the newly formed products) [5,6]. Thus, for a paradox, the capability of water ices to act as chemical catalysts is limited due to their relatively chemical inertness. In contrast, chemical catalytic properties can be found in interstellar refractory materials (e.g., silicates, iron sulfides, metallic grains…) due to the presence of transitions metals (e.g., Fe, Ni) that can activate the reactants [7,8]. In this contribution, different paradigmatic roles exerted by grains (ices and refractories) in different chemical reactions of astrochemical interest will be shown, which have been discerned thanks to the unique capabilities of quantum chemical simulations at providing exclusive atomic-scale information.

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Dissolution process of forsterite coexisting with interstitial water

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Inclusions of liquid water have been found in the samples collected from the carbonaceous asteroid Ryugu [1]. Though the origin of water is not conclusive, the deposited ice on mineral dust grains in interstellar molecular clouds could be a potential cause. In interstellar molecular clouds, mineral dust grains are covered with amorphous ice mantles [2]. The major component of the mineral dust grains is forsterite (Mg_2SiO_4) in glassy state [3], which is considered to undergo a mineral evolution through various processes to be a crystalline state in planets. Although most water molecules desorb from the mineral grains with heating during the formation of protoplanetary disk, residues can be confined in the grain boundaries as an interstitial water. The interstitial water of forsterite has unique properties. Kubo et al. [4] found that the interstitial water of glassy forsterite has higher density than that of ordinary water and exists as liquid state at high temperatures above the boiling point. However, the mechanisms of the structural change of the interstitial water have not yet been well understood. In this study, molecular dynamics (MD) calculations were performed to investigate the effects of thickness of water layer on structure of interstitial water and forsterite.

MD calculations were performed using the MXDORTO program developed by Kawamura [5]. Fundamental orthorhombic cells consisting of 484–3311 H_2O and 1176 Mg_2SiO_4 (forsterite in crystalline or glassy states) were used as the initial structures. The thicknesses of water layer d between the forsterite phases were controlled with the number of H_2O to be 1–6 nm at the initial structure. The MD code was run with an NTP ensemble at 280–670 K. The pressure was kept at 0.1 MPa. The structure was analyzed using the equilibrated states. For the comparison, the pure water system consisting of 360 H_2O was also calculated.

Dissolutions of Mg and Si from the glassy forsterite toward interstitial water were observed at temperatures above 280 K for the system with $d > 1$ nm. The dissolved Mg exists as MgO_6H_x unit and forms $Mg(OH)_2$ crystal by collisions of the MgO_6H_x units in water layer [4]. The dissolved Si maintained tetrahedral SiO_4 structure due to the strong Si–O bond.

For crystalline forsterite, in contrast, no dissolution of Mg and Si was observed at temperatures below 610 K. Only Mg dissolved at temperatures above 630 K for the system with $d < 1.5$ nm. The dissolution of Mg generates a defect on the surface of crystalline forsterite. The distortion of structure around the defects might promote an additional dissolution of Mg. The dissolution occurs for the systems with $d < 1.5$ nm, because the density of water increases as the thickness of the water layer decreases. The result suggests that the dense structure of interstitial water has an effect to enhance the decomposition of crystalline forsterite. Since the number of dissolved Mg was extremely small, the formation of $Mg(OH)_2$ crystal was not observed in the calculation period of the present study (3.0 ns).

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Chemical Evolution in Turbulent Disks: Stochastic Effect by UV photons

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Whether the complex organic molecules (COMs) detected within the disk are inherited directly from the protostellar stage or are chemically processed within the disk itself remains a topic of debate. Our research aims to shed light on this debate by studying the chemical evolution of COMs in these dynamic environments. First, we trace the grain motion (advection, turbulent diffusion, radial drift, and vertical settling) of individual dust particles for 10^6 yrs on a physical structure model of a protoplanetary disk[1]. Next, we solve a gas-ice chemical reaction network along the trajectories and obtain the temporal evolution of molecular abundances.

Our findings underscore the pivotal role of UV flux in the formation of COMs within turbulent disks. The journey of each grain particle, marked by its unique thermal and UV exposures, results in diverse chemical evolutionary among grains even if the cumulative UV dose is same. Contrary to the hypotheses of past research[1], there is not a direct proportionality between the abundance of COMs and cumulative UV exposure. High UV exposure convert oxygen into CO_2, diminishing the abundances of oxygen-bearing COMs. Nitrogen, however, is not locked into certain species, leading to the high abundances of COMs, even under intense UV exposure. Notably, a threshold UV fluence of around 500 [G_0 * years] signals the decline of COMs with oxygen, mirroring the reduction trend of the major source of radical, i.e. CH_3OH. Since COM abundances depend on the stochastic evolution of physical parameters, grains ended up in a similar disk radius will show significant diversity of COM composition.

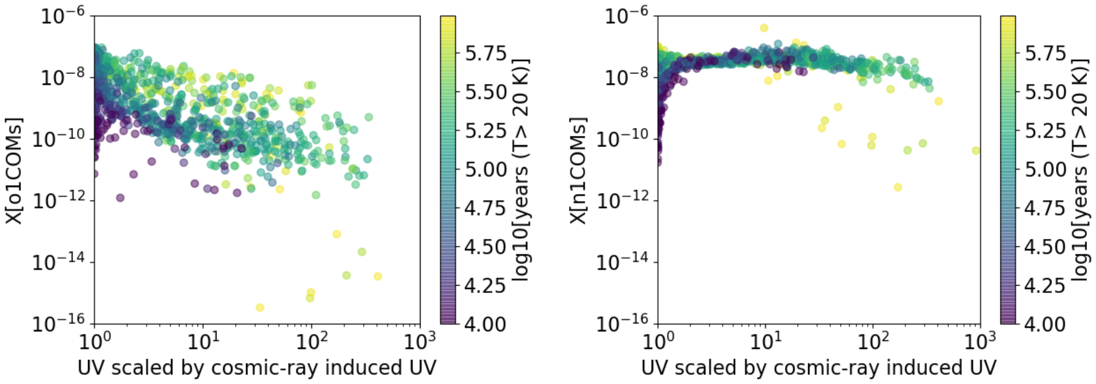

Figure 1: Abundance of COMs containing at least one O (excluding CH_3OH) and COMs containing at least one N, after 10^6 years of turbulent motion. The horizontal axis represents cumulative UV exposure.

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QUIJOTE: Q-band Ultrasensitive Inspection Journey to the Obscure TMC-1 Environment.

The chemical complexity of a cold dark cloud

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I will present the recent results obtained with the QUIJOTE line survey of the cold dark core TMC-1. The observations have been carried out with the YEBES 40m radio telescope in the Q-band. A new set of receivers have been installed in the telescope within the frame of the ERC synergy Nanocosmos project that allows to cover the whole 31-50 GHz band in dual polarization with a spectral resolution of 38.15 kHz. The sensitivity achieved so far varies between 0.08 and 0.20 mK, and allows to search for new molecules in a line by line (no stacking) detection procedure. These new data have permitted to detect many protonated species of abundant molecules, several sulfur-bearing species, cycles (benzyne, cyclopentadiene, indene), radicals, and long hydrocarbon chains. I will show the present chemical models we have performed to explain the chemistry of these species and in particular the possible reactions leading to the formation of these cycles. We suggest that a bottom-up approach starting with reactions of simple radicals, such as propargyl and the vinyl radical, with vinyl and allyl acetylene and other hydrocarbons could reproduce satisfactorily well the observed abundances. None of the new molecules found in TMC-1 are detected towards the carbon-rich evolved star IRC+10216.

Finally, I will show the SANCHO project which is devoted to the study of the spatial distribution of these molecules around TMC-1 with a sensitivity never achieved so far (4 mK).

Modeling Maser Activity of Organic Molecules toward Sgr B2

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Single-dish observations have revealed that the Sagittarius B2 molecular cloud at the Galactic Center hosts maser emission from several organic molecules, including CH_2NH [1], HNCNH [2], and $HCOOCH_3$ [3]. However, the lack of spatial information for these new maser species has prevented us from assessing their excitation conditions and pumping mechanisms. In this presentation, we introduce a cutting-edge tool for modeling and fitting the maser signals, leveraging non-LTE radiative transfer models and Bayesian statistics. This MCMC approach enables us to quantitatively assess the physical conditions of maser clumps under varying continuum background radiation levels. Our analyses suggest reference conditions for a gas clump to achieve the necessary population inversion for maser action, specifically a kinetic temperature of ~30 K, a gas density of $\sim 10^4$ cm^{-3}, and a molecular column density of 10^{16}-10^{17} cm^{-2} in the context of collisional pumped CH_3OH maser. In addition, the recent interferometric observations conducted with both ALMA and VLA enable us to compare the spatial origins and compact extents of maser emissions from several molecular species. We find a close spatial relationship between the 5.29 GHz CH_2NH maser and the 4.36 GHz CH_3NH_2 maser with the 84 GHz CH_3OH maser, supporting a shared collisional pumping mechanism.

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The chemistry in the starburst galaxy NGC 253 from the ALCHEMI survey

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Intense star formation, or starburst, characterizes the important phase of the galaxy evolution. Much is unknown about the properties of the interstellar medium (ISM) when the starburst is taking place, and when it is about to cease from the feedback. Astrochemistry is a useful tool to study these ISM properties.

By taking an advantage of the excellent capabilities of ALMA, we conducted a spectral line survey called ALCHEMI in the nearby starburst galaxy NGC 253 as a part of Cycle 5 ALMA large program. It covers most of ALMA Bands 3-7 that allowed the detection 1500 transitions.

Our results show that the central region of NGC 253 has at least three orders of magnitude higher cosmic-ray ionization rates than that in dense clouds in the Galactic disk[1,2,3]. We also found that the outskirts of the central molecular zone host intersections of galaxy orbits, and can be used as a laboratory of shock chemistry. We found that methanol, HNCO, HOCO+, and OCS are species that are enhanced in these regions[4,5,6]. From a statistical analysis on 150 integrated-intensity images using principal component analysis, we were able to identify the chemistry between young super star clusters and more developed ones.

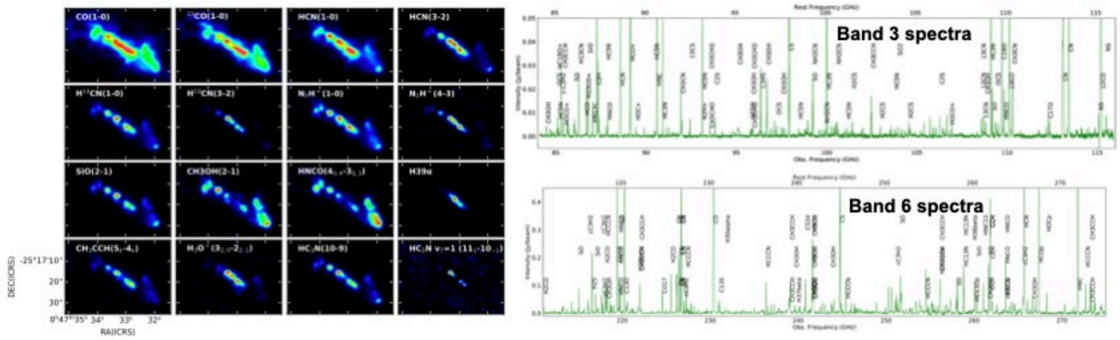

Figure 1: (Left) Selected velocity-integrated images and (right) spectra obtained from the ALCHEMI survey.

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From lab to space: An integrated rotational spectroscopy–quantum chemistry strategy

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Understanding the chemical evolution of the interstellar medium is one of the main aims of astrochemistry, and one of the biggest challenges (see Figure 1). The starting point for the development of astrochemical models is the knowledge whether a molecule is present in the astronomical environment considered and, if so, its abundance [1]. In this scenario, rotational spectroscopy plays a crucial role because most of the molecular species have been detected thanks to their rotational signatures. These, in turn, are accurately obtained from laboratory spectroscopy studies that are increasingly assisted by quantum-chemical calculations, also in the derivation of molecular abundances [2-6]. The subsequent step is understanding the chemical evolution: how the detected molecules were formed and how they can further react [1]. Accurate computational approaches play a fundamental role in this respect [7-10].

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

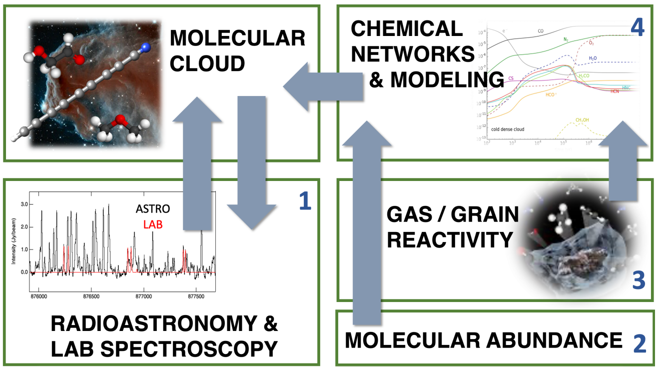

Figure 1: Chemical evolution – the required steps for the chemical characterization of a molecular cloud.

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Stability of diatomic carbon anion C_2^- in interstellar clouds: a time-resolved laboratory spectroscopy in a cryogenic ion storage ring

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The diatomic carbon C_2 is one of the most studied molecules as the simplest system having a C-C bond, and so are their ionic species C_2^+ and C_2^-. In astronomical observation, the A-X absorption line of neutral C_2 has been detected in the near-infrared spectrum of a luminous blue hypergiant Cyg OB2 No. 12. [1,2] On the other hand, C_2^+ and C_2^- are yet undetected so far, and their relevance to the C_2 abundance and chemical reaction network is not fully elucidated.

In this work, we carried out high-resolution rovibrational spectroscopy of C_2^- in a cryogenic ion storage ring RICE. [3] The photo-detachment spectrum in the 537.63 – 568.18 nm wavelength region (17600 – 18600 cm^{-1}) exhibited a lot of unassigned absorption lines, which were not ascribed to the known A-X and B-X transitions. Interestingly, these lines may or may not appear depending on how these C_2^- ions are produced in ion sources. Taking the unique advantage of the storage ring experiment, we analyzed the temporal evolution of the photo-detachment spectrum and identified a millisecond-order autodetachment process of C_2^-. [4]. The possible origins of these lines and their effect on the stability and reactivity of C_2^- in interstellar clouds will be discussed.

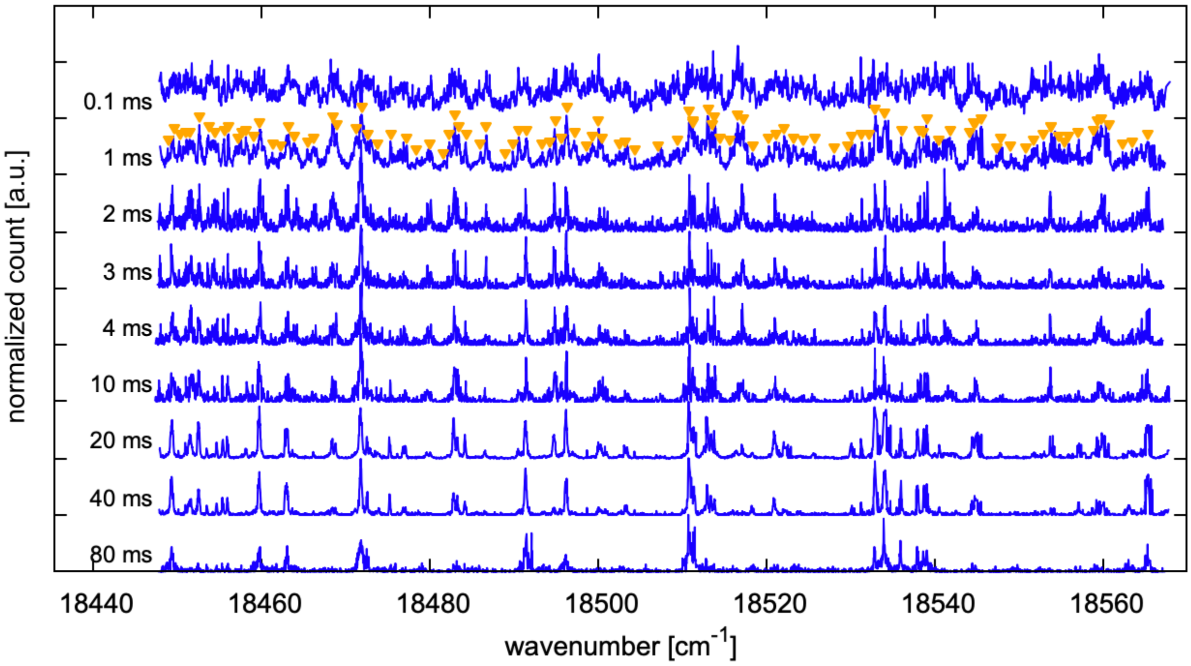

Fig1. A part of the C_2^- photo-detachment spectra recorded at different storage times.

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Possible observation of linear H_3^+ in the laboratory

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H_3^+ was discovered by J. J. Thomson in 1911 in the laboratory with a mass spectroscopic method, determined its structure by T. Oka in 1980 with infrared spectroscopy, and observed as an interstellar molecule by T. Oka in 1996. Now, we regard H_3^+ as one of the most critical species in interstellar clouds because many complex molecules are produced via the reaction involving H_3^+ [1].

We performed the ion mobility measurements after injecting H_2^+ into a drift tube filled with normal H_2 gas at the liquid nitrogen temperature of 77 K using a very low-temperature drift tube mass spectrometer [2]. The following ion-molecule reaction produces H_3^+ in the gas phase [3]:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

This is one of the important reactions that produce H_3^+ in molecular clouds, and it has been investigated in laboratories. We measured the arrival time spectra of H_3^+ at various H_2 gas pressures and electric field strengths in the drift tube to obtain the reduced mobility of H_3^+ in H_2 gas at 77K.

Arrival time spectra of H_3^+ surprisingly split two components in weak electric fields. As the mobility of molecular ions depends on their molecular structure, we consider that two peaks correspond to two isomers, namely triangle and linear structures of H_3^+. The ground state of H3+ has a triangle structure confirmed with spectroscopic observation, and theoretical calculations proposed the first excited triplet state with a linear structure [4]. However, the energy of this triplet state is too high to be produced in the low-energy collision of H_2^+ with H_2. Then the meta-stable linear structure in the electronic ground state will be the candidate. If this interpretation is correct, this result might be the first observation of linear H_3^+ ions in experiments.

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Pushing Astrochemistry into the Solar System through Mission Science

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In the past decade, astrochemistry has experienced an explosion of rich data from revolutionary observatories (ALMA, JWST), advances in experimental laboratory techniques, and the development of state-of-the-art computational calculations and models. Despite this remarkable growth, the value of this field to very relevant and neighboring fields of astronomy is not fully appreciated. Notably, as multimillion to multibillion-dollar space missions venture our solar system, the limited involvement of astrochemists in such missions has hindered the planetary science community's access to the insights of astrochemistry in interpreting solar system data. In this talk, I outline strategies undertaken at Southwest Research Institute to bridge the gap between interstellar and solar system chemistry. This includes plans to conduct pure interstellar chemistry experiments, notably atom chemistry, and initiatives to connect interstellar and solar system chemistry. These strategies will act as the foundations for the bigger goal of enhancing the visibility and value of astrochemistry among numerous solar system missions.

Methanol production through irradiation of low-energy CH_3^+ ions on an ice surface at low temperature

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To understand a variety of chemical species in molecular clouds, theoretical and experimental studies have been intensively performed. In a gas phase, it has been considered that ion-molecule reactions are indispensable. On the other hand, in a solid phase, it has been experimentally confirmed that reactions of hydrogen atoms adsorbed on an icy grain surface are essential for productions of hydrogen, water, methanol, and so on. Furthermore, reactions of other heavier radicals adsorbed on an ice surface attract many interests. Besides these reactions, recent theoretical investigations have suggested molecular formation through reactions of low-energy ions with an ice surface. In contrast to the theoretical investigations, little experimental investigations have been done because of difficulties in detecting the trace amount of reaction products with conventional methods. We have developed an experimental apparatus to sensitively detect those reaction products and performed experiments for the reactions of low-energy molecular ions with an ice surface. The CH_3^+ ions in the energy range of several electron volts impinged on an ice surface around 10 K. The reaction products on the surface were detected using pick-up reaction method by Cs^+ ions at ~40 eV. After CH_3^+ irradiation, methanol molecules were observed as the theoretically suggested. In addition, we also investigated ice-temperature dependence of methanol production. Little temperature dependence of detected methanol intensities was observed in the temperature range 12–60 K. We will also touch the results of our ab-initio molecular dynamics simulation with NVT ensemble and astrochemical model simulation in our presentation.

Formation of Sodium-bearing species in the interstellar medium

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Sodium-bearing species such as NaCl in the gas-phase have been observed in an assortment of stellar atmospheres and interstellar environments. [1],[2] However, their detection in relatively low-temperature regions has yet to be made. Here we emphasize NaCl via both gas-phase and grain-surface chemistry under assorted interstellar conditions. Two types of numerical gas-grain simulations have been run: models under isothermal conditions at temperatures from 10 K to 800 K with varied intervals, and three-phase warm-up models that consist of an initial isothermal collapse at 10 K, a warm-up phase, in which temperature reaches 200 K with varied intervals, and lastly a hot-core phase. The surfaces of dust grains contain water-ice using a base cluster of 17H2O. Desorption and barriers against diffusion were calculated with Gaussian 09 using B3LYP density functional theory. We found that for isothermal models over a broad parameter space, the fractional abundances of gaseous NaCl and NaOH can reach above 2 x 10(-10) and approximately 1 x 10(-10) respectively, which may be in the detection range of observational facilities such as ALMA and JWST. For warm-up models, we found that if we consider sodium-bearing molecules to be co-desorbed with water ice, then gaseous NaCl can reach a sufficiently large abundance for detection to be possible. However, more experiments and quantum calculations are needed to constrain the relevant reaction rates in our simulations better.

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Overview of ALMA Large Project FAUST
(Fifty AU STudy of the chemistry in the disk/envelope system of Solar-like protostars)

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A huge variety of planetary systems has been discovered in recent decades, and it likely related to the early history of their formation. Meanwhile, it has been recognized that protostellar cores show chemical diversity, especially in the composition of organic species. For instance, two distinct cases are well known: hot corino sources are rich in intestellar complex organic molecules (iCOMs), while warm carbon-chain chemistry (WCCC) sources are rich in unsaturated hydrocarbons. They are still unclear whether such a chemical diversity is seen in disk-forming regions (~50 au scale) and what kinds of molecular species are delivered into disks from envelope gas (~2000 au scale).

To tackle with the above problems, our ALMA large program 'FAUST' (P.I. S. Yamamoto) focuses on the early history of Solar-type protostars and their chemical diversity on a 50 au scale, where planets are expected to be formed. The main goal of this project is to reveal and quantify the variety of chemical composition of the disk/envelope system. We observed thirteen young (Class 0-I) protostellar sources as representatives of the chemical diversity observed on larger scales to obtain a homogeneous database of thousands of images from different lines and species. The analysis of this huge database is in progress (1) to disentangle the components of the 50-2000 au disk/envelope system, (2) to characterize the organic complexity in each source, (3) to probe their ionization structure, and (4) to measure their molecular deuteration. We are going to present the overview compiling the results in 13 sources.

ALMA Observations of the Young Bursting Star V883 Ori: Chemistry of Complex Organic Molecules in the Protoplanetary Disk

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Complex organic molecules (COMs), potential precursors of prebiotic molecules, are key to understanding the chemical evolution from the interstellar medium to planetary systems. Recent interferometric observations suggest that COMs are abundant in the warm inner envelopes around low-mass protostars. However, complex organic chemistry in protoplanetary disks, the immediate birthplace of planets, is still poorly understood because COMs are frozen out and thus hidden from view in archetypal disks [1].

Recent ALMA detections of thermally sublimated COMs in the warm disk around the young bursting star V883 Ori have opened a new window to probe the complex organic chemistry in protoplanetary disks [2][3]. We will present our new observations of COMs toward V883 Ori in ALMA Band 3 at an angular resolution of ~0.3" (or ~120 au). We detected ten oxygen-bearing COMs including ^{13}C isotopologues in the disk. We measured the abundance ratios of COMs with respect to CH_3OH and the isotopic ratios ($^{12}C/^{13}C$ and D/H) of COMs for the first time in a protoplanetary disk. The abundances of COMs are systematically higher than those in the warm envelopes of IRAS 16293-2422. The $^{12}C/^{13}C$ ratios of different COMs are consistently lower (~20-30) than the canonical ISM ratio (~69). The upper limits of COM D/H ratios (< 0.01) are also lower than those in IRAS 16293-2422. These high abundances of COMs and peculiar isotopic ratios could be explained by the efficient (re-)formation of COMs on the lukewarm dust grain surfaces from the ^{13}C-enriched CO due to the exchange reaction with $^{13}C^+$.

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Photochemistry of Sulfur-species in ice mantles

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Sulfur chemistry is a trending topic in Astrochemistry. Several S-species are commonly detected in the gas toward interstellar and circumstellar environments, such as SO_2, SO, CS, OCS, H_2S, C_2S and H_2CS, but their total observed abundance in the dense interstellar medium is more than one order of magnitude lower than the sulfur cosmic abundance. Refractory sulfur in dust grains is summoned to account for the S-depletion in dense clouds and protoplanetary disks. This refractory form of sulfur, however, remains a mistery. Laboratory experiments involving irradiation of H_2S in the ice, theoretical models, and the detection of S_2, S_3 and S_4 in comet 67P during the Rosetta mission, suggest that S-chains is a potential source of refractory sulfur in the dust.

Figure 1 displays the thermal desorption of an irradiated H_2S ice sample [1]. Each mass over charge (*m/z*) value corresponds to the molecular ion of a species or to a fragment of a larger species. The desorption temperatures of S_x molecules are indicated by the solid vertical lines, while dashed lines indicate the desorption of H_2S_x species. Apart from the molecular ion of each species, the *m/z* values of the main fragments used to confirm the presence of these species are displayed.

A brief overview of experiments mimicking the photochemistry of H_2S and other S-bearing species in the ice will be presented. We use the experimental data and modeling to interpret the observational results. The study of S-species in the ice serves to prepare the observations of refractory sulfur and to interpret the gas phase observations accounting for the desorption of S from the ice. In addition to thermal desorption when the dust temperature is high enough, other mechanisms were proposed for the release of solid S-species to the gas phase, among them are chemical desorption [2] and photodesorption [3] . The latter mechanism will also be discussed in our presentation.

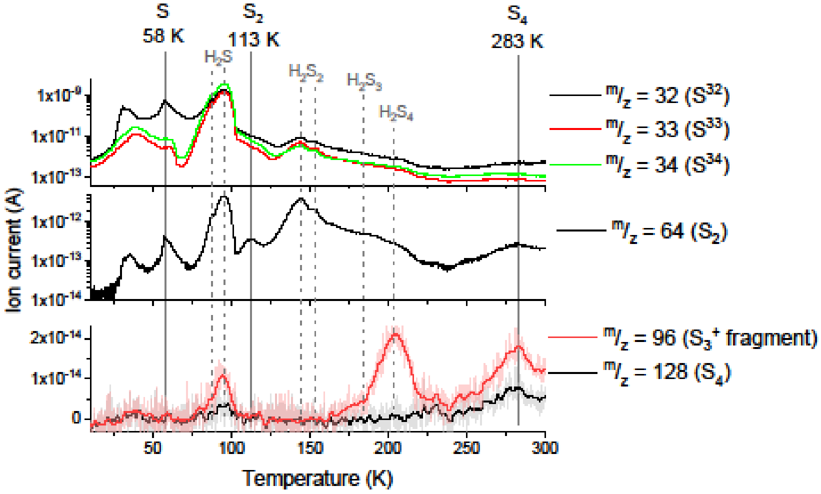

Figure 1: Desorption of S-photoproducts during warm-up of a previously UV-irradiated H_2S ice layer, adapted from [1].

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VUV photodesorption of H_2S ices

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Hydrogen sulfide (H_2S), one of the most abundant sulfur-bearing species detected in the interstellar medium (ISM), can be considered a precursor to certain biochemical molecules. Within the dense clouds, the significant energetic source stems from the secondary vacuum ultraviolet (VUV) field generated by the interaction of cosmic rays with molecular hydrogen. Oba et al. (2018) conducted measurements of chemical desorption caused by H atom incidents and speculated that it should surpass VUV photodesorption [1].

In this study, we investigated the VUV-induced desorption of H_2S ices and assessed the impact of structural factors by depositing ices at two different temperatures, 13 K and 70 K (both of which were subsequently irradiated at 13 K). Our findings indicate that amorphous H_2S ice deposited at 13 K exhibited a higher depletion cross-section and VUV-induced desorption yield compared to crystalline ice deposited at 70 K. Moreover, the VUV photodesorption yield of H_2S ice was influenced by both energy transfer length and surface purity of H_2S [2]. The VUV photodesorption yield measured in this study was found to be comparable to the chemical desorption yield measured through hydrogenation, especially when both values are applied to simulate conditions in dense cloud environments.

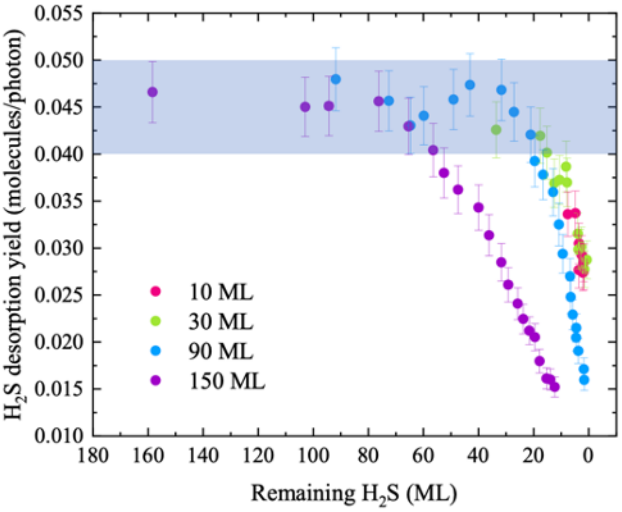

Figure 1: VUV photodesorption yield for different initial column densities as a function of remaining column density of H_2S ice.

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Chemical pathways of Methyl Mercaptan (CH_3SH) with Hydrogen atoms on Interstellar Ice

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There have been about 30 sulfur (S)-bearing species identified in the interstellar medium (ISM). Since the observed abundance of S-bearing species in the gas phase is lower than the cosmic abundance of S[1], it is often considered that there might be a source of "missing S" on interstellar grains. Based on an assumption that physico-chemical processes of S-bearing species on interstellar grains would be a key to constrain their presence in the ISM, several laboratory studies have been performed and our understanding has been significantly improved on the surface processes of S-bearing species at low temperatures[2,3]. In the present study, we shed light on the behavior of other S-bearing species, methyl-mercaptan (CH_3SH), via chemical reactions of CH_3SH and H atoms without external energies on interstellar ices at low temperatures (typically 10 K) using experimental and computational methods.

We found that chemical reactions of CH_3SH with H atoms proceeded via multiple channels: $CH_3SH + H \rightarrow CH_3 + H_2S$, $CH_3S + H_2$, or $CH_2SH + H_2$. The major channel was the dissociation of C-S bond in CH_3SH with the activation barrier of 0.05 eV on amorphous solid water, eventually resulting in the formation of methane (CH_4) by further hydrogenation to CH_3[4]. The hydrogen abstraction channels lead to the formation of CH_3S and CH_2SH radicals, and further hydrogenation to these radicals would result in the formation of CH_3SH again. Chemical desorption of CH_3SH was not positively identified via these processes, implying the presence of other processes for the desorption of CH_3SH from interstellar grains at low temperatures.

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Chemical evolution from the interstellar medium to the solar system: Insight from the analysis of asteroidal materials

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More than 180 interstellar molecules have been identified by radio telescopes, and recently, the presence of interstellar molecules having more than 10 atoms such as glycolamide ($NH_2C(O)CH_2OH$) and propanol (C_3H_7OH) has often been reported in literature [1,2]. Although the presence of further complex interstellar molecules may be detected in future astronomical observations, it is still widely accepted that interstellar molecules have much less complex structures compared to molecules in the solar system. Since all materials present in the solar system should have their ultimate origin in the interstellar medium (ISM) where it was born, it is straightforward to consider that the relatively simple interstellar molecules should have become more complex through the evolution from the ISM to the solar system.

Organic molecules in carbonaceous meteorites have been regarded as a good target for understanding the “end member” of chemical evolution in space since they are the most pristine solar system materials that can be analyzed in the laboratory. Moreover, the recent great successes in the recovery of materials from carbonaceous asteroids Ryugu and Bennu should provide researchers precious opportunities to analyze the most primordial solar system materials without terrestrial contamination [3,4].

The initial analysis of the Ryugu samples detected various kinds of organic molecules such as amino acids and nucleobase, which provides strong evidence for the presence of such biologically relevant molecules in extraterrestrial environments [5,6]. In this talk, I would like to show further findings on the organic contents in the samples recovered from Ryugu. In addition, several potential pathways for the formation of organic molecules in asteroids/meteorites will be discussed based on the distribution of organics in those materials and laboratory experiments.

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Intensity-calibrated molecular spectroscopy and determination of intrinsic line intensity $S\mu^2$ for CH_2DOH

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Isotopic fractionation in molecules is known as one of the powerful tools to trace the molecular evolution during the Solar system. Among various interstellar species, methanol is the most abundant saturated-organic molecule and is known as an important species to form more complex organic molecules in interstellar clouds. Observing isotope fractionation ratios of methanol is especially useful to reveal reaction pathways of such organic molecules [e.g., 1, 2]. Despite its importance, current spectroscopic information is not enough to determine their abundances accurately even for the methanol isotopologues. For example, CH_2DOH significantly suffers from the uncertainty of intrinsic line intensities ($S\mu^2$) due to their floppy nature. Although $S\mu^2$ of each transition line is a critical parameter to derive accurate column density and temperature of the molecular gas, they are not easy to be evaluated theoretically for the asymmetric-top asymmetric-frame isotopologue. With our emission-type spectrometer, SUMIRE [3], using technique developed for radio astronomical observations, we can now derive $S\mu^2$ and transition frequency for various isotopologues of methanol by laboratory spectroscopy in the millimeter-wave region from 216 GHz to 264 GHz [4,5]. In the *b*-type transitions of CH_2DOH, significant systematic errors were found between theoretical and experimental $S\mu^2$ for three torsional sub-state, e_0, e_1 and o_1 as shown in Figure 1. This study will enable us to trace deuterium fractionation of COMs along the star formation.

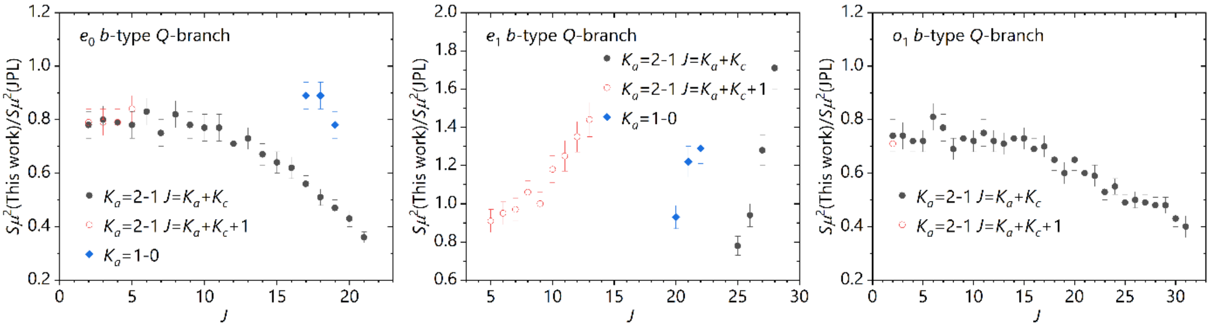

Figure 1: Ratios between the $S\mu^2$ values derived in this study and those listed in the JPL database for the *b*-type *Q*-branches in CH_2DOH.

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Microwave spectroscopy of CH_2Cl_2

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Dichloromethane (CH_2Cl_2) is a known organic solvent and atmospheric molecule. In recent studies, there are two astronomy-related reports of CH_2Cl_2. In 2008, it was reported that the Phoenix Mars lander collected three soil samples and confirmed the presence of CH_2Cl_2[1]. In 2010, Navarro-González *et al.* found CH_2Cl_2 in Martian soil which had been previously considered to be terrestrial contaminant.[2].

So far, studies have been conducted to obtain laboratory molecular data on CH_2Cl_2. For example, in 1952, Myers and Gwinn measured the microwave spectra of seven isotopic species of CH_2Cl_2 and determined the dipole moment-and the chlorine nuclear quadrupole coupling constants [3]. In 1981, Gerry measured microwave spectrum of CH_2Cl_2 up to $J = 80$ to get centrifugal distortion constants [4]. Later, Tullini measured far-infrared spectra in the region between 10 and 75 cm^{-1}, and assigned rotational transitions [5].

However, the current available data do not possess sufficient accuracy. Therefore, we performed measurement and analysis to provide sufficiently accurate rest frequencies. In this study, we used microwave spectroscopy to measure and analyze the spectrum of CH_2Cl_2 to improve the data. The frequency region from 50 to 750 GHz was measured with a measurement error of 50 kHz at the University of Toyama and at the University of Wisconsin-Madison. More than 7000 transition frequencies were assigned up to $J = 99$ and $K = 5$. As a result, the parameters that were determined in this study were the rotational constant and centrifugal distortion constants. We plan to extend the range of K values.

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The microwave spectroscopy of *trans*-ethyl methyl ether

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1.Introduction

Trans-ethyl methyl ether ($CH_3CH_2OCH_3$) is the next simplest ether structure after dimethyl ether (CH_3OCH_3), and dimethyl ether has been observed in many spectra as an interstellar molecule. It was identified in Orion KL [1]. The rotational structure of this molecule is very much complicated because it has two internal rotors and there are many low-lying vibrational excited states. One rotational level splits into 5 sublevels (AA, AE, EA, EE1, and EE2). In a laboratory microwave study, Hayashi and Kuwada measured in the frequency range of 8.5 - 34 GHz, and gave molecular constants, dipole moment, and the molecular structure [2]. In addition, past study, K. Kobayashi and her collaborators analyzed this molecule in the first skeletal torsional excited state [3], v_{29} = 1 excited torsional state [4] and determined twenty-two molecular parameters composed of rotational constants, centrifugal distortion constants, internal rotation parameters and internal rotation tunneling parameters for the ground state, and three torsional states were also reanalyzed [5]. In this study, we extended and analyzed microwave spectra, providing effective molecular parameters of the AA sublevel in the ground state, and low-lying vibrational excited states.

2.Experiment

All the measurements were made using our conventional frequency modulation spectrometer in the frequency range of 330 - 360 GHz. The experiment was carried out at room temperature.

3.Results

The observed spectra were analyzed together with our previous 202 - 330 GHz data. Over 2500 transitions were newly assigned and analyzed over 6000 transitions in total. The highest J and K values of each vibrational states were 98, and 22 in the ground state, 98, and 19 in the skeletal torsional excited state, 99, and 16 in the C-CH_3 torsional excited state, and 98, and 17 in the O-CH_3 torsional excited state, respectively. We plan to further assign and analyze other sub-levels in the future.

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Development of a merged-beam apparatus to study the interstellar ion-neutral reactions

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Experimental determination of ion-neutral reaction cross sections and their internal state dependence is crucial to understanding interstellar gas-phase chemistry. A merged-beam experiment is capable of measuring the energy-dependent reaction cross-sections by merging the ion and neutral beams collinearly at low center-of-mass collision energies. We plan to conduct a merged-beam experiment on state-selective low-energy collisions of interstellar molecular ions with neutral atoms such as H, D, C, and O at 10 — 100 meV region.

An overview of the experiment is shown in Fig.1. The neutral beam of the ground-state atoms is produced by laser photo-detachment of a negative ion beam extracted from the duoplasmatron ion source, which generates about 100 nA of negative ions by a two-stage discharge process. The photo-detachment is done by an 808 nm laser diode array in a multi-reflection cavity. A cold-cathode PIG ion source is also under development for the production of molecular ion beams. The two beams are merged and mass-analyzed by electrostatic deflectors at the entrance and exit of the merged section.

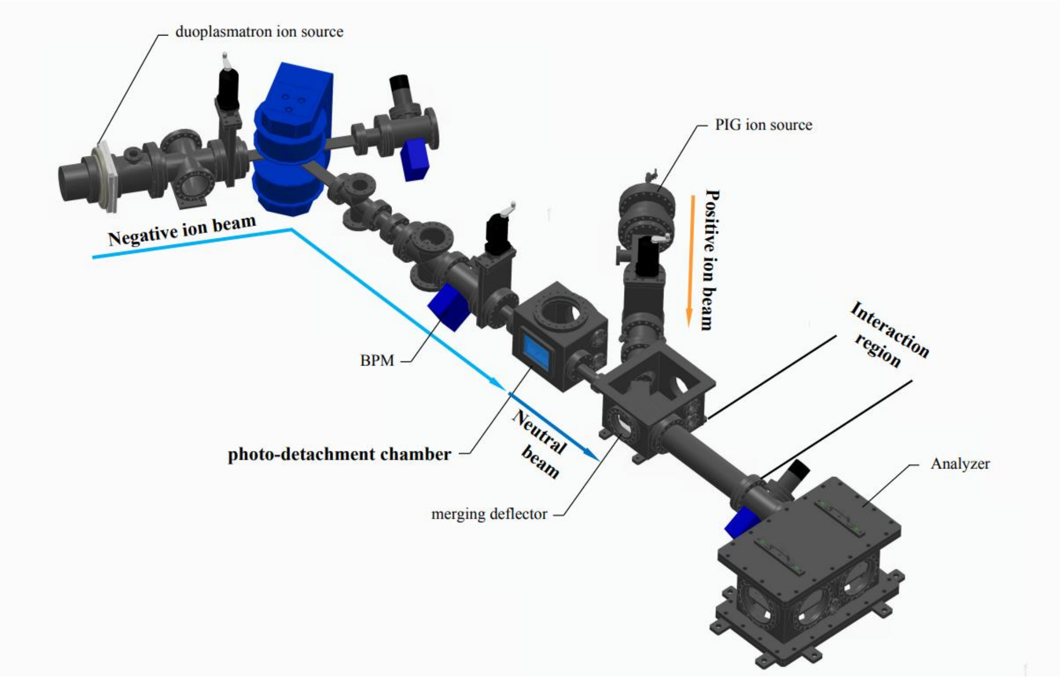

Fig1. Overview of the merged-beam apparatus

Development of far ultraviolet light source using laser-produced plasma

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In the photodissociation region of interstellar space, photoionization, dissociation, and isomerization occur due to the far-ultraviolet light (100-200 nm) from stars. Our goal is to quantitatively understand the reaction dynamics and measure rate constants. Laser-produced plasmas are expected to be a compact FUV light source. We have obtained emission spectra from plasmas of four different metal targets (Al, Fe, Cu, and Inconel (Ni/Cr/Fe)), which show characteristic profiles in the wavelength range 100-200 nm. From the intensity ratios of the obtained spectra, the electron temperature of the plasma was estimated to be 6.4 eV by using the Boltzmann Plot method. The obtained emission spectra were also compared with spectral simulations (Fig.1). In addition, a dedicated off-axis parabolic mirror was developed to collimate the light emitted from the plasma and incident on the monochromator. As a result, the FUV light intensity detected after passing through the monochromator was about 10^7 photons/pulse, an amplification of about 35 times (Fig.2). We plan to experimentally study the interaction of FUV light with polycyclic aromatic hydrocarbons (PAHs), which have few data on photoionization cross sections and reaction branching ratios among molecules in the photodissociation region, PAH molecules have high vapor pressure, and we are currently developing a mechanism to vaporize and pulse PAH molecules. We have also developed a mechanism for discharging the pulsed gas to induce a gas-phase reaction. The reaction routes that occur in this discharge are of interest for astrochemistry as possible growth pathways for PAHs [2]. In this presentation, we will report on the comparison of emission spectra obtained from the four targets with simulations, as well as the specifications of the developed off-axis parabolic mirror and future prospects.

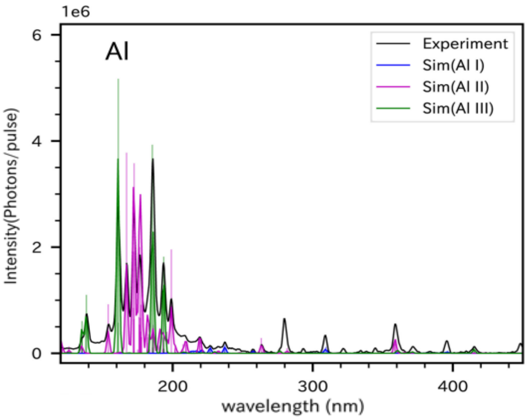

Fig1. Emission spectrum and simulation of Al [1]

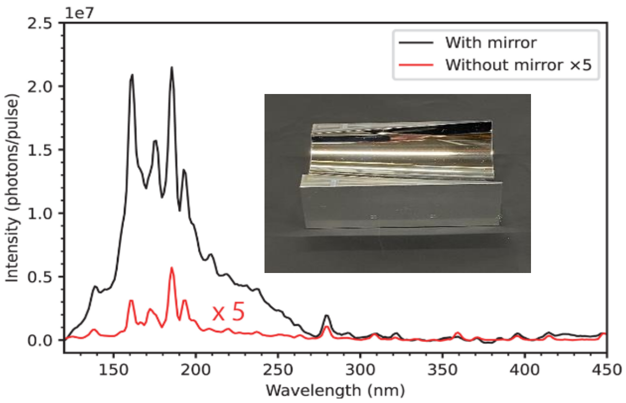

Fig2. Spectrum change by mirror [1]
Spectra from plasma produced by irradiating an Al target with a 532 nm pulsed laser

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A new approach for reaction rate measurements of cold ion-polar molecule reactions

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Low-energy ion–polar-molecule reactions are important chemical processes in interstellar matter. However, due to experimental difficulties, the reaction rate constants have not been sufficiently measured at low temperatures. In this context, we have been working on the reaction rate measurements of cold ion-polar molecule reactions by combining velocity-selected polar molecules and sympathetically cooled ions in a linear Paul trap [1]. Additionally, we have proposed a new approach that combines buffer-gas cooling of trapped ions in a cryogenic ion trap with a wavy Stark velocity filter [2, 3]. As a proof-of-principle experiment for this new approach, we measured the electronic state-dependent reaction-rate constants of $Ca^+(^2S_{1/2}, {}^2D_{3/2}) + CH_3F \rightarrow CaF^+ + CH_3$ at a translational temperature of about 110 K [3]. In addition, the rotational cooling effect on the rate constants was also observed by implementing a cryogenic buffer gas cell for the rotational cooling of polar molecules. Recently, we also measured the rate constants of $Ca^+(^2S_{1/2}, {}^2D_{3/2}) + C_2H_5OH$ at a translational temperature of about 90 K. Since this new approach can be applied to various ion-polar molecule reactions over wide ranges of translational and rotational temperatures of molecular ions and polar molecules, we have been constructing a new experimental setup based on this new measurement method by combining a wavy Stark velocity filter and a cryogenic linear octupole rf ion trap (Fig.1). In this poster presentation, we will present the recent results on the reaction rate measurements on cold ion-polar molecule reactions as well as the status of the new experimental setup.

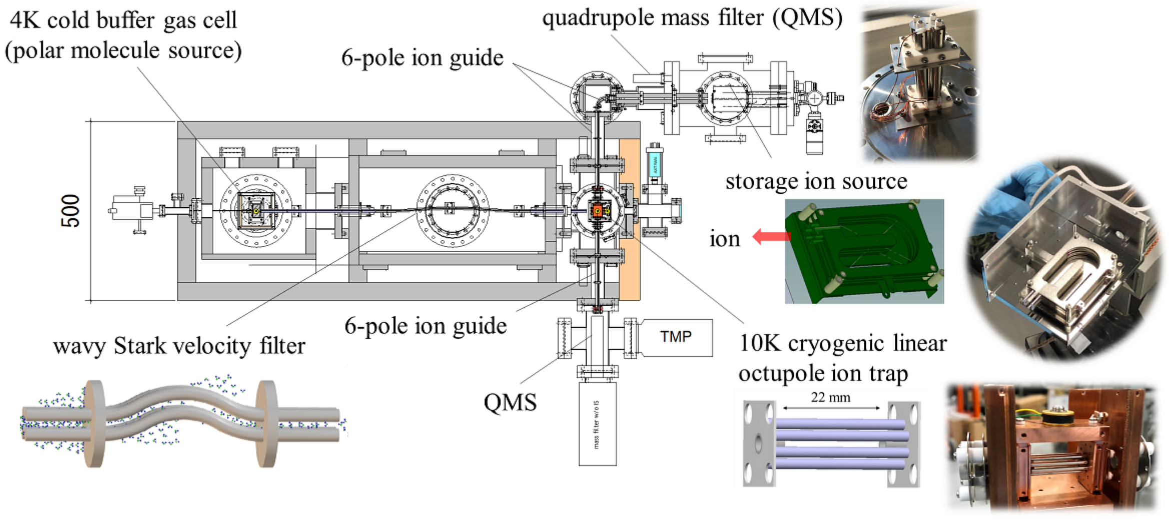

Figure 1: Wavy Stark velocity filter–cryogenic octupole ion trap apparatus with a storage ion source.

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Collisional excitation and collision-induced dissociation of astrochemically relevant molecules by ion impacts

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The collision-induced dissociation (CID) of small molecules by ion impacts such as

$$X^+ + AB \rightarrow \quad X^+ + A + B$$

plays an important role in the chemical evolution in molecular clouds [1-3]. Here we present a theoretical work on the energy transfer and fragmentation of molecules by ion impacts at hyperthermal energies. The classical trajectory (CT) calculation and the sudden-limit model [4,5] are applied to estimate the energy transfer from translational to internal degrees of freedom. Figure 1 represents the calculated excitation spectrum of CO molecule by proton impacts at the collision energy E=27 eV. The model predicts the energy-transfer from the translational to the internal degrees of freedom with less efficiency. The threshold energy for CID of CO molecule by ion impacts is calculated. The results are listed in Table I. When the projectile is much lighter than the target, the spectator model works well. The probability of CID depends strongly on the orientation angle at the moment of the contact. The CID takes place predominantly when an ion hits the molecule either perpendicular or parallel to the molecular axis. Calculation and analysis would be extended to other astrochemically relevant molecules.

Table I: Threshold energy (eV) for the collision-induced dissociation of CO by ion impacts obtained with the classical trajectory calculation and with the spectator model.

Projectile	CT calculation	Spectator Model
H^+	60	59
D^+	41	31
He^+	29	17
C^+	35	7

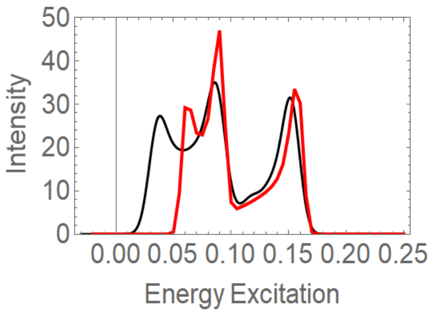

Figure 1: Calculated excitation spectrum of CO molecule by proton impact with incident energy of 27 eV. The black (red) curve is the result obtained with the classical trajectory (sudden limit model).

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Electron discharge chemistry in exoplanetary CO_2-rich atmospheres

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Electrical processes are expected to be a common process on planets. Lightning has been observed on Jupiter [1], Saturn [2], Uranus [3], Neptune [4], it is also possible in the atmospheres of Mars and Titan. Electrical processes may be crucial to increase chemical composition in prebiotic atmospheres.

In the present work we simulate the chemistry induced by electrical processes in CO_2 rich atmospheres. We study the influence of small amounts of NH_3 on the chemical network of these atmospheric analogues.

We irradiate a CO_2:NH_3 (10:1) gas mixture at a pressure of 20 mbar. The gas composition was measured in real time by mass spectrometry and the ionized fraction was monitored by UV spectroscopy during the electrical discharge. UV spectroscopy highlights optical phenomena such as self-absorption, which could obscure a fraction of the emitted spectrum. The residue formed after electrical processing of each gas mixture was compared and analyzed by IR spectroscopy.

We found that abiotic processes such as electrical discharge are capable of producing organic compounds. The solid residue formed in the gas phase and deposited is strongly influenced by the presence of small amounts of NH_3.

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Impurity contribution to photoabsorption of saturated fatty acids and its implications to tropospheric chemistry

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Saturated fatty acids are abundant surfactants in oceans and sea sprays, in which they concentrate at interfaces. Recent laboratory studies have reported that irradiating liquid saturated fatty acids with ultraviolet (UV) wavelengths longer than 295 nm produce various volatile organic compounds, which enhance marine aerosol formation by acting as precursors [1]. UV absorption spectra of liquid saturated fatty acids exhibit a weak shoulder absorption band centered at 270 nm and extending to 330 nm, in addition to the main band at around 210 nm, due to a singlet-singlet (S_0-S_1) $n \rightarrow \pi^*$ transition (Fig. 1). Various origins have been proposed for shoulder absorption, e.g., carboxylate anions, a singlet-triplet (S_0-T_1) $n \rightarrow \pi^*$ spin-forbidden transition of neutral molecules, and the formation of cyclic dimers [2]. However, no consensus has yet been reached, despite over 90 years of investigation [3].

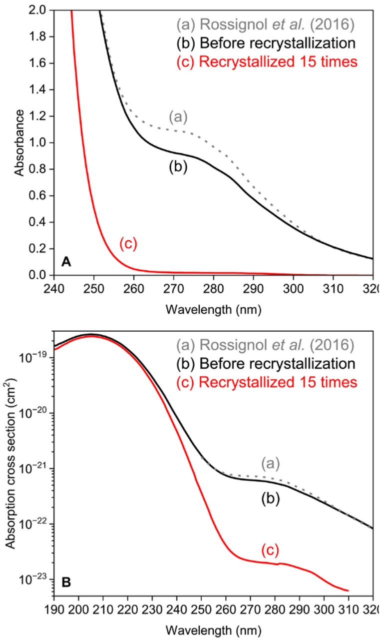

Fig. 1. UV absorption spectra and absorption cross sections of liquid nonanoic acid at room temperature. (A) UV absorption spectra of nonanoic acid: (a) reported by Rossignol et al. [1] for a commercial sample (purity, 97%) and measured here for a commercial sample (purity, >98.0%) (b) before and (c) after recrystallization. Optical path lengths were 10 mm. (B) The corresponding calculated absorption cross sections [3].

The present study of the absorption of wavelengths longer than 250 nm by nonanoic acid [$CH_3(CH_2)_7COOH$], a representative fatty acid present in the sea-surface microlayer, demonstrates that the weak absorption band originates from trace amounts of impurities (0.1% at most) intrinsically contained in nonanoic acid reagents (Fig. 1). We developed a unique recrystallization purification system and purified commercial nonanoic acid by 15 recrystallizations. As a result, the absorption band at 250−330 nm completely disappeared (Fig. 1A). The absorption cross section at 295 nm (1.3×10^{-23} cm^2) was found to be three orders of magnitude smaller than those typical for atmospherically relevant organic molecules such as formaldehyde (H_2CO, 4.4×10^{-20} cm^2), acetaldehyde (CH_3CHO, 4.3×10^{-20} cm^2), and acetone ($CH_3(CO)CH_3$, 3.4×10^{-20} cm^2) at 295 nm (1 nm average) in the gas phase [2]. Our results show that purified fatty acids are photochemically inert in the troposphere, in contrast to previous predictions. This study also suggests that more accurate evaluation about the effects of impurities is required for scientific research. This is particularly important in research of photochemical systems because impurities and contaminants can act as photosensitizers when they are selectively excited by photons.

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Chemical Composition of Interstellar Amorphous Silicate Dust

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Absorption features at ~10 µm and ~18 µm of interstellar dust indicate the majority of interstellar silicate dust is amorphous and the upper limit to the fraction of crystalline silicates in the diffuse interstellar medium is 2.2 ± 0.2 % by mass [1, 2]. Synthetic optical constants such as "astronomical silicate" [3] and "interstellar dust" [4] have been widely used in the interpretation of observational data. These optical properties, however, do not represent real solid materials because they are arbitrarily synthesized from the combination of the observation and laboratory data. Various dust analogs have been produced in laboratories [e.g., 5, 6] but still cannot replace the astronomical silicates. Thus, the nature of amorphous silicate dust in the circumstellar and interstellar environments, such as chemical composition and structure, cannot be derived from discussions using astronomical silicates.

In this study, we conducted gaseous condensation experiments of dust analog nanoparticles in the system of Na-Al-Ca-Mg-Fe-Ni-Si-O using the induction thermal plasma (ITP) system (JEOL TP-40020NPS, [7]). The chemical compositions of the starting materials are shown in Table 1. The products were analyzed by XRD (Rigaku RINT-2100), FT-IR (JASCO FT/IR-4200), and EPMA (JEOL JXA-8530F) and partly observed by TEM (JEOL JEM-2800). We report IR spectral dependence on the chemical compositions of amorphous silicates and discuss the chemical composition of interstellar silicates by comparing the experimental products with astronomical silicates and observations.

Table 1: Chemical Composition of the Starting Material

	Mg	Si	Al	Ca	Na	Fe	Ni
$Ca_{0.06}MgNa_{0.06}Al_{0.08}Si$ w/ Fe, Ni	1.03	1	0.08	0.06	0.06	0.85	0.05
$Ca_{0.06}MgNa_{0.06}Al_{0.08}Si$ w/o Fe, Ni	1.03	1	0.08	0.06	0.06	-	-
$MgAl_xSi$(x=0.75) w/ Ca, Na	1.03	1	0.75	0.06	0.06	-	-
$MgAl_xSi$ (x=0.64)	1.03	1	0.64	-	-	-	-
$MgAl_xSi$ (x=0.31)	1.03	1	0.31	-	-	-	-
$MgAl_xSi$ (x=0.08)	1.03	1	0.08	-	-	-	-
$Ca_{0.5}Mg_{0.5}Al_xSi$ (x=0.08)	0.515	1	0.08	0.515	-	-	-
$CaAl_xSi$ (x=0.08)	-	1	0.08	1.03	-	-	-
$CaAl_xSi$ (x=0.64)	-	1	0.64	1.03	-	-	-

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Kinetic isotope effects in high-temperature evaporation in protoplanetary disks

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Interstellar dust grains are building blocks of planetary materials but are likely to be thermally processed in protoplanetary disks before they accrete to form planets. The most intensive processing in inner hot regions of disks results in vaporization of dust grains, and their chemical compositions are significantly altered when they are partially vaporized. The metal-bearing molecules (e.g., SiO, AlO and NaCl) observed in a high mass young protostar candidate (Orion Source I) are likely to be the molecules evaporated from dust [1-3].

Evaporation is a kinetic process that governs the timescales of such solid-vapor partitioning and thus is important in understanding chemical evolution of planetary materials. Kinetic isotope effects (KIEs) associated with evaporation lead to isotopic fractionation of the residual phase, providing information about evaporation experienced by extraterrestrial samples. For example, calcium-, aluminum-rich inclusions (CAIs) with igneous textures found in chondrites show enrichment of heavy isotopes of Mg and Si, which is attributed to evaporative isotopic fractionation in the protosolar disk [4]. The KIE in evaporation can be theoretically predicted by the ratio of the thermal velocity of the evaporating molecules, i.e., the square root of their inverse mass ratio. However, experimentally determined KIEs are usually smaller than the theoretical prediction [5,6].

In this study, we newly formulated the KIE in evaporation by using the expression of the evaporation rate based on conventional transition state theory (CTST) [7,8]. We found that the KIE in evaporation at the high-temperature limit is expressed by the square root of the inverse ratio of the reduced mass for the motion along the reaction coordinate at the transition state. This result is consistent with the theory previously proposed for KIEs in general chemical reactions [9] and explains the experimental KIEs in evaporation smaller than the conventional prediction. By considering the motion along the reaction coordinate as vibration with an imaginary frequency, we further evaluated the KIE in evaporation using normal-mode vibration analyses for the transition state. The result suggested that the KIE is smaller than the conventional prediction when the activation barrier exists for the bond dissociation. This suggests that the different degrees of KIEs of metallic iron and silicates obtained by experiments might indicate the presence of an activation barrier for the dissociation of an ionic bond that originates from the avoided crossing of potential energy curves.

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Development and preliminary results of the low-temperature gas evaporation method to understand nucleation conditions of water ice and related materials

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In our previous studies, we have shown that the key factors governing nucleation from the gas phase are the melting point depression of nanoparticles and sticking probability (dimer formation) [1,2]. In long years, nucleation theory has been known to be completely unable to explain the results of experiments and molecular dynamics simulations. In contrast, we have clarified that the latest nucleation theory can explain experimental results by using appropriately determined sticking probabilities and surface free energies of nanoparticles as physical parameters [1], and by including chemical potential differences that consider the nucleation pathway [2].

To understand the nucleation processes of ice, we developed a low-temperature gas evaporation method to determine the sticking probability and surface free energy of nanoparticles of ice. The gas evaporation method has been used to make nanoparticles of refractory materials through homogeneous nucleation during the cooling process of high-temperature vapor generated by heating and evaporating the starting material [3]. By applying interferometry to this method, two physical quantities (surface free energy and sticking probability), which are essential for understanding the nucleation process, can be obtained. In addition, infrared spectral measurements can reveal the nucleation pathways.

The low-temperature nucleation chamber has a double-tube structure. The inner chamber, where ice nucleation takes place, is filled with neon gas to reduce the mean free path and cooled by liquid nitrogen. The evaporation source was also cooled with liquid nitrogen. The space between the inner and outer chambers is evacuated to thermally insulate them and prevent condensation.

Water vapor generated by heating and sublimating ice in the low-temperature nucleation chamber is cooled by neon gas, and after becoming supersaturated, it undergoes homogeneous nucleation to form nanoparticles. This process was observed in situ using a double-wavelength Mach-Zehnder laser interferometer and an infrared spectral system. The interferometer can quantitatively determine the temperature and concentration fields from evaporation to nucleation. The infrared system can investigate the changes in the crystal structure of water and ice particles during the nucleation process.

In the experiment, the interferometer succeeded in capturing the moment of nucleation, and the infrared system also succeeded in capturing the temporal change in absorption intensity. This means that the nucleation process of ice nanoparticles from water vapor was captured. This achievement is expected to lead to the construction of a nucleation model that can predict the state of ice dust formation that repeatedly sublimated and condensed in the primordial solar nebula 4.6 billion years ago.

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Returned sample from carbonaceous asteroid Ryugu and its astrochemical implications

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The Hayabusa2-returned C-type asteroid Ryugu samples [1] are the chemically most pristine material in the Solar System as they have not been exposed to terrestrial conditions [e.g., 2-9]. The Ryugu samples have the bulk elemental compositions similar to those of the Sun and CI chondrites, which are the chemically most primitive meteorites [1], suggesting that Ryugu formed from the Solar System's original elemental ingredients without experiencing elemental fractionation except for highly volatile elements such as H, C, N, and noble gases.

The carbon abundance of the bulk Ryugu samples ranges from 3.2 to 6.8 wt % [2, 5, 8, 9], which is similar to that in CI chondrites and among the highest in the meteorite samples. About 2/3 of this carbon is in organic matter [1]. The organic matter in Ryugu records the molecular evolution from the Sun's parent molecular cloud chemistry to the asteroidal aqueous alteration [e.g. 7-9]. The Ryugu samples contain organic matter having hydrogen and/or nitrogen isotopic compositions highly enriched/depleted in D and ^{15}N [7]. These distinct isotope compositions of macromolecular organics may have been inherited from the chemistry in the Sun's parent molecular cloud or the cold outer Solar System.

The N/C ratio of the Ryugu's macromolecular organic matter ranges from 0.01 to 0.035 [5]. Thosee N/C ratios of the Ryugu's macromolecular organic matter are within the range of thoseN/C ratios found inof insoluble organic matter (IOM) in carbonaceous chondrites and those inof organic particles from comet 67P/Churyumov-Gerasimenko [e.g., 10]. It is thus suggested that the macromolecular organics with the N/C ratio lower than the solar N/C ratio was present with those having the high N/C ratios in the Sun's protoplanetary disk, and the organics with the lower N/C ratio was incorporated into the Ryugu's parent body and comet 67P/Churyumov-Gerasimenko [10].

We review the results of Ryugu sample analysis and discuss the evolution of organic matter in the early Solar System by comparing with the recent radio and infrared observations of protostars and protoplanetary disks.

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Infrared spectra of isomers of protonated and hydrogenated phenanthridine isolated in solid *para*-hydrogen

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Abstract

Large polycyclic aromatic hydrocarbons (PAH) and polycyclic aromatic nitrogen heterocycles (PANH) have been proposed to be potential carriers responsible for the unidentified infrared (UIR) emission bands in the interstellar medium.[1] The nitrogen atom in PANH induces a blue shift of the CC-stretching mode of the PAH, occurring around 6.3 μm. In addition to PANH, several protonated polycyclic aromatic hydrocarbons (H^+PAH) and the corresponding nitrogen heterocycles (H^+PANH) also exhibit blue shifts.[2] Therefore, the CC-stretching band of the H^+PANH might agree better with the UIB band at 6.2 μm and H^+PANH might be potential candidates that contribute to the UIR bands.

We report the infrared (IR) spectra of two isomers of protonated phenanthridine ($H^+C_{13}H_9N$) and seven isomers of mono-hydrogenated phenanthridine ($HC_{13}H_9N$), produced upon electron-bombardment of a mixture of phenanthridine ($C_{13}H_9N$) and *para*-hydrogen (*p*-H_2) during matrix deposition at 3.2 K. IR spectra of protonated species $C_{13}H_9NH^+$ and 4-$H^+C_{13}H_9N$ were observed. In addition to the hydrogenation on the N atom of $C_{13}H_9N$ to form $C_{13}H_9NH$, mono-hydrogenation at six carbon sites to form 1-, 2-, 3-, 7-, 9-, and 10-$HC_{13}H_9N$, respectively, were also observed. To confirm the spectral identification of hydrogenated phenanthridine, additional experiments on a $C_{13}H_9N/Cl_2/p\text{-}H_2$ matrix were performed; the matrix was irradiated at 365 nm to generate Cl atoms, followed by IR irradiation to generate H atoms via $Cl + H_2 (v = 1) \rightarrow HCl + H$. The H atoms thus generated propagated throughout the matrix and reacted with $C_{13}H_9N$ via quantum tunneling. In these experiments, six hydrogenated phenanthridine species, except the one hydrogenated at the carbon site 3, were clearly observed. Spectral groupings were achieved according to the behaviors of lines upon secondary photolysis at various wavelengths, chosen according to the vertical electronic transitions of various isomers of $HC_{13}H_9N$ predicted with the TD-B3LYP/6-311++G(d,p) method. The spectral assignments were supported via comparison of the experimental results with the vibrational wavenumbers and IR intensities of possible isomers predicted with the B3LYP/6-311++G(d,p) method. All spectra of $H^+C_{13}H_9N$ and $HC_{13}H_9N$ are new.

For $H^+C_{13}H_9N$, major observed lines are at 2.95, 6.22 and 12.53 μm; the CC-stretching band of $C_{13}H_9NH^+$ was observed at 6.22 μm, blue shifted from that of the corresponding PAH, 10-$C_{14}H_{11}^+$. For $HC_{13}H_9N$, major lines were observed at 13.43, 13.16, and 13.55 μm for $C_{13}H_9NH$, 9-$HC_{13}H_9N$, and 2-$HC_{13}H_9N$, respectively. Based on the overall spectral pattern, these protonated and hydrogenated species are unlikely to be the carriers of the UIR bands, characterized by emission bands near 3.3, 6.2, 7.7, 8.6, 11.2, and 12.0 μm.

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Photochemistry of six-membered hydrocarbons in solid parahydrogen

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Photochemical reactivities of cyclic hydrocarbons are interested in natural sciences, biological sciences, and astrochemistry, because the investigation of these ring molecules give us the useful information about the noble or unstable species formation and chemical reactions. In particular, since polycyclic aromatic hydrocarbons (PHAs) are one of the potential candidates for the carrier of diffuse interstellar bands (DIB) [1-3], it is important to understand the UV photochemical behavior of PHAs because interstellar molecules are constantly exposed to strong UV radiation. In this study, we investigate the photochemistry of six-membered hydrocarbons: benzene (Bz) [4], one of the simplest and most widely studied aromatic hydrocarbons, and 1,3-cyclohexadiene (1,3-CHD) [5] and 1,4-cyclohexadiene (1,4-CHD) [6], two double bonding at different position in ring, trapped in solid parahydrogen by a joint use of Fourie transform infrared spectroscopy and density functional theory (DFT) calculations, aiming to compare the photochemical stability, reactivity and photochemical products among three molecules. The mixture of hydrocarbons and parahydrogen were condensed on the cold substrate (4.2 K) cooled down by closed-cycle GM refrigerator. The sample was them irradiated by 193 nm photons of an ArF pulsed laser, and photoproducts were detected by and FT-IR spectrometer. In order to confirm the spectral assignment of reactants and products, DFT calculations were also performed. In the IR spectra of 1,4-CHD in solid parahydrogen after ArF laser irradiation, we observed peaks of 1,3-CHD and Bz as photoproducts. Further irradiation using ArF, we observed the cyclohexadienyl radical, hexatriene derivatives, and small photofragment molecules. Comparing with the photochemical behavior of three six-membered hydrocarbons, the photochemical products and reactions mechanism of three molecules will be discussed.

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Quantitative analysis for the branching ratio of CH_3O and CH_2OH radicals formed from CH_3OH + OH reaction on ice surface

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Complex organic molecules (COMs) with CH_3O incorporated into their structure, such as methyl formate ($HCOOCH_3$) and dimethyl ether (CH_3OCH_3), have been found in various astronomical objects including cold molecular clouds. For these COMs formation, radical reactions on the surface of interstellar dust would play an important role. Recent experiment suggested that the surface reaction of methanol and OH formed promotes the formation of CH_3O-bearing COMs on ice [1]. That is, of the following two reactions, the branch to CH_3O radical formation would be the major.

$$CH_3OH + OH \rightarrow CH_3O \text{ and/or } CH_2OH + H_2O$$

However, while this reaction in the gas phase has been extensively studied [2, 3], little information is available for that on ice surfaces. Since information of branching ratios is needed for constructing better chemical evolution models, we measured the branching ratio of CH_3O and CH_2OH produced by CH_3OH + OH reaction on water ice surface at 10 K.

For trace radical detection, we used a newly developed high-sensitive "Ion Pickup" apparatus. In this method, low-energy Cs^+ ions (~20 eV) nondestructively pickup adsorbates on the ice surface. The adsorbate was then detected as a Cs^+-molecule complex in a quadrupole mass spectrometer, and its mass number was obtained by subtracting the Mass 133 of Cs [1, 4]. Thanks to our various improvements, this apparatus has a sensitivity of ~0.0001-0.001 ML, which is much higher than conventional methods like FT-IR.

The experimental procedure of present study is shown in Figure 1. We first prepared OH radicals on ice surface by UV irradiation at 30 K, where most H atom did not remain on the surface. Then, after UV was turned off, the reaction was triggered by depositing methanol on the ice at 10 K. The radicals formed by this procedure were monitored using Ion Pickup. We also performed experiments with isotopologues (CH_3OD and CD_3OH) to distinguish the products of CH_3O and CH_2OH. Quantitative analysis shown the branching ratio (CH_3O/CH_2OH) of 4.3 ± 0.6 (i.e., CH_3O ~ 80 %) [5].

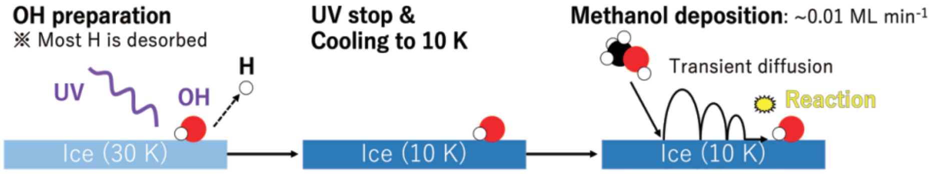

Figure 1: Experimental procedure for the reaction of methanol and OH on ice surface

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Laboratory development for the study of interstellar surface chemistry

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It is suggested that interstellar complex organic molecules (COMs) may give rise to the chemical complexity on planetary surface. These COMs are proposed to be formed on the ice surface of dust grains in molecular clouds. We present the experimental apparatus designed for simulating the environments of the interstellar clouds to study the chemical process underlying the formation of these COMs. The apparatus includes a main ultra-high vacuum chamber with 10^{-10} mbar base-pressure. The experiments will be conducted by feeding gas into the chamber through gas deposition lines, onto the liquid nitrogen-cooled substrate to form an interstellar ice analog. The ice will be irradiated by VUV, with a source equipped to the chamber. Then, mass spectroscopy and FTIR spectroscopy will be used to identified the chemical products. Finally, we present the progress of the manufacturing process as well as the development plan of the apparatus.

Visible light-induced photodesorption of OH radicals adsorbed on water ice surface

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In cold interstellar medium, the OH radical would be one of the most predominant reactive species on ice dust because it is readily produced by the photolysis of H_2O or surface reaction of H and O atoms. At low temperatures, OH radicals can take part in various chemical activities on the ice dust surfaces, while once they are released from the surface, gas phase chemistry like O_2 formation can be enhanced [1]. However, because the OH radical is highly reactive and thus easily consumed by reactions with other adsorbates at higher temperatures, its thermal desorption as intact may hardly happen. Instead, the photodesorption induced by UV and X-ray photons, which often follow the photodissociation of H_2O, has been investigated for a long time. In contrast, visible light has not been considered as the trigger of photodesorption, because both isolated water molecules and OH radicals are transparent in a visible region. Recently, we observed the photodesorption of OH radical on water ice at 532 nm through combining photostimulated desorption (PSD) and resonance-enhanced multiphoton ionization (REMPI), the PSD-REMPI method [2]. According to quantum chemical calculation, the absorption of 532 nm photons is triggered by the OH strongly bonded with surrounding H_2O through three hydrogen bonds, indicating that the photodesorption strongly depends on the adsorption sites of OH on the water ice surface.

In this study, we extended the wavelength of visible light in the range of 410 to 700 nm to measure the photodesorption efficiency of OH radicals on ice surface, which would be contributed by the population of OH adsorption sites and the photodesorption cross section. The multiplication of the population and cross section represents the effective cross section for each wavelength, which was found to explain the trend of photodesorption efficiency as a function of wavelength very well.

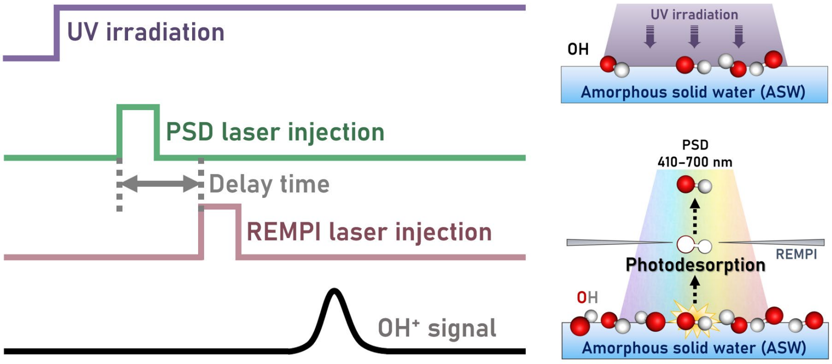

Figure 1: The schematic diagram of OH radicals photodesorb from water ice surface by the visible light.

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Laboratory studies on the infrared emission spectra of fullerene C$_{60}$ thin films

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Fullerene C$_{60}$ has been detected in interstellar objects at late stages of the stellar evolution, such as post asymptotic giant branch (post-AGB) stars, protoplanetary nebulae (PPNe), planetary nebulae (PNe), reflection nebulae, and young stellar objects (YSOs) [1-3]. It is natural to consider that the relative intensity of multiple emission bands of a single molecular species in the infrared (IR) spectra can be exploited as a probe for vibrational temperature of an ensemble of the molecules. Concerning C$_{60}$, variations are observed for the relative intensity of bands for four IR-active vibrational modes of T$_{1u}$ symmetry. The thermal emission mechanism [1] and the UV-induced fluorescent mechanism [2] are proposed. However, the observations do not simply follow either mechanism. There must be another factor to be taken into considerations.

We have conducted laboratory studies on the measurement of IR emission spectra of fullerene C$_{60}$ at elevated temperatures. Using a commercial FTIR spectrometer, power spectra of heated samples of a thin film of C$_{60}$ deposited on a KBr slab were recorded in a range of 300–400 K. Theoretical simulations were performed under the assumption of Boltzmann distributions of molecules in vibrationally excited states up to seven vibrational quanta. Figure 1 depicts an image of contribution of vibrationally excited molecules to the IR emission of bands for T$_{1u}$ modes of C$_{60}$ at ambient temperature.

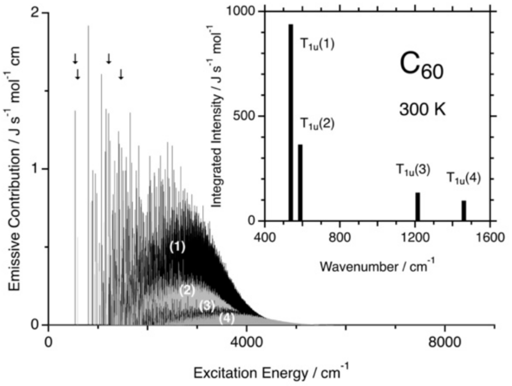

Figure 1: The simulated IR emission intensity of four vibrational T$_{1u}$ modes of the fullerene C$_{60}$ molecule. Contributions from vibrationally excited states including 46 fundamentals and their overtones and combinations with excitations up to seven vibrational quanta are taken into considerations.

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A Laboratory-Demonstrated Model that Explains the Galactic Extended Red Emission: Graphene Exposed to Far-ultraviolet Light

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Extended red emission (ERE) is a broad feature in spectral region 500~900 nm commonly observed in a wide range of circumstellar and interstellar environments [1]. Although the observational constraints for ERE are well established, definitive identifications of the carriers and associated processes complying these constraints remain unanswered. We report a plausible two-step model involving far-UV irradiated single-layer graphene (SLG), considered as large polycyclic aromatic hydrocarbons, to meet these constraints and supported by laboratory experiments. The far-UV-treated SLG, producing structural defects and graphene quantum dots, showed photoluminescence excitation spectrum extending from far-UV to UV–visible region, hence meeting the requirements of far-UV light and high photon-conversion efficiency. Furthermore, a photoluminescence band shifted from ~585 nm to ~750 nm for high-dose-exposed SLG agrees with the observed red shift of the ERE band in regions under a greater far-UV radiation density [2,3]

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In situ electron diffraction analysis of stacking sequences in ice I under interstellar conditions

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Infrared (IR) observations toward interstellar molecular clouds reveal that water ice without a long-range ordered structure (amorphous water) is the dominant solid component in icy dust grains. At high temperatures, amorphous water is crystallized into ice I, which consists of stable hexagonal ice Ih, metastable cubic ice Ic, and their mixed structure. Although the morphology of water ice affects the reactivity of chemical reactions in icy dust grains [1], the selection rule of those different ice structures is not completely understood yet.

In laboratory, interstellar ice analogues are usually prepared by deposition of a water vapor onto a cold substrate (vapor-deposition). Crystallinity of water ice depends not only on the temperature of a substrate but also on the deposition rate of a water vapor [2]. Recently, the formation of crystalline ice is reported even at extremely low temperatures by a method arranged from vapor-deposition (for details, see ref. [3]). However, because the previous study [3] analyzed the ice only by IR spectroscopy, the amount of cubic or hexagonal stacking sequences in the ice is still unknown. *In situ* diffraction analysis is crucial to determine the extent of stacking sequences in ice I.

By using newly developed reflection high-energy electron diffraction (RHEED), we found that the amount of hexagonal stacking sequences in the ice I formed by the new method at 13 K was lower than that in the ice I prepared by annealing vapor-deposited amorphous water at 143 K (Fig. 1) [4]. The formation of less hexagonal stacking sequences in ice I at higher supercooling degree is qualitatively in line with the study of cubic ice Ic formation by using classical thermodynamics theory [5]. In the session, we will introduce further information about the experiment and its astrophysical implications.

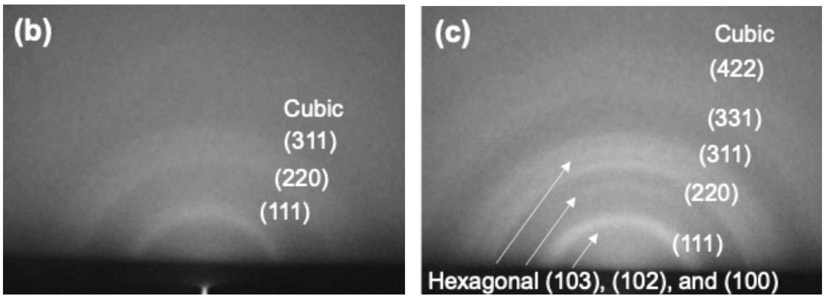

Figure 1: RHEED images of ice I obtained by the new method at 13 K (left), and ice I obtained by annealing vapor-deposited amorphous water at 143 K (right).

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Atomic force microscopy measurement of local contact potential difference of amorphous solid water deposited at 15 and 100 K

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Icy dust particles, which are mineral nanoparticles covered with an amorphous ice mantle primarily composed of H_2O, play an important role in chemical evolution in space. This is because the surface of icy dust surface facilitates a variety of molecular syntheses involving processes such as adsorption, diffusion, reaction and desorption of atoms and molecules [1, 2]. However, it is difficult to say that our understanding of the amorphous solid water (ASW) is sufficiently comprehensive.

ASW films formed by vapor deposition onto a cold surface are known to have negative surface potentials due to spontaneous polarization, which varies depending on the temperature and film thickness [3,4]. However, the mechanisms underlying this polarization, responsible for the surface potentials, remain unclear. Although previous studies that used Kelvin probe measurements have proposed the polarization model of ASW named tilted dipole model, the direct evidence confirming accuracy of this model has not been obtained yet due to limitation of spatial resolution. To overcome this limitation in spatial resolution, we used FM-AFM to measure variations in the negative surface voltage of ASW with nanoscale resolution depending on the surface structures.

We conducted measurements on two types of ASW formed by water vapor deposition at 15 and 100K on a Si (111) 7×7 substrate in ultra-high vacuum conditions. The topographic images of the surface structure showed temperature dependence, attributed to the differences in diffusion length of water molecules on the surface until reaching stabilization at the measurement temperature. We also measured the local contact potential difference between probe tip and 400 measurement points set on ASW surface within a 200 nm x 200 nm are, respectively. On both ASW surfaces, the local contact potential difference varied at each measurement point without correlation with local thickness (topographic height). This suggests that this polarization phenomenon cannot simply attributed to the thickness of ASW but depends on the local structure. Our observations with nanoscale resolution imply that the tilted dipole model is a plausible representation of the spontaneous polarization of ASW.

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Poster 23

Preliminary study of radiation-induced morphological alteration to water ice (Ih)

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A large fraction of amorphous solid water is expected to be crystalline phase in protoplanetary disks (PPDs) [1]. Two variant crystal structures of the water ice are potentially formed around the snow line at PPDs: hexagonal ice (Ih), which is produced above 150 K by condensation of water vapor and/or above 140 K by annealing of amorphous solid water (ASW), and cubic ice (Ic), which is produced above 130 K by condensation of water vapor and/or 130 to 140 K by annealing of ASW [2], depend on the temperature of the snow line.

Cosmic rays from a central star irradiate the upper layer of a PPD where gas and dust are decomposed and altered by the high-energy solar wind [3]. The consequence of the radiolysis depends on the physical state and the composition of the dust. In the case of crystalline water, tiny-cavities are formed due to immediate clustering of myriad vacancies generated by diffusion of hydrogen and oxygen atoms from their lattice sites, which are a direct result of the electron-induced radiolysis of water ice [4]. The tiny-cavities produced by radiolysis can serve as additional surface on the water ices.

It is widely supposed that the surface of water ice works as a catalysis for gas-solid phase chemistry in interstellar environments [5]. To understand radiation-induced alterations to water ice, we observed a time-evolution of tiny-cavities in water ice (Ih) with a liquid-cell transmission electron microscopy (LC-TEM). Figure 1 shows a moment of the time-evolutions of tiny-cavities in the ices around −15 °C obtained by a 200 keV TEM (JEM-2100F). The tiny-cavities were discerned their shapes at the beginning of the observation and then clearly recognized in a period of the observation due to a simultaneous disappearance of the mother ice body. We found that the size, the shape, and the evolution path of the tiny-cavities were changed depend on the thickness of the mother ices that was estimated from 17 to 500 nm.

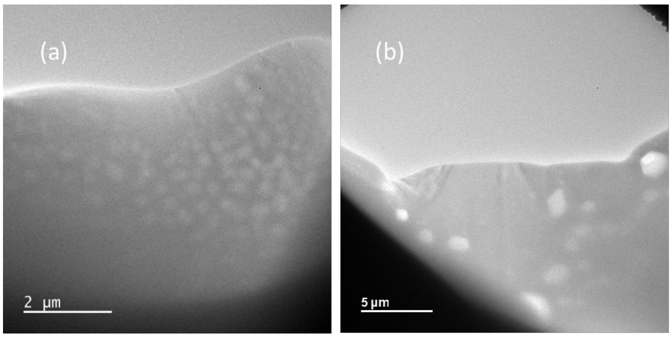

Figure 1: Bright field TEM images of selected frames in each video of tiny-cavities evolution in ice Ih encapsulated between electron-transparent SiN windows. The relative dark fields correspond to ice at a range of the estimated thickness 17 to 35 nm for (a) and 70 to 150 nm for (b). The relative bright fields are possibly filled with gas generated by the radiolysis of the ice.

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In situ cryogenic transmission electron microscopy observation on the formation of hydrogen-ordered hexagonal ices and its astrophysical implications

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Water ice is ubiquitous in molecular clouds, protoplanetary disks, and icy bodies of the outer solar system. In addition to the formation of various molecules on water ice in molecular clouds, water ice also has an important role for the formation of planetesimals in protoplanetary disks. It is therefore essential to clarify how the ice exist (e.g., phase) under such low-temperature and low-pressure environments. To investigate the ice under such environment, here we developed ultra-high vacuum cryogenic transmission electron microscopy [1] and observed water ice and its structural changes [2].

Two types of ice, cubic ice I (ice Ic) and hexagonal ice I (ice Ih), were observed while annealing under the microscope. First, ice was deposited on the 5 nm amorphous SiN_x membrane by controlling the partial pressure of H_2O at 140 K for ice Ic, and 150 K for ice Ih. Then, the ice was annealed at 83-130 K for ice Ic and 120-150 K for ice Ih. During annealing, electron diffraction patterns were acquired to investigate its structural changes.

Many diffraction spots in the electron diffraction patterns appeared with time, some of them do not belong to either ice Ic or ice Ih. To determine the origin of these diffraction spots, we calculated the *d*-spacings and diffraction intensities of several ice polymorphs that form under the experimental conditions. Then we found that the possible origin of these diffraction spots was hydrogen-ordered phases, that the ice Ic or Ih having specific hydrogen positions. We plan to discuss the formation of these ice phases and their impacts on chemical and physical evolution in a planetary system.

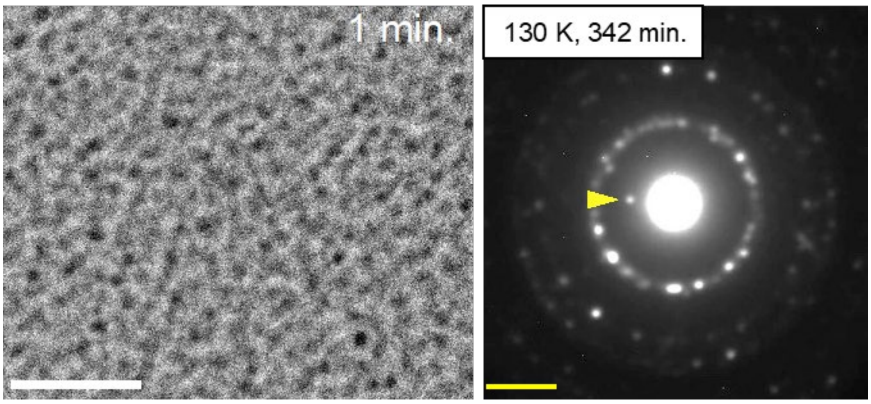

Figure 1: Examples of a TEM image of initial water ice sample of ice Ic crystals (left) and an electron diffraction pattern with a diffraction spot not observed in ordinary ice Ic and Ih (right). The TEM image was taken immediately after the start of annealing (1 min later), and the electron diffraction pattern was acquired by annealing at 130 K for 342 min. The arrowhead on the right indicates the diffraction spot corresponding to *d*-spacing of 6.4 Å, which is not observed in ordinary ice.

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Nuclear quantum effect in the phase transition between Ice VII and ice X

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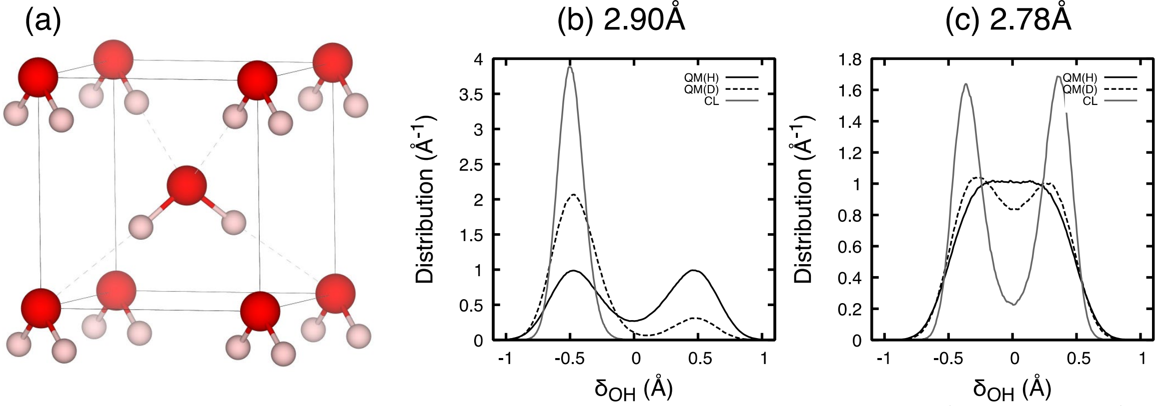
Water is one of the most abundant and essential substances on Earth, playing a critical role in the diversity of nature and natural phenomena, including the existence of life. Despite being composed of a single molecule, H_2O, ice is a complex substance with 17 different stable structures. As a result, it is an important model for studying hydrogen modeling[1]. At room temperature and pressure between 2 and 60 GPa, ice VII is a stable crystalline phase, where the oxygen atoms form a body-centered cubic structure, with the hydrogen atoms being delocalized between the two oxygen atoms (Fig. 1(a)). Infrared spectroscopy has confirmed that above 60 GPa, ice VII undergoes a phase transition to ice X, in which the hydrogen atoms lie midway between the two oxygens[2]. Although the phase transition from ice VII to ice X is a change in the symmetry of the hydrogen atom, the behavior of the hydrogen atom is still unknown due to the difficulty of conducting neutron diffraction experiments under high-pressure conditions. To address the gap, this study uses the path integral molecular dynamics method (PIMD), which can treat the nuclear quantum effect, to theoretically clarify the behavior of hydrogen atoms in the phase transition from ice VII to ice X.

We conducted three types of PIMD simulations to study the impact of the nuclear quantum effect: the simulation for hydrogen atoms (QM(H)), for deuterium atoms (QM(D)), and the classical simulation without nuclear quantum effect (CL). To analyze the phase transition, we used the difference in distance between the two oxygen atoms and the hydrogen atom (δ_{OH}) as a guide. At a lattice constant of 2.9 Å, the hydrogen atoms in the CL simulation were found to be localized on one oxygen atom, while in the QM(H) and QM(D) simulations, the hydrogen atoms were delocalized, and the distribution at $\delta_{\mathrm{OH}} = 0$ Å was increased. Across all simulations at a lattice constant of 2.9 Å, the distribution displayed two peaks, indicating the phase was ice VII. Upon reducing the lattice constant to 2.78 Å, the distribution in QM(H) displayed only one peak, suggesting that the nuclear quantum effect promotes the phase transition. Futher details will be presented in a poster.


(a)

(b) 2.90Å

(c) 2.78Å

Figure 1: The structure of ice VII (a), distribution of δ_{OH} at a lattice constant of 2.90 Å (b) and 2.78 Å (b)

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The cold path to saturation:
hydrogenation of cyanoacetylene towards ethyl cyanide in dark molecular clouds

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

Rovibrational transitions in HCl due to collisions with H_2: spin-free and hyperfine-resolved transitions

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Hydrogen chloride (HCl) is a key repository of chlorine in the interstellar medium. Accurate determinations of its abundance is critical to assessing the chlorine elemental abundance and constraining stellar nucleosynthesis models. To aid in modeling recent and future observations of HCl rovibrational spectra, we present cross sections and rate coefficients for collisions between HCl and molecular hydrogen. Transitions between rovibrational states of HCl are considered for temperatures ranging from 10 to 3000 K. Cross sections are computed using a full dimensional quantum close-coupling (CC) method and a reduced dimensionality coupled-states (CS) approach. The CS results, benchmarked against the CC results, are used with a recoupling approach to calculate hyperfine-resolved rate coefficients for rovibrational transitions of HCl induced by H_2. The rate coefficients will allow for a better determination of the HCl abundance in the interstellar medium and an improved understanding of interstellar chlorine chemistry. We demonstrate the utility of the new rate coefficients in a non-thermodynamic equilibrium radiative transfer model applied to observations of HCl rovibrational transitions in a circumstellar envelope.

Capturing the Essence of Interstellar Icy Grains: Unveiling Computed Binding Energies and Frequency Distributions of Significant S-Bearing Species

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Binding energies (BEs) are crucial parameters to understand the evolution of molecular species in dense clouds, determining whether a species is frozen onto the grain surfaces or free in the gas phase. Nowadays, BEs are usually provided as single point values. However, the predominant amorphousness of icy grains gives rise to a distribution of BE sites and values. Until now, several grain models have appeared in literature, but they lack a comprehensive physical and systematical description. Recently, ACO-FROST, an automatic procedure to simulate realistic icy grains has been released.[1] This code allows us to build up models of amorphous ice up to 1,000 atoms and to simulate a large variety of BE sites (see Figure 1 – left panel).

In the present contribution, the aforementioned procedure was applied to compute BE distribution of high relevant S-bearing species, i.e., H_2S, OCS, CH_3SH. S-species were selected in order to contribute to a long-standing issue in the field: the sulphur depletion problem.[2] BEs were computed at DFT level (B97-3c) and then refined with one of the highest level of theory available (DLPNO- CCSD(T)). The previous reported BE values are overestimated with respect to our new BE distribution,[3] (see Figure 1 – central panel). Besides, frequency distribution was calculated for OCS molecule and compared to the James Webb Space Telescope (JWST) observations[4] (see Figure 1 – right panel). The computed distribution outstandingly reproduces JWST data indicating the robustness of the model studied and thus defining a novel computational tool to predict icy species vibrational features.

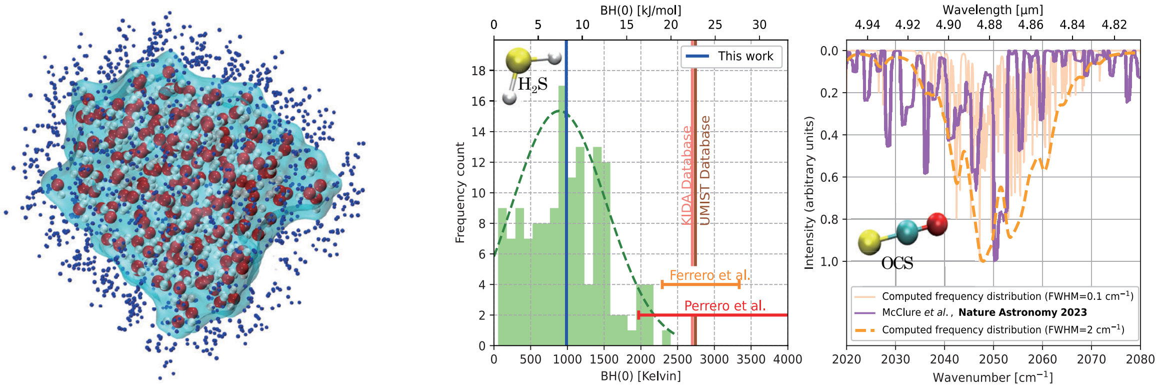

Figure 1: Left panel: 200-H_2O grain covered by a grid of 486 BE sampling sites. Central panel: BE distribution of H_2S compared with previous results. Right panel: Computed frequency distribution for OCS molecule compared with JWST observations.

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Insights into the Third-Body Role of Interstellar Water Ices Mantles in Formamide Formation Route

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Ice mantles covering dust particles provide a solid-state support for chemical reactions in the Interstellar Medium. Such water ice surfaces can act as third bodies by absorbing the energy released by surface reactions [1]. Indeed, the ability of ice mantles to absorb the energy released by surface reactions is a crucial factor that will determine the fate of the newly formed species. These species can either remain adsorbed on the ices or be desorbed and ejected into the gas phase, as is commonly assumed by astrochemical models [2-4]. In this contribution, we analyze the third-body role of water ice mantles for a particular reaction: the radical-radical coupling between NH_2 and HCO leading to the formation of formamide. This mechanism presents a low energy barrier and is largely exothermic [5]. Its potential energy surface has been characterized on an amorphous water ice model using static quantum chemical methods. Ab initio molecular dynamics simulations have been performed to elucidate how the nascent reaction energy is dissipated through the amorphous water ice model. Results indicate that the energy release by the reaction is effectively absorbed and dissipated by water ices, and therefore, the energy reaming on the newly formed formamide is not large enough to cause its ejection into the gas-phase.

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Cracking the Puzzle of CO_2 Formation on Interstellar Ices

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The formation of an ice layer on top of interstellar dust grains is a central topic in astrochemistry. The chemical composition of interstellar ices varies over time [1], and the dominance of polar or apolar fractions in them is important for several surface properties, like adsorption, diffusion or reaction. Among the most abundant components of interstellar ice we find H_2O, CO, CH_3OH or CO_2, to give some examples. These molecules can be formed *in situ* on interstellar ices, as it is the case of H_2O or CH_3OH, or can land on the ices after formation in the gas, like CO. Experiments show that CO_2 mainly forms *via* surface reactions (see, for example [2]), e.g. the $CO + OH \rightarrow CO_2 + H$ reaction. In this talk I will review our recent calculations on such reaction [3]. I will cover the reactivity on a CO and H_2O ice, showing that the reaction does not proceed directly in neither of them. In reality, the reaction stops at the very stable HOCO radical that may be later transformed into CO_2 via a H abstraction reaction. The H_2O ice is found to be a better substrate for the formation of HOCO, which can be behind the higher abundance of the polar component of CO_2 found in astronomical observations, in comparison with the apolar one [4].

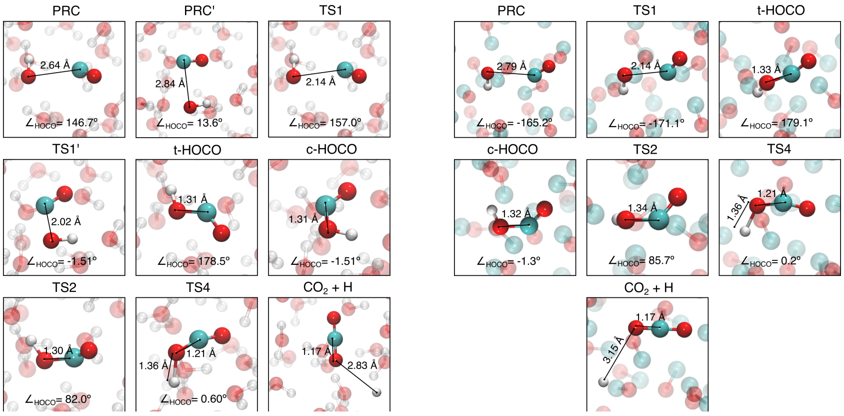

Figure 1: Stationary points in the potential energy surface for the $CO + OH \rightarrow CO_2 + H$ reaction on water (left) and CO ice (right).

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Studying shell structure in CO outflows in the eDisk survey

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In star formation, jet and outflows play a key role, as they extract angular momentum from the protostar-disk system while injecting energy and momentum into the surrounding cloud and envelope [1]. In many sources, evidence for variation in the mass-loss rate of the protostar is seen, most commonly in the form of series of knots along the axis of the jet, which are thought to be caused by internal shocks in the jet due to variations in the jet velocity. Since the accretion rate and mass-loss rate of protostars are thought to be closely related, these variations in mass-loss rate are therefore thought to trace variations in the accretion rate of the protostar. As well as knots in the jet, variation in the mass-loss rate has been seen in the form of wide-angle shell structures in molecular outflows, such as in the HH 46/47 outflow, which are believed to trace the entrainment of ambient gas by a series of outbursts in a wide-angle wind from the protostar and disk[2][3].

We take advantage of the high-resolution 12CO data obtained in the ALMA Large Program "eDisk" to search for similar shell structures in molecular outflows from low-mass protostars. Out of the 19 sources, 6 sources seem to show some level of shell structure in their outflows similar to that seen in previous studies. For three of these source: CB68, GSS30 IRS3, and IRAS32, we were able to fit the shell structure seen with a model which assumes that the shells are caused by previous outbursts in the outflow which entrained ambient gas, as was seen in HH46/47. In CB68, shell models fitted to the data suggest two previous outbursts occurred ~160 yrs ago and ~300 years ago respectively. In Figure 1, the position-velocity diagram along the axis of the outflow shows the two shell models which were fitted. For the other 3 sources, where shell structure was detected, it wasn't possible to fit the shells observed with the entrained ambient gas model, and so alternative explanations are required for the structure detected.

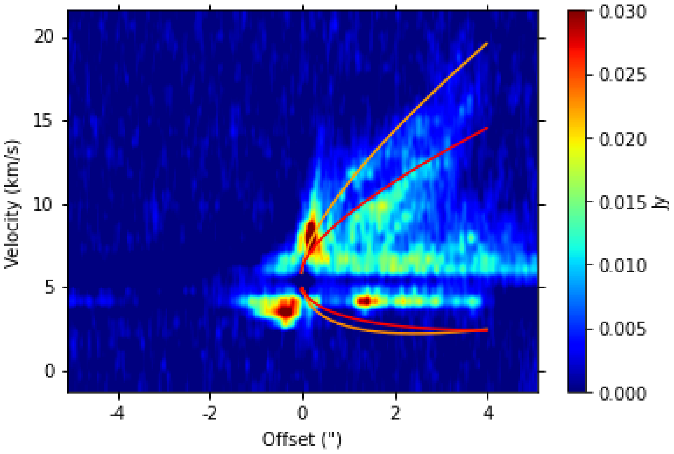

Figure 1: The position-velocity diagram along the outflow axis of CB68 showing the two shell models fitted to the data, tracing the outbursts launched ~160 years ago (red) and ~300 years ago (orange).

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ALMA Unbiased Spectral Line Survey of an Organic-poor High-mass Protostar in the Large Magellanic Cloud

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Because cosmic metallicity is increasing in time with the evolution of the Universe, understanding interstellar chemistry in low metallicity environments is crucial to unveil chemical processes in past metal-poor galaxies and the early Milky Way Galaxy.

We here present a high-sensitivity spectral line survey towards a high-mass protostellar object located in a nearby low-metallicity galaxy, the Large Magellanic Cloud (LMC). The survey was conducted by the Atacama Large Millimeter/submillimeter Array (ALMA). The frequency coverage of the survey is from 333 to 364 GHz and the spatial resolution is about 0.4 arcseconds, which corresponds to 0.1 pc at the distance of the LMC. The target source, ST11, is reported to harbor a hot molecular core [1].

As a result of the spectral line survey, we have obtained a high-quality wide-band submillimeter spectral and continuum data for this low-metallicity high-mass protostar. Its physical and chemical characterstics are investigated in detail using the detected various molecular lines. The high gas density (>10^6), high temperature (>100 K), and small source size (<0.1 pc) observed in ST11 suggest that its physical characteristics are consistent with those of known normal-metallicity hot cores in the inner Galaxy. However, unlike typical hot cores, the source does not show any emission line of complex organic molecules such as CH3OH even after the stacking analysis of multiple lines. Only small organic molecules such as H2CO are detected. On ther other hand, inorganic molecules such as SO and SO2 are abundantly detected in the source. Several hydrogen recombination lines are also detected.

In this poster, we present the results of the initial analysis of the spectral line survey, and discuss the nature of this organic-poor high-mass protostar.

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Millimeter emission in the methanol maser flare source G24.33+0.14

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In September 2019, a sudden brightening of the 6.7 GHz methanol maser line (methanol maser flare) was reported for the high-mass young stellar object (HMYSO) G24.33+0.14. It is suggested that this event would be caused by a transient mass accretion burst event in HMYSOs as reported for other HMYSOs, S255IR NIRS3, NGC6334I-MM1, and G358.93-0.03-MM1. Among them, G24.33+0.14 seems to be a unique case because it has been identified a past maser flare event with an interval of 8-year. In the case of another recent methanol maser flare event in G358.93-0.03-MM1, several methanol transitions from centimeter to submillimeter wavelengths also showed flare activities. To study time-variability of methanol maser lines at millimeter wavelengths in G24.33+0.14, we conducted target-of-opportunity (ToO) observations using the Atacama Large Millimeter/submillimeter Array (ALMA) as a director's discretionary time (DDT) [1]. We observed the millimeter continuum and molecular lines at Band 6 (217-230 GHz) toward G24.33+0.14 in the pre-flare phase in August 2016 (Cycle 3) and the mid-flare phase in September 2019 (Cycle 6 DDT) at resolutions of about 300 milliarcseconds.

We identified 3 continuum sources in G24.33+0.14, where the brightest source, C1, is associated with the 6.7 GHz maser emission. The continuum sources show only marginal increases in flux density with a mean flux ratio (Cycle 6/Cycle 3) of 1.16. In addition, we also compared the total 26 millimeter transitions from 13 molecular species between the Cycle 3 and Cycle 6 data and found similar levels of flux differences of ~12%. Considering the flux calibration accuracy of ALMA, 10%, these differences would not be significant. On the other hands, we investigated 8 methanol lines identified in our observing band including a ^{13}C isotopologue and a torsionally excited transition and found an average flux ratio (Cycle 6/Cycle 3) of 1.23+/-0.13. There is a possible tendency that the higher excitation lines show a larger flux increase in Cycle 6. If this systematic trend is real, it would suggest radiative heating close to the central HMYSO caused by the accretion event which could expand the size of the emission region and/or change the excitation conditions.

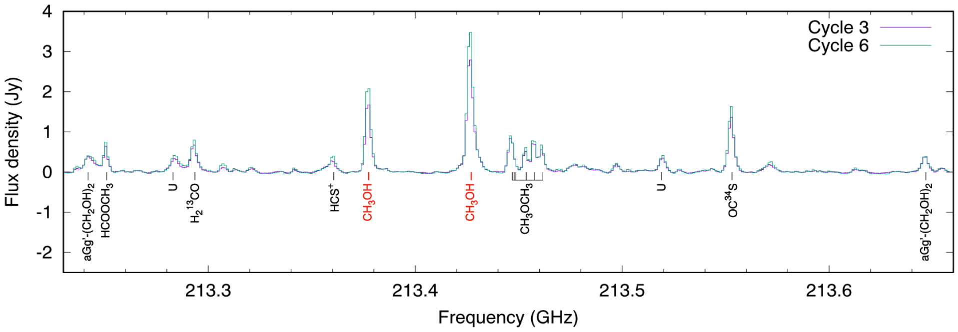

Figure 1: A sample spectrum of G24.33+0.14 [1].

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50 au-scale Chemical Composition of R CrA IRS7B-a: FAUST

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The diversity of chemical compositions among Solar-like protostars has been recognized by recent high angular resolution and high sensitivity observations of ALMA. R CrA IRS7B is a low-mass protostar in the Class 0/I stage in Corona Australis (*d* = 152 pc: Galli et al. 2020). The protostar is thought to be strongly irradiated by a Herbig Ae star R CrA at a distance of about 4000 au from IRS7B-a. In fact, the temperature of extended molecular gas component around the protostar is estimated to be about 50 K, which is higher than that of typical dense molecular clouds, by H_2CO observation with APEX and SMA (Lindberg et al. 2012). Moreover, CCH and CN, which are characteristic molecular species in the photodissociation region, are strongly detected at the protostar position by spectral line survey observations ASTE and APEX telescopes (Watanabe et al. 2012, Lindberg et al. 2014).

We have observed the protostar IRS7B at a scale of 50 au, as one of 13 target sources of ALMA large program FAUST (Fifty AU STudy of the chemistry in the disk/envelope system of solar-like protostars). The ALMA observation detected two continuum sources as Ohashi et al. (2023) reported. SO and $C^{18}O$ are associated with the strongest continuum peak IRS7B-a and show a rotation motion of a Keplerian disk. On the other hand, the emission lines of CH_3OH and CS are weakly detected and no complex organic molecules (COMs) found in Hot Corinos are detected at IRS7B-a. One possible origin of the deficiency of COMs is that the formation of COMs is suppressed due to inefficient adsorption of molecules under the high-temperature environment by strong UV radiation during the starless phase. Moreover, we found that carbon-bearing sulfur molecules, such as CS, H_2CS, and OCS are deficient in IRS7B-a compared with a typical Hot Corino source IRAS 16293-2422 while the abundance of SO_2 relative to SO is similar to each other. In this poster, we will discuss the chemical characteristics in this source at a scale of 50 au.

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Amides inventory towards the G+0.693-0.027 molecular cloud

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Interstellar amides, species that contain peptide-like bond, have attracted significant attentions as they are potential precursors for a wide variety of organics essential to life. However, detection of several amides from the same regions are still relatively sparse and they are mostly biased towards the physical conditions of star-forming regions (e.g. [1-3]. The chemical networks that include amides may therefore lack of further constraints to elucidate the chemical link between these species and the interplay with the physical conditions especially at earliest stage of star formation.

In this talk I will report the detection of a series of amide species, including $HC(O)NH_2$, $CH_3C(O)NH_2$, CH_3NHCHO, and $NH_2C(O)NH_2$ towards the chemically rich Galactic Centre molecular cloud G+0.693-0.027 [4]. From the comparison with other sources as well as works from laboratory experiments and chemical models, we find constant abundance ratios independently of the evolutionary stages, suggesting that amides related chemistry is triggered in early evolutionary stages of molecular cloud and remain unaffected by the warm-up phase during the star formation process.

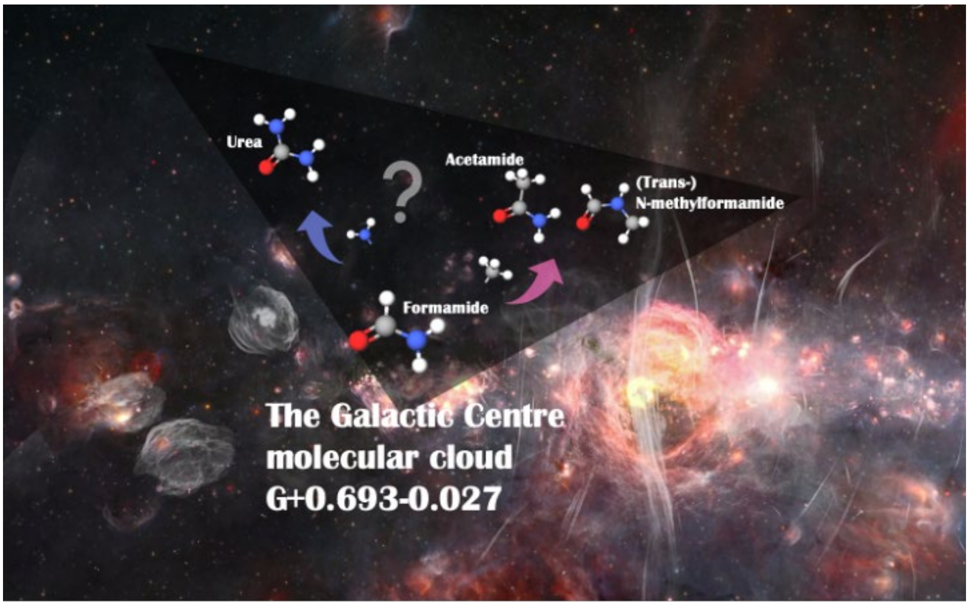

Figure 1: Amides species detected towards the molecular cloud G+0.693-0.027 as a result of the deep unbiased spectral survey conducted with the Yebes 40m and IRAM 30m telescope.

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Detection of 13C17O line emission in the disk around the young outbursting protostar V883 Ori by ALMA observations

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Understanding the spatial distribution of gas and mass evolution in protoplanetary disks are essential for elucidating the formation and evolution processes of planetary systems. Therefore, a lot of statistical observations of the disk gas distribution using 13C16O and 12C18O emission lines have been carried out (e.g., [1]). However, if these emission lines are optically thick, the disk gas mass will be underestimated. Here, by using the 13C17O emission line, which is the rarest and thus most optically thin among the stable carbon monoxide isotope species, it becomes possible to measure the gas mass with higher precision, including disk midplane. In recent ALMA observations, the 13C17O emission line was detected for the first time in two protoplanetary disks (HD 163296: [2]; HL Tau: [3]), and the estimated disk masses are about 2-10 times heavier than those estimated from previous 12C18O emission line observations. In this presentation, we report the detection of the 13C17O J=3−2 emission line by ALMA observations (Band 7 (~0.9 mm), spatial resolution: ~0.3-0.4”) in the disk around the Class I protostar V883 Ori, a typical young outbursting FU Ori type star. We found that the 13C17O line emission has ring-like distribution within the disk surrounding the optically thick dust emission (radius r~40 au) near the protostar, similar to the 12C17O line emission line obtained in past observations ([4]). In addition, the 13C17O line emission extends further to the outside of the disk (r~200 au) compared with H2O and CH3OH line emission (r~80 au). We derived the column density and the total gas surface distributions in the disk radial direction, and discuss the gas to dust mass ratio G/D, Toomre Q values (= Index of gravitational stability in the disk), and 12C/13C isotope ratio in the V883 Ori disk. We also conduct the comparative discussion of the 12C/13C ratio between CO (this study) and complex organic molecules (Yamato, Notsu et al. in prep.).

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Complex Carbon Isotope Fractionation in a Protoplanetary Disk

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Chemical information is vital to understanding material evolution during planetary system formation. Specifically, isotopologue ratios are of interest because they could conserve the formation history of molecules, linking the planetary system bodies and their birth environment, protoplanetary disks. Hereafter, we focus on the carbon isotope ratio, $^{12}C/^{13}C$, in the gas phase of the nearest protoplanetary disk around TW Hya. Recent measurement suggests that significant carbon isotope fractionation occurred in this disk while the $^{12}C/^{13}C$ ratio in the local interstellar medium (ISM) is ~70. Zhang et al. (2017) and Yoshida et al. (2022) found significantly low $^{12}C^{18}O/^{13}C^{18}O$ and $^{12}CO/^{13}CO$ of 20-40. On the other hand, $H^{12}CN/H^{13}CN$ is estimated to be ~86 by Hily-Blant et al. (2019).

In this talk, we present the first spatially-resolved detection of ^{13}CN with the Atacama Large Millimeter/sub-millimeter Array. By combining archival ^{12}CN observations, we derived the $^{12}CN/^{13}CN$ ratio to be ~70 with non-local thermal equilibrium (non-LTE) modeling. Additionally, we found tentative evidence of a dip of $^{12}CN/^{13}CN$ at ~100 au, where the ratio decreases to ~50.

Different molecules exhibit different carbon isotopologue ratios in the TW Hya disk. In terms of the molecular column densities, the main carbon carrier in the gas phase is CO. Therefore, if the bulk carbon isotope ratio is the same as the ISM value, there are significant amount of hidden ^{12}C in the solid phase. This might be caused by an isotope exchange reaction between CO and carbon ions under the environment where the carbon-to-oxygen ratio (C/O) is larger than unity in the past. The higher isotopologue ratios found in other molecules would be explained by the isotope exchange reaction and/or vertical variation of the C/O ratio. Indeed, our non-LTE modeling implies that the CN line traces the disk atmosphere rather than near the midplane where CO isotopologue measurement traces. This study sheds light on complex carbon isotope fractionation patterns, requesting a more detailed understanding of the isotope chemistry.

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Molecular Formation in Low-Metallicity Hot Cores

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The chemical complexity in low-metallicity hot cores has been confirmed by observations. We investigate the effect of varying different physical parameters, such as temperature, density and cosmic ray ionization rate (CRIR), on the molecular abundance evolution in the low-metallicity hot cores using UMIST gas-phase chemical model. CRIR has the strongest effect on the molecular abundances. The resulted molecular abundances were divided into three categories with different trends in time evolution. We compare our results with the observations of hot cores in Large Magellanic Cloud (LMC). Our model fits the best with the observations at a time around 10^5 years after the evaporation of ices and at the CRIR of 1.36×10^{-16} s^{-1}. The resulted abundances of the oxygen-bearing Complex Organic Molecules (COMs), such as CH_3OH, $HCOOCH_3$ and CH_3OCH_3, don’t fit with observations in the same physical condition and may locate in different physical environment. Our results suggest that investigating the CRIR value is crucial in predicting the molecular evolution in the LMC hot cores.

Theoretical investigation of the formation pathways of (Z)-1,2-ethenediol and glyceraldehyde

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

A set of reactions leading to formation of (Z)-1,2-ethenediol and its evolution to glyceraldehyde both in the gas phase and on grain surface has been considered. We model grain surface reactions using a two-water molecule cluster model. We report possible formation pathways of (Z)-1,2-ethenediol from simple radical species and discard enolization of glycolaldehyde. The addition of the OH radical to vinyl alcohol furnishes two stable species, that following H-insertion and abstraction reactions, yield cis-ethyleneglycol and (Z)-1,2-ethenediol under ISM conditions. Formation of L and D-glyceraldehyde is also proved successful from (Z)-1,2-ethenediol and glycolaldehyde.

This work provides an efficient and cost-effective view of the formation of key prebiotic species in the RNA-world scheme. Further work on the OH addition to vinylol is currently been performed, focusing on the improvement of the ice-slab and its relationship with the stereoselectivity of the formation of 1,2-ethenediol.

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Chemistry of Forming Molecular Clouds: Comparison with Molecular Absorption Lines

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Molecular clouds are formed by the compression of atomic gas by interstellar shockwaves. This process is intensively studied using MHD simulations in recent years (e.g. [1]). While these studies include the formation and destruction of major coolants (e.g. O atom, C+, and CO), they do not include less abundant molecules (e.g. carbon-chains) that are observed and used for chemical diagnosis of molecular clouds. So far more than a hundred molecular species are detected in interstellar clouds, and their abundances and spatial distributions are used to investigate the physical conditions and evolutionary stage of clouds.

We aim to fully understand the chemistry in the molecular cloud formation process, including the less abundant molecules for the chemical diagnosis. In the present study, we investigate the chemistry in the shock-compressed layer of Av ≤ a few mag, which corresponds to diffuse clouds, as a first step. We perform 3D MHD simulations of converging atomic gas flow. We analyze the results to derive the 1D mean flow, along which we solve the detailed chemical reaction network. Compared with previous studies on 1D shock model of cloud formation (e.g. [2], [3]), we cover a wider range of shock parameters such as initial gas density, velocity, and the angle between the gas flow and magnetic field.

We derive the column densities of various species such as HCO+ and C3H2 along the mean flows and compare them with the observations of molecular absorption lines of diffuse clouds observed toward field stars and quasars (e.g. [4]). The column densities vary among the shock parameters, depending on density structures of post-shock regions and timescales of Av. They show reasonable agreement with the observations. We also investigate the dependence of chemistry on cosmic-ray ionization rate, elemental abundance, and PAHs.

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From Stardust to Life: Decoding the Role of Ionic Minerals on the Formation of Prebiotic Molecules

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Interstellar grains and cometary and meteoritic seeds have undoubtedly been found to be key for the formation of interstellar simple and complex organic molecules (iCOMs) [1]. To this date, over 200 molecular species have been identified in our galaxy and beyond [2]. Many studies have focused on identifying the effect that the interstellar bodies play on the formation process of these molecules; however, computational studies have mainly focused on the role of the icy surfaces that usually surround them, for at initial stages of planetary formation, these have been shown to provide surface sites where primordial molecules adsorb, diffuse and eventually react.

In our study, the vast diversity of materials present in the currently analysed stellar objects and the predicted presence of liquid water and exposed mineral surfaces in the latter stages of planetary evolution [3] led us to assess how the solid surface of interstellar, cometary and meteoritic grains interact with the molecular species in the interstellar medium. While the former are usually composed of silicates and pyroxenes of different compositions, *ca.* 275 different minerals have been found to constitute the latter two [4]. In order to thoroughly study this variety of surface compositions and interacting molecular species, we propose a novel and unexplored approach to automatically investigate, using state-of-the-art quantum chemistry simulations, how most molecules in the observed universe interact with the known surface compositions. This thorough analysis will lay down the path to rationalise the abundance of certain molecular species in meteoritic samples, as well as provide a foundation for the investigation of how very complex molecular species, such as amino acids and sugars, are formed along the planetary formation stages.

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Gas-Grain Model for Carbon Isotope Fractionation of COMs in Star-Forming Cores

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Understanding the isotopic composition of ice molecules in star-forming cores is a powerful tool for investigating the origin of organic molecules in solar system objects. Recent high-resolution ALMA observations have measured the carbon isotopic ratios ($^{12}C/^{13}C$) of Complex Organic Molecules (COMs) in the Class 0 low-mass protostellar object IRAS 16293-2422B. The measured isotopic values are comparable to the average values in the local interstellar medium or show lower values, that is enriched in ^{13}C. Several model calculations , observations, and laboratory experiments suggest that COMs are formed on the dust grain surface during star-formation. However, there are no model calculations of carbon isotope fractionations of COMs, and the origin of observed fractionations is not well understood.

In this study, we use a physical model of a star-forming core undergoing gravitational contraction, and performing chemical reaction network calculations considering three phases: the gas phase, the grain surface, and the ice mantle. And then we systematically investigate the carbon isotopic fractionations of COMs including formation of icy COMs prior to star formation and subsequent their sublimation into the gas phase following star formation.

Before the protostar formation, the $^{12}C/^{13}C$ ratios of icy small carbon species exhibit bimodal profile: the derivative species from CO are slightly enriched in ^{13}C, while those succeeded from C and C^+ are depleted in ^{13}C owing to isotope exchange reactions. Icy COMs, originating from simpler species, also show this bimodality or deviation from it due to mixing. Sublimated COMs reflect the $^{12}C/^{13}C$ ratios of their icy counterparts. However, parts of COMs originate from radical and ionised species at higher temperature ($T > 20$ K), which change the $^{12}C/^{13}C$ ratios of the molecules from that of their ice in the prestellar phase. Eventually, in our base model COMs exhibit more fractionated rather than the observed value. The additional Eley-Rideal (ER) reactions, which is a grain surface reaction having occurred at shorter timescales relative to isotope exchange reactions, lead to formation of COMs originated from less fractionated atomic carbon.

Consequently, the ER reactions mitigates isotope fractionation, and roughly reproduces the non-fractionated observed values. Nonetheless, further investigation is necessary to reproduce the observed values more comprehensively.

The impact of high-mass protostellar accretion bursts on the physical conditions in the ISM in high-mass star forming regions

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High-mass protostellar accretion bursts are rare and energetic events which drive increased radiation. Due to the scarcity of studied events their impact on the surrounding ISM is not well documented. However, very recently a handful of accretion events have been investigated and clear evidence of the effects of irradiation has been observed in both the 10-1000 AU regions within the disk of the accreting protostars, out to influencing the physical conditions of other protostars 1000s of AU away. In this contribution we present evidence of the affects of high-mass protostellar bursts on the ISM regions of high-mass star formation.