

# Periodic Dust Formation around WR 140; Dust Properties Examined by the Multi-Epoch Mid-Infrared SED Analyses

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Massive stars are expected to play an important role in predominately supplying metal elements and dust particles into the interstellar space in the early universe due to their short lifetime in the main sequence. The amount of newly formed dust in the ejecta of a supernova obtained from the observational results, however, remains only in a range of  $10^{-3}$ - $10^{-5}M_{\text{sun}}$ , which is much smaller than the amount of dust needed for a SN to form to account for the dust content in the early universe. Recent observations of dust-forming type-Ib supernova 2006jc made with AKARI and Spitzer have shown that the newly-formed dust in the SN ejecta is also only in the range of  $10^{-4}$ - $10^{-5}M_{\text{sun}}$  (Sakon et al. 2009; Mattila et al. 2008), but they recognize the presence of pre-existing circumstellar dust possibly formed in the mass loss wind associated with the events prior to the SN explosion. Recent studies reveal that many of the Wolf-Rayet stars form in binary system and that around 10% of WR stars may form carbon-rich dust in their wind-wind collision zone whenever the secondary passes by the periastron point of the primary. Therefore, whether or not such WR binary systems should have made significant contribution toward supplying dust particles in the early universe has to be verified from the observational point of view. In this presentation, we present the results of the multi-epoch Mid-Infrared observations of a long period ( $P=7.93$ years; Williams 2011) colliding-wind Wolf-Rayet binary system WR140 with Subaru/COMICS. The observations have been carried out over 3 years since after the last periastron event in 2009. The properties of dust in the expanding concentric arc structures (see Fig. 1) formed during the 2001 and 2009 periastron events are examined based on the mid-infrared SED analyses.

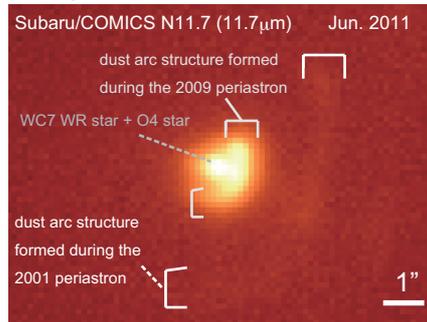


Figure 1: Subaru/COMICS N11.7 band image of WR140 on June 2011 (orbital phased =0.3)

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# Growth of Dust Aggregates in Protoplanetary Disks and Reexamination of Particle Interaction model

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Dust growth is the first step of planet formation in protoplanetary disks. Dust growth also influences temperature structure and chemical reactions in protoplanetary disks. However, we still have a large uncertainty in the dust growth process. This uncertainty mainly comes from unknown factors in dust internal structure and collisional outcomes. The dust structure and the collisional outcome would be closely related with each other. In recent years, many theoretical studies on aggregate collisions and growth have been done. In the present talk, we introduce remarkable results in these theoretical studies, mainly focusing on numerical simulations of dust collisions done by our group. We obtained the following results from our numerical simulations. (1) Icy dust aggregates can grow for high-speed collisions with up to 60m/sec [1]. (2) Dust aggregates compressed with collisions have a structure with the fractal dimension of 2.5 [2,3,4] (also see Fig1). (3) Because of the low fractal dimension of compressed aggregates, collisional compression is not effective, which makes the bulk density of dust aggregates extremely low ( $\sim 10^{-5}$  g/cm<sup>3</sup>)[3,5]. These rather surprising results in our numerical simulations are dependent on the interaction model between sub-micron constituent particles of dust aggregates. We also have started the reexamination of the particle interaction model, by performing molecular dynamics simulation of particle collisions. We report the preliminary results of our molecular dynamics simulations, too. Our preliminary results support the particle interaction model in the previous studies [6].

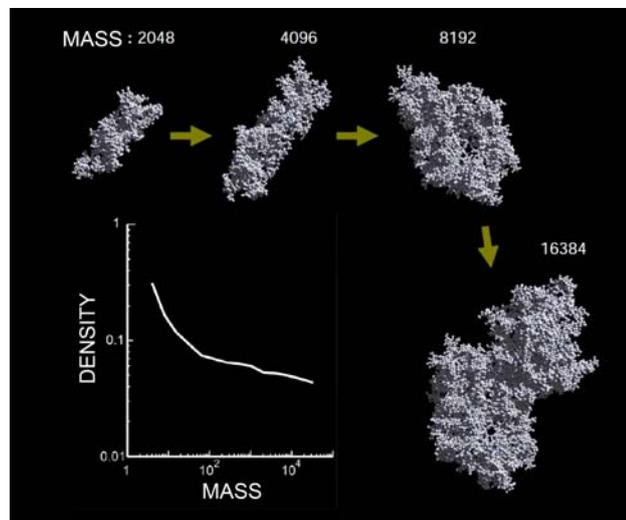


Figure 1: Structure and the bulk density of growing dust aggregates in numerical simulations[3].

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# Observations of Interstellar Ices

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The icy grain mantles in dense interstellar and circumstellar environments are formed by a complex interplay of chemical and physical processes. Key questions on the formation and evolution of the ices must be answered by the combination of observations, chemical modeling, and laboratory experiments. Recent infrared (2-30 micron) spectroscopic surveys of large samples of Young Stellar Objects (YSOs) [1] and background stars tracing quiescent cloud material [2] have shown that the ice abundances and absorption band profiles vary considerably as a function of environment. Using laboratory spectra in the identification process (Figure 1), it is clear that a rather complex mixture of simple species (CH<sub>3</sub>OH, CO<sub>2</sub>, H<sub>2</sub>O, NH<sub>3</sub>, CO) exists even in the quiescent cloud phase. In particular, our discovery of frozen CH<sub>3</sub>OH in some isolated dense cores, and its absence in others, show that local physical conditions (CO freeze out) and time scales (CH<sub>3</sub>OH formation) are key factors in the chemistry before star formation occurs. Sublimation and thermal processing of the ices are dominant processes during the YSOs evolution. The identification of several ice absorption features is still disputed. I will outline laboratory work needed to further constrain the ice band identification as well as the thermal and chemical history of the carriers. Such experiments will also be essential to interpret future high spectral resolution SOFIA and JWST observations.

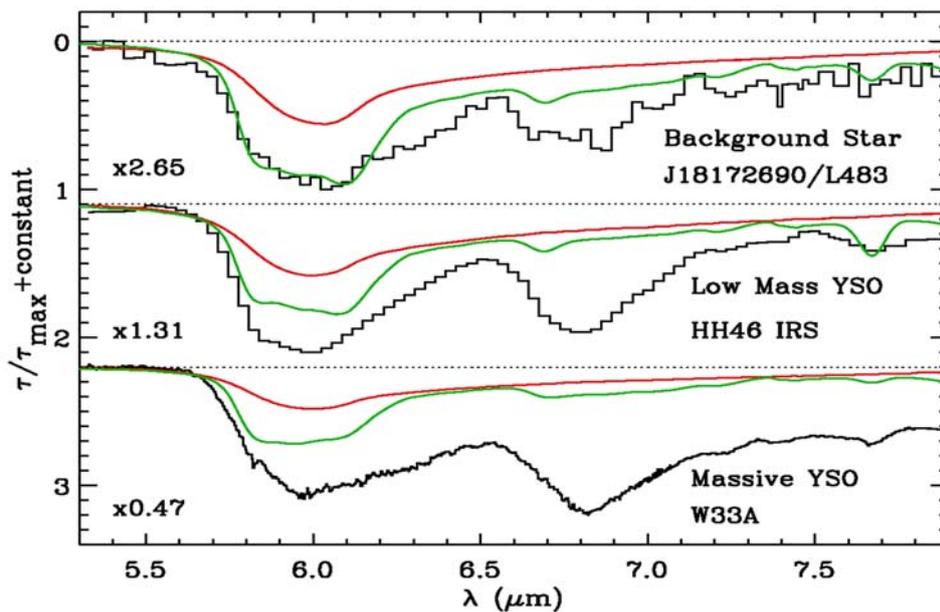


Figure 1:

Mid-infrared spectra of a star tracing quiescent cloud material (top), a low mass YSO (middle) and a massive YSO. For each source, the smooth red line is a laboratory spectrum of pure amorphous H<sub>2</sub>O ice at 10 K. The green line below that includes laboratory spectra of frozen H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>4</sub>, CO<sub>2</sub>, NH<sub>3</sub>, HCOOH, and H<sub>2</sub>CO. Clearly, a significant fraction of the absorption remains unexplained.

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## Ice chemistry in the Magellanic Clouds

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Recent advances in infrared observational instruments enable us to detect spectral information of young stellar objects (YSOs) in extragalaxies. Star-/planet-formation activities can occur in various types of galaxies which differ in various points such as size, shape, and environment. In order to understand the diversity of materials in the universe, it is very important to investigate how galactic characteristics affect the properties of materials around YSOs.

The Large and Small Magellanic Clouds are the nearest galaxies to our Galaxy (~50 kpc for LMC, and ~60 kpc for SMC). Metallicities of the LMC and the SMC are known to be approximately 1/2 and 1/5 compared to the solar neighborhood. Thus, YSOs in the Magellanic Clouds enable us to investigate how the different metallicity environments affect the properties of circumstellar materials. Chemical evolution of the universe is, as a first-order approximation, the evolution of metallicity. In this respect, it is especially important to investigate YSOs in low-metallicity environments.

For the last few years, it has been pioneer days for spectroscopic studies of YSOs in the Magellanic Clouds. A number of embedded YSOs are spectroscopically identified in the LMC and SMC, and their infrared ice features are investigated in detail (e.g., [1], [2], [3]).

In this presentation, I'm going to discuss the properties of circumstellar ices around high-mass YSOs in the LMC and SMC based on infrared spectroscopic data obtained with the *AKARI* satellite. It is shown that ices around YSOs in the Magellanic Clouds possess different properties in terms of molecular abundances and column densities for such major species as water, carbon dioxide, and carbon monoxide. In addition to the observational discussions, I'm going to present the preliminary results of numerical simulations on dust surface reactions under the unique environment of the Magellanic Clouds. The effect of galactic environment on the ice chemistry will be discussed from the point of view of observations and chemical calculations.

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## Systematic study of interstellar ices in nearby galaxies

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Many important spectral features are included in a near-infrared (IR) wavelength range, which enable us to investigate the interstellar environments of galaxies. In particular, spectral absorption features due to interstellar ices, especially H<sub>2</sub>O and CO<sub>2</sub> ices, provide us crucial information on the present and past interstellar environments, and thus the evolutionary histories of galaxies. More specifically, we can derive information on temperature, chemical condition, and radiation history of the interstellar medium from ices. Before AKARI, however, few detections of ices were reported for nearby galaxies. The AKARI's unique capability of near-IR spectroscopy with high sensitivity enables us to systematically study ices in nearby galaxies.

We explored many near-IR spectra (2.5 – 5.0 microns) of the 211 pointed observations, which were carried out within the framework of the AKARI mission program, "ISM in our Galaxy and Nearby galaxies (ISMGN)". As a result, out of 122 nearby galaxies, we have significantly detected H<sub>2</sub>O ice from 36 galaxies and CO<sub>2</sub> ice from 9 galaxies. It is notable that the ices are detected not only in late-type galaxies but also in early-type galaxies. We have evaluated the column densities of the ices, visual extinctions ( $A_V$ ), and spectral feature intensities of polycyclic aromatic hydrocarbons (PAHs) and Br $\alpha$  from the spectra. Then we find a global correlation between the column densities of the H<sub>2</sub>O ice and the Br $\alpha$  intensities, but no correlation between those and  $A_V$ . In this presentation, we show the results of our systematic study on ices in nearby galaxies, and discuss their physical implications for the interstellar environments of the galaxies.

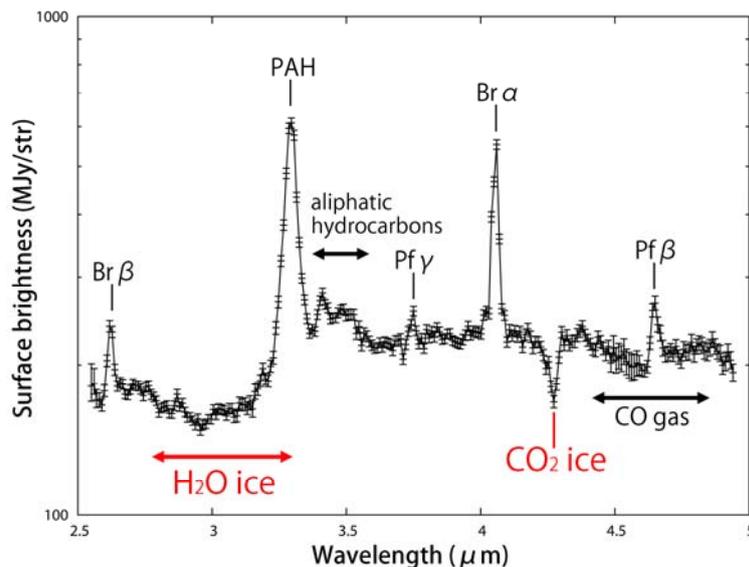


Figure 1: Example of the AKARI near-IR spectra obtained for the central region of M 82.

## **The chemistry of interstellar ice: the case of purely thermal reactions.**

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Complex organic molecules are widely observed in star formation regions, although their formation mechanisms are not well understood. Although solid-state chemistry is thought to play a dominant role in their formation, the solid-state reaction network is poorly known. We want to emphasize the role of purely thermal reactions involving stable reactants. These reactions lead to the formation of complex organic molecules, which are either released into the gas phase or incorporated into an organic residue. Unlike non-thermally induced reactions, thermal reactions are important because they are not limited by the UV or particles flux, and can occur despite the slow diffusion of the reactants. Moreover, both surface and mantle molecules can react. However, these reactions have large activation energies, the astrophysical relevance of which can be measured experimentally. Thermal reactions represent an important step towards the formation of complex organic molecules and need to be included as supplementary reactions in existing grain chemistry networks.

# Interaction of Charged Particles with Kuiper Belt Ices and Astrobiological Implications

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The Kuiper Belt consists of about 70,000 icy bodies, which extend beyond the orbit of Neptune at 30 AU. These bodies are thought to have maintained low temperatures (30-50 K) since the formation of the Solar System and therefore hold a well-preserved record of the primitive volatiles from which the solar system formed. While the icy inventory consist of water, observations have also confirmed the presence of methane, ammonia, carbon monoxide, nitrogen, carbon dioxide, and methanol. These surfaces have been exposed to galactic cosmic radiation (GCR) and solar wind particles, which are thought to produce biologically important species. Since KBOs are also considered as ‘precursor objects’ to short periodic comets, KBOs might be also a source to bring such molecules to the primordial Earth, perhaps helping to instigate the origin of life. Our research has been focused on trying to understand how these ices have evolved over the age of our solar system under the chemical processing – primarily of species containing the atoms carbon, hydrogen, oxygen and nitrogen – and to what extent the variation of composition and temperature may help explain these observations and enable us to trace backwards, to determine the primordial composition of the solar system. Results on the formation of simple sugars such as glycolaldehyde, amino acids like glycine, carboxylic acids, and molecules carrying the peptide bond (form amide, dipeptides) will be presented. We also present new results from the newly commissioned W.M. Keck Research Laboratory in Astrochemistry at the University of Hawai‘i at Manoa. This lab comprises a next generation ultra-high vacuum experimental set-up which allows the study of the interaction of monoenergetic photons and charged particles with icy surfaces using a plethora of complementary analytical techniques within a single machine including Fourier Transform Infrared, Raman, and UV-VIS spectroscopy, as well as quadrupole and time-of-flight mass spectrometry coupled with soft vacuum ultraviolet photoionization. Here, we present recent results regarding the formation of high molecular weight ( $\sim C_{18}$ ) hydrocarbons starting from pure, simple hydrocarbons ices upon interaction of these ices with ionizing radiation: methane ( $CH_4$ ), ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ) and n-butane ( $C_4H_{10}$ ). Specifically, we have utilized for the very first time a novel application of reflection time-of-flight mass spectrometry to observe the nature of high mass hydrocarbons as a function of their respective sublimation temperature. Coupled with soft vacuum ultraviolet photoionization of the subliming products at 10.5 eV, generated via tripling in a pulsed xenon jet of the 355 output of a Nd:YAG laser, our results indicate that larger, more complex hydrocarbons up to C18 are formed easily under conditions relevant to the environment of Kuiper Belt Objects which may help elucidate part of the puzzle regarding the ‘colors’ of these objects along with the formation of carbonaceous material throughout the interstellar medium.

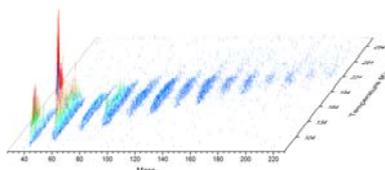


Figure 1: Time-of-Flight spectra as a function of temperature of the newly formed hydrocarbon species from the energetic processing of a pure amorphous ethane ice taken at a photoionization energy of 10.5 eV.

## Proton transfer reaction at the air-water interface

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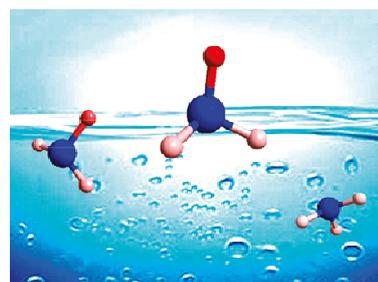
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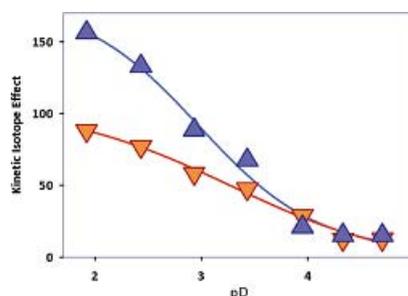
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Proton transfer (PT) through and across aqueous interfaces is a fundamental process in chemistry and biology. Unveiling the mechanism will help to understand the ubiquitous nature of PT at other interfaces, such as vacuum-ice interfaces. Notwithstanding its importance, it is not generally realized that interfacial PT is quite different from conventional PT in bulk water. Here the mechanism of PT across air-water boundaries is investigated in experiments in which the protonation/deprotonation of gaseous trimethylamine (TMA)<sup>1,2</sup>, n-hexanoic acid (PCOOH)<sup>3</sup>, nitric acid (HNO<sub>3</sub>)<sup>4</sup> and isoprene (ISO)<sup>5</sup> upon collision with liquid water microjets is monitored by online electrospray mass spectrometry as a function of bulk pH.

We found, although PCOOH(aq) is a very weak base ( $pK_{BH^+} < -3$ ), PCOOH(g) is converted to PC(OH)<sub>2</sub><sup>+</sup> on pH < 4 water via a process that ostensibly retains some of the exoergicity of its gas-phase counterpart, PCOOH + H<sub>3</sub>O<sup>+</sup> = PC(OH)<sub>2</sub><sup>+</sup> + H<sub>2</sub>O,  $\Delta G < -22$  kcal mol<sup>-1</sup>. We infer that H<sub>3</sub>O<sup>+</sup> emerges at the surface of pH < 4 water and behaves as a *superacid* (Fig. 1). The extremely large kinetic isotope effects (KIE) observed on H<sub>2</sub>O/D<sub>2</sub>O microjets and their inverse dependences on pH indicate that protonation of PCOOH(g) on water (1) involves tunneling, (2) is faster than H-isotope exchange, and (3) is progressively confined to the outermost layers as water becomes more acidic (Fig. 2). PT across steep water density gradients appear to be promoted by both dynamic and thermodynamic factors.



**FIGURE 1** Hydronium becomes a superacid once it appears at the water's surface.



**FIGURE 2** Extremely large KIE for the protonation of gaseous PCOOH(g) on H<sub>2</sub>O/D<sub>2</sub>O (5/95) microjets as functions of bulk pD.

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## COM's and Their Formation in Assorted Sources

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Complex organic molecules (COM's) are partially saturated molecules with six or more atoms [1] found in the gas phase of assorted interstellar sources such as hot cores and corinos, cold dense cores, and infra-red dark clouds. Perhaps the best-known molecule of this class is methyl formate (HCOOCH<sub>3</sub>). Although these species are detected in the gas, their formation involves both grain surface and gas-phase chemistry. In hot cores and corinos, COM's are most likely formed during the warm-up phase of protostellar sources as gas and dust collapse towards the central protostar or towards a growing protoplanetary disk [2]. Here the rising temperature is necessary to allow fragment radicals, formed by photolysis, to diffuse on grain surfaces and recombine with each other rather than with hydrogen atoms, and to allow the newly formed COM's to desorb into the gas phase. In cold cores, the formation of COM's likely depends upon transitory heating of grains allowing both reactions and desorption of the products before cooling. In protoplanetary disks, COM's can be formed even on cold icy grains because of the high densities compared with interstellar clouds, which result in a reduction of the normally significant amount of atomic hydrogen on cold surfaces [3]. In these sources, however, most of the COM's remain in the ice because the temperature never rises to their sublimation points and photodesorption is generally inefficient. In infrared dark clouds, the mechanism for formation of these species, which have been newly detected, is unclear although one possibility is shock desorption from grain surfaces, as has also been posited for the galactic center.

In the talk, I will discuss how COM's are formed and how abundant they can become in both the gas and in granular ices for assorted sources. New work on their possibly high abundance in protoplanetary disks will be emphasized with the goal of understanding the original organic inventory of planets and other objects such as comets.

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## Water and organic molecules in protoplanetary disks

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Protoplanetary disks surrounding young stars provide peculiar environment for astrochemistry. The disk surface is exposed to strong UV and X-ray irradiation from the central star, while the outer region of the disks is cold and molecules are frozen onto dust grains to form more complex species via surface reactions. The gas density is much higher than molecular clouds, and dust grains are thought to stick together as well as settle towards the disk midplane to lead to planet formation, which also makes specific environment.

We have studied the chemical structure of protoplanetary disks using a comprehensive astrochemical reaction network, based on a detailed model for the gas and dust temperature and density profiles, which takes into account UV and X-ray irradiation from the central star. Here we especially focus on abundance profiles and line emission of water and organic molecules in the disks with considering effects of some physical processes, such as dust evolution and turbulent mixing. Water and some organic molecules are basically formed via endothermic reactions in the hot gas in the inner disk surface, while they are photodesorbed from dust grains in the cold outer disk. Our results show that turbulent mixing enhances water at the hot surface layer of the inner disks, while it doesn't affect very much in the cold outer disk. On the other hand, the dust evolution changes the gas temperature and amount of radiation field so that it makes water-abundant-region shrunk in the hot surface layer of the inner disks, while it enhances water near the midplane in the cold outer disk. Grain surface reaction has a significant effect on formation of complex organic molecules, and some photodesorbed organic molecules could be detectable with ALMA. We compare the results of our model calculations of water line fluxes with the Spitzer and Herschel observations, which suggests that observed water line fluxes can be reproduced only when molecular hydrogen formation rate on warm grains is small or dust grains are significantly less abundant.

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## Finding of large-sized, nitrogen-rich organic materials in ultracarbonaceous Antarctic micrometeorite

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Ultracarbonaceous Antarctic micrometeorites (UCMMs), first discovered by [1], represent large sizes of high carbon contents. It has been reported extreme D-rich organic matter with both crystalline and amorphous silicates from a UCMM, which appears to be compatible to cometary origin [2]. However, little has been known about the nature of UCMMs. In this study, for an UCMM collected in 250 kg of the surface snow at the Dome Fuji Station, Antarctica, we have carried out the systematic studies applying isotope microscopy, focused ion beam (FIB) extraction, scanning transmission x-ray microscope (STXM) and transmission electron microscopy (TEM) observation to study the origin and formation of UCMMs. Isotope imaging has detected a large-sized, nitrogen-rich organic material of  $\sim 10 \times 20 \mu\text{m}^2$ . The distribution of sulfur is associated with with the organic material. There is no significant difference in carbon, hydrogen, and nitrogen isotopic compositions of the UCMM from those of epoxy resin. A STXM C- and N- maps of the FIB section show that organic N-rich and poor regions coexist in the object with a sharp boundary. N-XANES spectra of the N- rich regions exhibit intense peaks of imine (C=N), nitrile (C $\equiv$ N), and amide (NHx(C=O)C), while that of N-poor region shows a less characteristic spectrum that is similar to those of typical chondritic and IDP organics [3]. It is noted that the N-XANES spectral patterns of the N-rich regions are very similar to those observed from the three samples of Comet 81P/Wild 2 dust particles [4]. Furthermore, the organic features of the UCMM in its size and N- functional chemistry are very similar to those of CR3 chondritic organic material [5]. Thus, the organic chemistry of the UCMM implies the very early stage of parent body aqueous alteration or before.

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## **Recent Results from the HEXOS GT Key Program**

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I will present recent results from the Herschel GT key program entitled Herschel Observations of EXtra Ordinary Sources (HEXOS). In particular, I will focus on results stemming from a "full band analysis" of a complete 1.2 THz wide spectral survey toward the Orion Kleinmann-Low nebula (Orion KL). This massive dataset, obtained using the HIFI instrument, spans a frequency range of 490-1900 GHz and contains approximately 20,000 spectral lines from over 30 molecules. Consequently, we have modeled the molecular emission over an unprecedented range in excitation energy and, in some cases, used thousands of lines to constrain our models. Our collection of molecular fits have: (1) yielded a chemical inventory for different spatial/velocity components toward Orion KL, (2) produced robust abundances for each molecule, (3) provided D/H ratios for some species (e.g. H<sub>2</sub>O, H<sub>2</sub>CO, and CH<sub>3</sub>OH), and (4) allowed us to determine which molecules are emitting in the hottest gas possibly in close proximity to an embedded massive protostar. In addition, detailed modeling of the light hydride H<sub>2</sub>S points to the presence of a hidden source of luminosity toward the Orion hot core. If time allows, I will also present preliminary results from a similar analysis of the HIFI spectral scan toward Sgr B2 (N), an equally rich spectrum which presents its own unique challenges. This work was undertaken with the aid of the HEXOS Orion KL and Sgr B2 (N) full band analysis teams.

# Spectral Line Survey toward Spiral Arm in Nearby Galaxy M51

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For a thorough understanding of the galactic star formation history, one of the key issues is formation and evolution of giant molecular clouds (GMCs) and giant molecular associations (GMAs), because they are intermediate structure connecting the galactic structure and individual star formation. We are going to investigate the evolutionary history and the physical states of GMCs on the basis of their chemical compositions. As the first step, we have conducted an unbiased spectral line survey toward a spiral arm in M51 to grasp the averaged chemical composition of GMCs.

M51 ( $d = 8.4$  Mpc) is a well-studied nearby galaxies for star formation and gas dynamics (*e.g.* Koda et al. 2009), because it has a prominent spiral arm and a plenty of molecular gas in a disk. The observed frequency ranges are 83-116 GHz and 130-146 GHz (Figure 1). We detected 17 molecular species ( $c\text{-C}_3\text{H}_2$ , CCH, HNCO, HCN,  $\text{H}^{13}\text{CN}$ ,  $\text{HCO}^+$ , HNC,  $\text{N}_2\text{H}^+$ ,  $\text{CH}_3\text{OH}$ , CS,  $\text{C}^{34}\text{S}$ , SO,  $\text{C}^{18}\text{O}$ ,  $^{13}\text{CO}$ , CN,  $\text{C}^{17}\text{O}$  and  $^{12}\text{CO}$ ) in the 3 mm band, and 4 molecular species (HNCO,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$  and CS) in the 2 mm band. It is remarkable that CCH, HNCO,  $\text{CH}_3\text{OH}$ ,  $\text{N}_2\text{H}^+$ , CN, and  $\text{H}_2\text{CO}$ , which are unfamiliar in observations of extra-galaxies except for those toward the nuclear region of the starburst galaxies and AGNs, are detected in the spiral arm region. The spectrum pattern is much different from that found in massive star forming regions like Orion KL (*e.g.* Tercero et al. 2011), indicating that the observed chemical composition cannot simply be interpreted in terms of the sum of contributions from embedded star forming cores. We will present the chemical compositions of M51 and comparisons them with other galactic and extra-galactic sources.

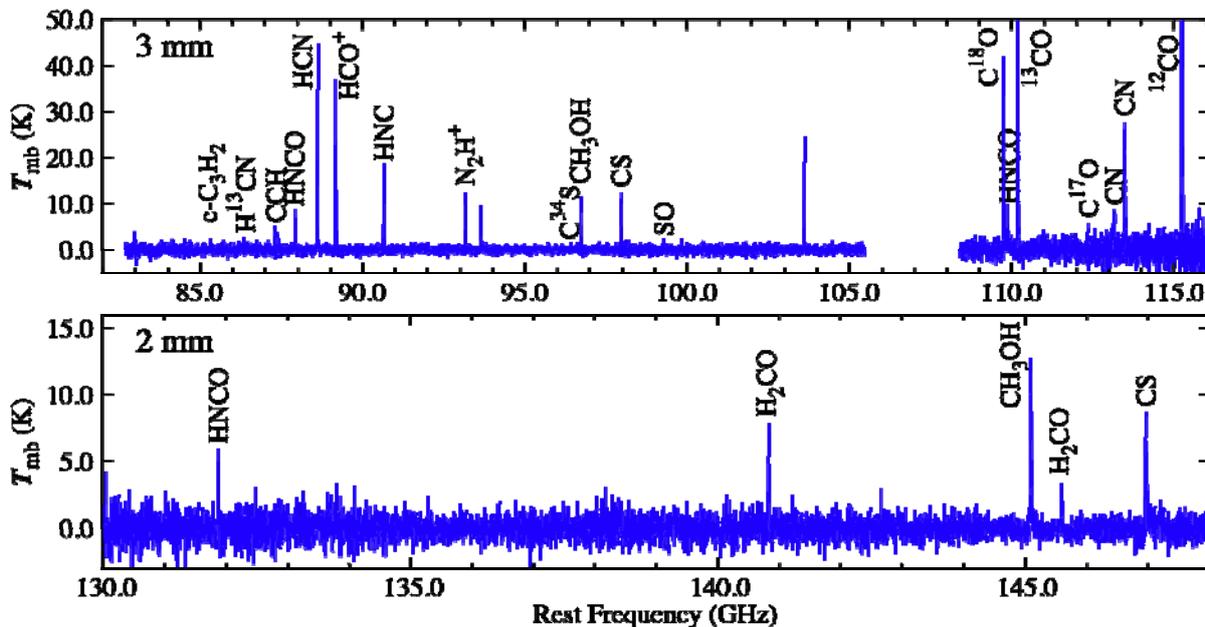


Figure 1: Spectrum of a spiral arm in M51 (upper: 3 mm band, lower: 2 mm band).

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## Ice deuteration: models and observations to interpret the protostar history

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Extremely large deuteration of several molecules has been observed around low-mass protostars for a decade. Among them, formaldehyde and methanol present particularly high deuteration, with observations of abundant doubly and triply deuterated isotopologues seen with ground-based millimetric telescopes [1]. The Herschel Space Telescope, launched in 2009, is now providing measures of the deuterium fractionation of water. First results towards the protostellar prototype, IRAS 16293, revealed that water shows HDO/H<sub>2</sub>O and D<sub>2</sub>O/H<sub>2</sub>O ratios of ~3 and ~0.1 % respectively [2]. Although water shows a higher deuteration than the cosmic deuterium reservoir (10<sup>-5</sup> relative to H nuclei), these values remain lower than the deuteration seen in formaldehyde and methanol. Water, formaldehyde, and methanol are believed to be mainly produced on interstellar ices in cold dark clouds. In this presentation, I will discuss 1) a theoretical model and 2) new interferometric observations of the water deuteration.

1) We have developed a macroscopic time-dependent gas-grain model, called GRAINOBLE [3], to study the formation and the deuteration of interstellar ices. The model follows the multilayer formation of ices distinguishing the chemical processes that occur in the mantle inert bulk and on the reactive surface. For this purpose, a comprehensive chemical network producing deuterated water, formaldehyde, and methanol has been considered following recent experiments and theoretical calculations [4] [5]. A grid of several thousands of models has been run and compared to observations toward low-mass protostars. The low deuteration of water compared to formaldehyde and methanol, can be explained by their different chemical history. Water is mainly formed during a translucent phase at low density while formaldehyde and methanol are rather formed in denser and colder prestellar cores, where the CO depletion is high [4] [5].

2) Interferometric mapping of HDO has been carried out with the PdB interferometer toward two low-mass protostars, IRAS2A and IRAS4A [6]. In both sources, the HDO emission is compact and unresolved in the PdB 2 arcsec synthesized beam. LVG analysis of the integrated line emission as well as other HDO lines from single dish observations [7] and H<sub>2</sub><sup>18</sup>O line from PdB observations [8] allows us to estimate the most reliable HDO/H<sub>2</sub>O ratio in low-mass protostars. We found a deuterium fractionation of water in IRAS2A and IRAS4A higher to that found in IRAS 16293 [2], suggesting a water formation at high densities.

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## HNCO 2(0,2)-1(0,1) line emission from methanol maser clouds

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We completed a large survey of class II methanol maser sources in the Galactic plane using the class I methanol line at 44.069 GHz with the Nobeyama 45m telescope. In this course of survey, we accidentally detected the 2(0,2)-1(0,1) line of isocyanic acid, HNCO, at 43.963 GHz in the same spectrometer with a band width of 250 MHz for 7 sources, most of which exhibit strong 44 GHz methanol maser emission. Though the 5(0,5)-4(0,4) and 4(0,4)-3(0,3) transitions of HNCO at higher frequencies have been observed in a number of molecular clouds [1] and are known to be associated with molecular outflows, detection of the 2(0,2)-1(0,1) line at 43.963 GHz was reported only as a private communication [2], or its spectrum was shown only for TMC1 [3]. Here we report on the observations of this transition of HNCO in a part of the methanol maser survey.

A dichotomy of methanol maser sources into class I and class II [4] has often been used for star forming regions; the former emits 36, 44, and 96 GHz methanol masers, and the latter 6.7 and 12 GHz methanol masers. However, some maser sources exhibits both characteristics. To investigate this phenomenon, we surveyed 214 IRAS sources with the 6.7 GHz methanol emission (Class II) using the 44 GHz methanol line (Class I) at Nobeyama, and detected 89 sources in the 44 GHz line. In addition, we detected very strong 44 GHz methanol maser in the dark cloud G359.94+0.17 toward the Galactic center [5].

Emission from the HNCO 2(0,2)-1(0,1) line was found in 7 sources, 6 of which exhibits relatively strong 44 GHz methanol maser line. Among them, IRAS 18321-0843 shows a very broad line width of about 30 km/s, which indicates an association with the rapid outflow. This cloud also exhibits SiO thermal emission at 43.4 GHz, and very broad ammonia emission at 23.7 GHz. These facts show strong evidence that isocyanic acid and methanol molecules are both evaporated from ice grains which were hit by shock in outflow.

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# First light observation of GIGMICS (germanium immersion grating mid-infrared cryogenic spectrograph) by Kanata 1.5-m Telescope at Higashi-Hiroshima Observatory

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We have developed a germanium immersion grating mid-infrared cryogenic spectrograph (GIGMICS) designed for the Nasmyth focus stage of NAOJ Subaru 8.2-m telescope, which operates at N-band (8-13 $\mu$ m) in wavelength with maximum resolving power  $R (\equiv \lambda/\Delta\lambda) \sim 40,000$ . A single crystal germanium echelle immersion grating (30 $\times$ 30 $\times$ 72 mm) for collimated beam size of 28 mm $\phi$  was fabricated by utilizing ultra-precision micro-grinding method coupled with the ELID (Electrolytic In-process Dressing) technique (Ohmori, H. 1992[1], Ebizuka et al. 2003[2], Tokoro et al. 2003[3]).

After the critical test for the application to the laboratory gas-phase IR high-resolution spectroscopy (Hirahara et al. 2010[4]), we have conducted the “first light” astronomical observation of GIGMICS by the Kanata 1.5-m telescope at Higashi-Hiroshima Observatory from January to April, 2011. Toward many astronomical objects such as the Moon, Venus, Jupiter, circumstellar envelopes of late-type stars, proto-planetary nebulae in the vicinity of star-forming regions, we conducted spectroscopic observations in the N-band region.

As a result, we detected 24 lines of <sup>12</sup>CO<sub>2</sub> ( $\nu_1, \nu_2^1, \nu_3$ )=(0, 1<sup>1</sup>, 1)  $\leftarrow$  (1, 1<sup>1</sup>, 0) and 11 lines of <sup>13</sup>CO<sub>2</sub> (0, 0<sup>0</sup>, 1)  $\leftarrow$  (1, 0<sup>0</sup>, 0) transitions in Venus (Fig. 1). Among these two transitions, 13 lines were detected for the first time (Hirahara et al. 2012[5]). Toward the planetary nebula NGC7027, We detected [S IV] forbidden emission line (<sup>2</sup>P<sub>3/2</sub> $\rightarrow$ <sup>2</sup>P<sub>1/2</sub>) at 10.510 $\mu$ m, and investigated the spatial distribution for the first time in the ground based observation.

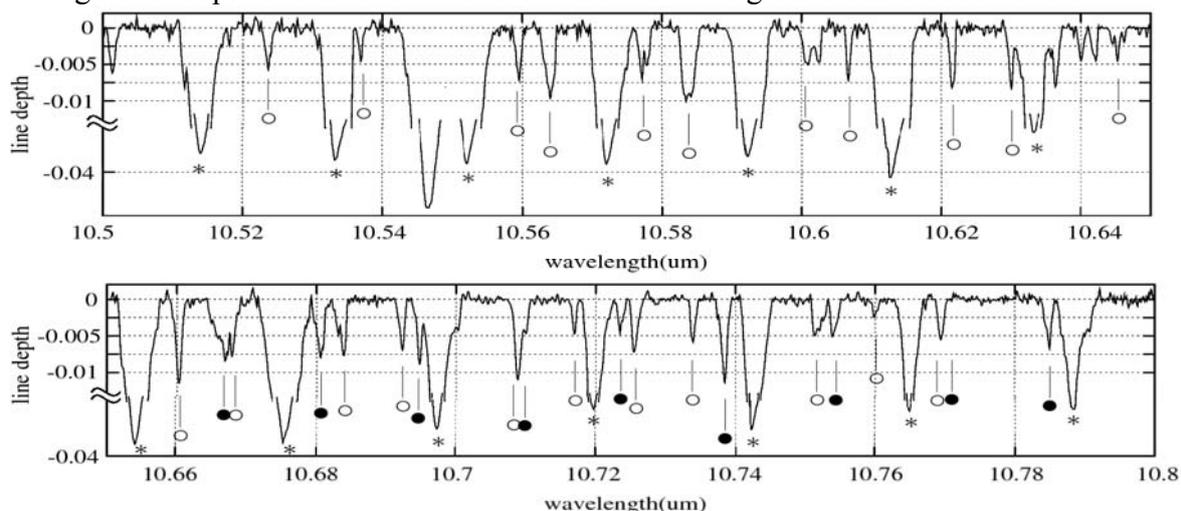


Figure 1. Spectrum of the Venusian <sup>13</sup>CO<sub>2</sub> (0, 0<sup>0</sup>, 1)  $\leftarrow$  (1, 0<sup>0</sup>, 0) (•) and <sup>12</sup>CO<sub>2</sub> (0, 1<sup>1</sup>, 1)  $\leftarrow$  (1, 1<sup>1</sup>, 0) (o) rotational and vibrational transitions. The strong absorption marked with \* show the telluric CO<sub>2</sub> lines.

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## Cold ion chemistry using the ion trap technique

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The cold ion-molecule reactions play important roles in synthesis of interstellar molecules, and their reaction-rate constants are important information for studying the chemical evolution of interstellar clouds [1]. Therefore, the databases of the rate constants were developed for astrochemistry and some reaction network models were proposed to understand the synthetic mechanisms of interstellar molecules [2, 3]. Recently, the present state of knowledge concerning the reaction-rate constants and their uncertainties for the major gas-phase chemical processes was reviewed [4]. It was pointed out that most of the measurements of ion-neutral reactions were only at room temperature or at a restricted range of temperatures near room temperature, even though the reactions occur actually at very low temperatures in interstellar clouds. Especially, the cold ion-polar molecule reactions have not been studied extensively in the laboratory, owing to some experimental difficulties, such as condensation of polar gases at relatively high temperatures. For that reason, we planned to measure the reaction rates of cold ion- molecule reactions using the ion trap technique. The main purpose of the present study is the contribution to the astronomical databases.

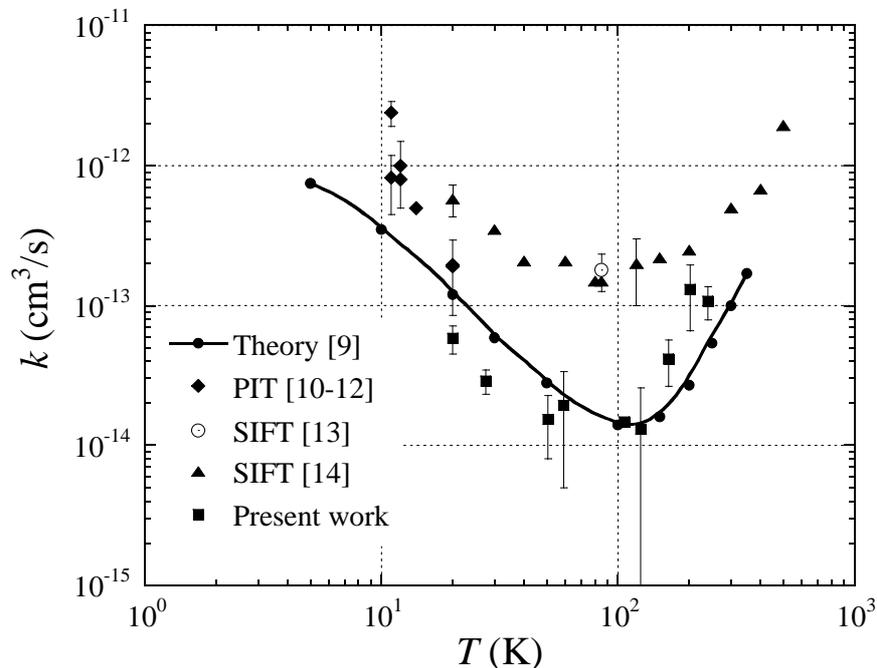


Figure 1: A summary of the temperature dependence of the reaction-rate constant in the  $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$  reaction. PIT: Penning ion trap, SIFT: Selected Ion Flow Tube.

We report two experimental approaches by the ion trap technique: one is a conventional method to measure the ion-molecule reactions by combining a cryogenic linear multipole rf ion trap with the cold buffer-gas cooling method [5], and the other is a new method to measure cold ion-polar molecule reactions using a Stark velocity filter and the laser cooling

technique [6]. The latter method can be extended to the reaction-rate measurements between sympathetically cooled molecular ions and slow polar molecules.

In the experiment using the cryogenic linear octupole rf ion trap, we have measured the temperature dependence in the reaction-rate constant of  $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$  [7], which is known as a bottleneck of the gas-phase ammonia synthesis in interstellar clouds [8]. The summary of the present measurement is shown in Fig.1. We also plot the data taken from Refs. [9-14]. The present result well agree with the theoretical values [9]. The experimental method and the measurement procedure will be described. We will also report recent experimental development for studying cold ion-polar molecule reactions [15-17]. We actually performed the reaction-rate measurement between sympathetically cooled molecular ions ( $\text{N}_2^+$ ,  $\text{N}_2\text{H}^+$ ) and slow  $\text{CH}_3\text{CN}$  molecules, which were produced by a Stark velocity filter [18]. The sequential fluorescence images of the  $\text{Ca}^+$  Coulomb crystal including  $\text{N}_2^+$  ions during the cold  $\text{CH}_3\text{CN} + \text{N}_2^+ \rightarrow \text{products}$  reaction are shown in Fig.2. The shadowed area progressively decreases with increasing the reaction time. Since the number of  $\text{N}_2^+$  ions in each image can be determined from the structure of the images, the reaction rate can also be determined. Preliminary results and the discussions will be presented.

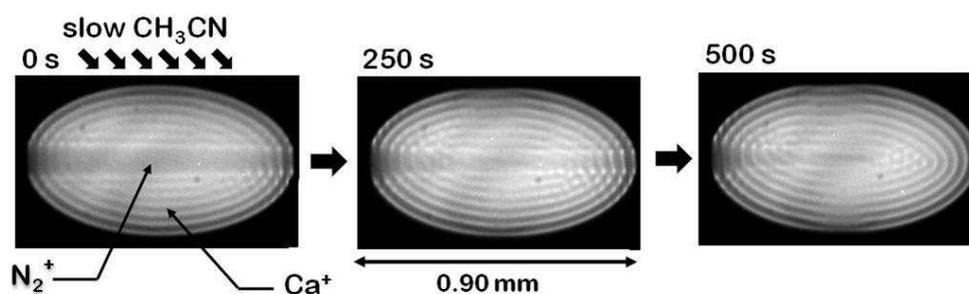


Figure 2: Sequential fluorescence images of the  $\text{Ca}^+$  Coulomb crystal (bright) including  $\text{N}_2^+$  ions (shadowed) during the cold  $\text{CH}_3\text{CN} + \text{N}_2^+ \rightarrow \text{products}$  reaction. The number of  $\text{Ca}^+$  was roughly estimated to be  $1.8 \times 10^3$ .

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## The Cologne Database for Molecular Spectroscopy: Recent Developments and Outlook for ALMA

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More than 10 years ago, the Cologne Database for Molecular Spectroscopy, CDMS, was founded to provide in its catalog section rest frequencies with sufficient accuracy on mostly molecular species which have been or may be observed in space by largely radio astronomical means. Entries are usually generated from critically evaluated laboratory data employing established Hamiltonian models. Each molecule has a separate entry, minor isotopic species are always, excited vibrationally states are usually presented separately. The CDMS is available on the internet free of charge [1], and a very early [2] as well as a more recent account have been published.

As of September 2012, the CDMS has more than 650 entries, of which at least 280 have been detected in space. Moreover, they make up a large fraction of the more than 170 different molecules which have been detected in the interstellar medium or in circumstellar envelopes of late-type stars. Access to the CDMS has increased steadily, and it is at present at a level of around 2000 accesses each month.

Future entries will be generated in particular to support observations with ALMA. Hence, the focus will shift to complex molecules as well as vibrational or isotopic satellites of known interstellar molecules, which will be important in observations of star-forming regions, and to metal containing or other refractory molecules which may be observed increasingly in circumstellar envelopes of late-type stars.

Initially, entries were created as ascii tables. About 3 years ago, a process has been initiated to put the CDMS into a database environment in the framework of the Virtual Atomic and Molecular Data Centre (VAMDC) [4,5]. The release of a test version is intended for September 2012. The advantages of this transition as well as various aspects of the CDMS will be presented.

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## Radio Searches for Interstellar Carbon Chains HC<sub>4</sub>OH and H<sub>2</sub>CCC

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We have made a sensitive search for the rotational transitions of the interstellar carbon chains HC<sub>4</sub>OH and H<sub>2</sub>CCC.

The carbon-chain alcohol HC<sub>4</sub>OH have searched in the frequency range from 21.2 to 46.7 GHz in the star forming region L1527 in Taurus with rich carbon-chain chemistry [1]. The incentive of this observation was a laboratory detection of HC<sub>4</sub>OH by the microwave spectroscopy [2]. Despite achieving an rms of several mK in antenna temperature by the 45m telescope at Nobeyama Radio Observatory, the search for HC<sub>4</sub>OH was negative, leading to a 5 sigma upper limit corresponding to the column density of  $4 \times 10^{12} \text{ cm}^{-2}$  based on the excitation temperature of 12.3 K. The upper limit indicates that the [HC<sub>4</sub>-OH]/[HC<sub>4</sub>-CN] ratio is less than 1.0. The ratio suggests that the cyanide species with carbon-chain structure is dominant in comparison with the hydroxyl one in L1527, which can be the opposite case of saturated compounds, *e.g.* CH<sub>3</sub>OH and CH<sub>3</sub>CN, in hot cores and dark clouds.

In order to clarify the authenticity of a recently proposed identification of H<sub>2</sub>CCC (*linear*-C<sub>3</sub>H<sub>2</sub>) as a diffuse interstellar band carrier [3], we searched for the rotational transition of H<sub>2</sub>CCC at a frequency of 103 GHz toward HD 183143 using the 45m telescope at Nobeyama Radio Observatory [4]. Although an rms noise level of 32 mK in the antenna temperature,  $T_A^*$ , was achieved, detection of H<sub>2</sub>CCC was unsuccessful, producing a  $3 \sigma$  upper limit corresponding to a column density of  $2.0 \times 10^{13} \text{ cm}^{-2}$ . The

upper limit indicates that the contribution of H<sub>2</sub>CCC to the diffuse interstellar band at 5450 Å toward the star HD 183143 is less than 1/25; thus, it is unlikely that the laboratory bands of the B<sup>1</sup>B<sub>1</sub>-X<sup>1</sup>A<sub>1</sub> transition of H<sub>2</sub>CCC and the diffuse interstellar bands at 5450 Å (and also 4881 Å) toward HD 183143 are related.

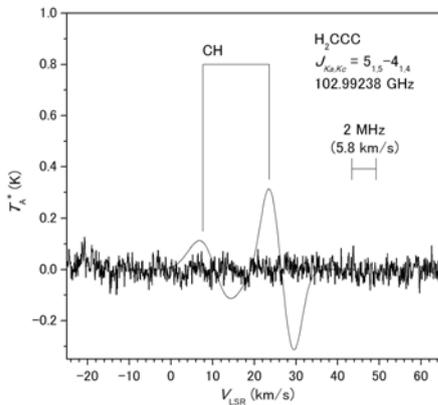


Figure 1: Spectrum at the line position of H<sub>2</sub>CCC searched toward HD 183143. Solid vertical lines indicate positions of the two velocity components of CH. Solid curve shows a line profile of H<sub>2</sub>CCC simulated in arbitrary intensity.

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# High Resolution Infrared Spectra of Protonated Polycyclic Aromatic Hydrocarbons and their Neutral Counterparts in Solid Para-hydrogen

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Identification of infrared (IR) spectra of protonated polycyclic aromatic hydrocarbons ( $H^+$ PAH) is important in understanding the unidentified IR emission bands (UIR) of interstellar media. We use protonated benzene ( $C_6H_7^+$ ) and protonated naphthalene ( $C_{10}H_9^+$ ) [1,2] to demonstrate a new method that has advantages over the Ar-tagging IR photodissociation or the IR-multiphoton-dissociation methods currently used.  $H^+$ PAH was produced on electron bombardment of a mixture of PAH and *para*-hydrogen during deposition onto a target at 3.2 K. IR absorption of the matrix sample shows lines mainly due to  $H^+$ PAH and its neutral form, HPAH. Lines of  $H^+$ PAH decreased in intensity when the matrix was irradiated at 365 nm or maintained in darkness, whereas those of HPAH increased in intensity. Observed wavenumbers, relative IR intensities and deuterium isotopic shifts agree with those predicted theoretically. This method, providing a wider spectral coverage with narrower lines and accurate relative IR intensities, can be applied to larger PAH which are difficult to study with other methods.

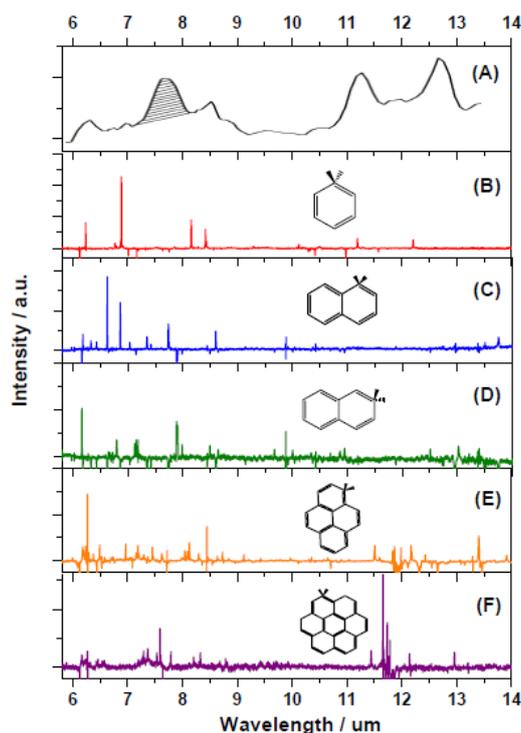


Figure 1: (A) UIR spectrum toward VV 114 [3] and IR spectra of (B) protonated benzene, (C) a-protonated naphthalene, (D) b-protonated naphthalene, (E) protonated pyrene, and (F) protonated coronene isolated in solid parahydrogen.

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## Terahertz spectroscopy of $\text{H}_2\text{F}^+$

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Rotational transitions of  $\text{H}_2\text{F}^+$  were observed in the THz region by using an Evenson-type tunable far-infrared (TuFIR) spectrometer [1] which is based on the difference frequency generation of two  $\text{CO}_2$  laser lines.  $\text{H}_2\text{F}^+$  ion was generated in an extended negative glow discharge cell [2] by a proton transfer reaction from  $\text{H}_3^+$  to HF. HF was produced from  $\text{HKF}_2$  powder in a heating tube [3]. A trace of the spectral line from the lowest rotational level ( $1_{11} \leftarrow 0_{00}$ ) is shown in Fig.1. A fitted line profile with a base line correction is also shown in the figure. Frequencies of 7 rotational lines below 1.9 THz were measured with the present spectrometer as shown in Table 1.

Present frequency data were analyzed together with 5 lines from submillimeter-wave measurement [3] and 122 combination differences for the ground state derived from the infrared data [4,5]. Sixteen adjustable parameters of the Watson's A-reduced Hamiltonian were determined.

Based on the TuFIR and submillimeter measurements,  $\text{H}_2\text{F}^+$  lines are to be searched for with Herschel Space Observatory.

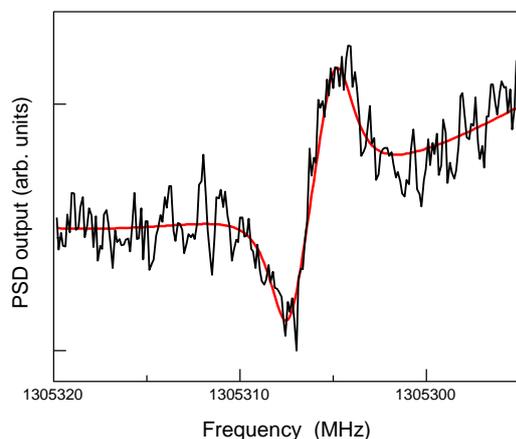


Figure 1: The  $1_{11} \leftarrow 0_{00}$  line of  $\text{H}_2\text{F}^+$ .

Table 1. Rotational lines of  $\text{H}_2\text{F}^+$  measured with TuFIR spectrometer.

transition	frequency (MHz)
$1_{11} \leftarrow 0_{00}$	1305306.503(73)
$3_{03} \leftarrow 2_{12}$	1370911.418(48)
$4_{13} \leftarrow 4_{04}$	1425857.036(59)
$5_{23} \leftarrow 5_{14}$	1737165.499(66)
$4_{22} \leftarrow 4_{13}$	1748027.582(85)
$3_{21} \leftarrow 3_{12}$	1823629.057(70)
$2_{12} \leftarrow 1_{01}$	1850081.989(50)

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# Distribution of CCS and HC<sub>3</sub>N in L1147, A Less Evolved Molecular Cloud

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The ratio “CCS/NH<sub>3</sub>” is a good indicator of molecular cloud age. A CCS-rich cloud is relatively young, while a NH<sub>3</sub>-rich cloud is old<sup>[1-3]</sup>. Suzuki et al. (1992) found Carbon-chain producing regions (CCPRs), where carbon-chain molecules are abundant but NH<sub>3</sub> is poor<sup>[4]</sup>. These regions are considered to be in younger phase of cloud evolution.

In 2009, Hirota et al. observed 40 molecular clouds and found five CCPR candidates. These candidates showed high “CCS/NH<sub>3</sub>” ratios, but their CCS abundances were lower than those of known CCPRs<sup>[5]</sup>. Molecular distributions in these clouds, which were not obtained so far, would provide us with key information regarding their evolution. Thus we made mapping observations in HC<sub>3</sub>N and CCS towards one of these CCPR candidates, L1147, to reveal molecular distributions and relation with associated star formation activity.

We observed a CCS line ( (J,N)=(4,3)→(3,2) ) and a HC<sub>3</sub>N line (J=5→4 ) by the Nobeyama 45m radio telescope. We found the followings: (1) CCS and HC<sub>3</sub>N are elongated in the NE-SW direction, (2) HC<sub>3</sub>N peak is located between two CCS peaks, and (3) the CCS and HC<sub>3</sub>N peaks are away from Spitzer 2040567+6723050. We also made column density maps by assuming that the lines are optically thin and the excitation temperatures are 5 K<sup>[4]</sup> (Figure 1). The column densities range in 10<sup>12</sup>~10<sup>13</sup> cm<sup>-2</sup> which agrees well with Hirota et al. (2009). It is noted that the “anti-correlation” between HC<sub>3</sub>N and CCS has been known toward only one source Hirota et al. (2009).

In the poster we will discuss evolution of molecular clouds in their very young phase.

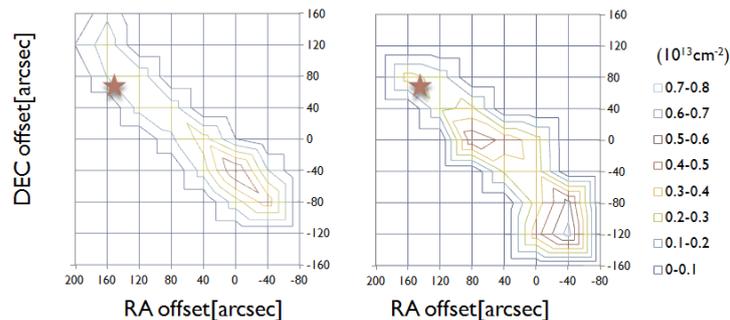


Figure 1: Column density distributions of HC<sub>3</sub>N (left) and CCS (right). The star mark corresponds to Spitzer 2040567+6723050. The reference position (0,0) corresponds to (RA(2000), Dec(2000))=(20h 40m 32 s, 67d 21 m 45 s).

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## Nobeyama 45 m telescope legacy project: Line survey

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Line surveys are of fundamental importance in astronomy not only for complete understanding of molecular abundances, but also for finding out new observational tools (spectral lines) probing interstellar medium. We carried out a new line survey project at the 3 mm region. The new wide band system (2SB receivers, 4-8 GHz IF lines, 3 bit 4 GHz sampling AD converters, and 2 GHz band width x 16 spectrometers) was used in the late stage of the survey, and the survey speed was accelerated. The target sources are the low-mass star-forming region in L1527, the shocked region in L1157 B1, the infrared dark clouds G28.34+0.06, and the external galaxies NGC 1068, NGC 253, and IC 342. The main results are as follows.

(1) L1527: This is an interesting star-forming region with high abundances of carbon-chain molecules [1]. The survey from 80 to 117 GHz has been completed. We detected many lines from 39 species including various carbon-chain molecules, isotopic species (D,  $^{13}\text{C}$ ) of some carbon-chain molecules, and unidentified species. In particular, we detected the lines of cyclopropanone and propynal as well as those of cyclic- $\text{C}_3\text{D}_2$  and  $^{13}\text{C}$  substituted cyclic- $\text{C}_3\text{H}_2$ .

(2) L1157 B1: This is a prominent region of interactions between a molecular outflow from the protostar and ambient clouds [2, 3]. This is an ideal region to study shock chemistry. The survey was finished from 78.1 to 115.5 GHz. We detected 130 lines from 44 species including  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_2\text{DOH}$ , carbon-chains, and PN [4, 5, 6].

(3) G28.34+0.06 (possible high-mass star-forming regions): Three interesting positions called MM1, MM4, and MM9 were selected, and the survey almost covered from 80 to 110 GHz. Toward MM1 and MM4 line wings were found in SiO and so on. These wings indicate outflow activities. In addition,  $\text{CH}_3\text{CHO}$  was detected only in MM1 and MM4, though  $\text{N}_2\text{D}^+$  was detected only in MM9. Based on these results, MM1 and MM4 are thought to be active and more evolved objects.

(4) NGC 1068 is a nearby galaxy with X-ray radiation from the active galactic nucleus, and NGC 253 and IC 342 are also nearby galaxies with prototypical starbursts. The survey was finished from 85 to 116 GHz. We detected 21-23 species depending on the galaxies including several new detections (e.g. cyclic- $\text{C}_3\text{H}_2$  and  $\text{C}_2\text{H}$  in NGC 1068 [7]). The intensities of HCN and CN relative to  $^{13}\text{CO}$  are significantly strong in NGC 1068 compared to those in NGC 253 and IC 342.

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## Spectral-Line Surveys at mm and submm Wavelength toward Outflow-Shocked Region, OMC2-FIR4

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Enormous progress has been achieved in the past few decades in studying the chemical composition of dense molecular gas associated with star-forming regions. The chemical composition and evolution in the dense interstellar medium themselves are of particular great interest. In addition, they are very useful for the diagnostics of protostar or protoplanetary disk evolution, also of interstellar shocks. Shock chemistry is one of keys to understand chemical compositions of interstellar medium because shock waves are ubiquitous. Shock chemistry is, however, still obtained in protostellar outflows and jets, although many theoretical studies have been extensively made since 1980's [1][2].

OMC2-FIR4(d=400pc) is one of the most suitable targets to investigate the shock chemistry, because the NMA(Nobeyama Millimeter Array) and ASTE(Atacama Submillimeter Telescope Experiment) observations have revealed that the FIR3 outflow interacts with the dense gas associated with FIR4 on the basis of the following three pieces of evidence [3]. The first is morphological one that the distribution of the southern lobe of the FIR3 outflow coincides with that of the FIR4 dense gas. The second is chemical one that the emission of the shock tracers of SiO and CH<sub>3</sub>OH is distributed at the tip of the outflow. The third is kinematical one that the increment in the velocity width of the H<sub>13</sub>CO<sup>+</sup>, SiO, CH<sub>3</sub>OH, and CO lines is seen at the interface between the outflow and the dense gas.

To obtain more evidence for the shock chemistry in FIR4, we have completed 3-mm (82-106GHz) and 850- $\mu$ m (335-355GHz) line surveys of FIR4 (i.e., the southern lobe of FIR3 outflow) as well as FIR3 and FIR3N (the northern lobe) using the NRO 45m and ASTE telescopes. FIR4 is proved chemically enriched remarkably. Our 3-mm and 850- $\mu$ m line surveys detected 122 lines and 21 species including CH<sub>3</sub>CCH and C<sub>3</sub>H<sub>2</sub> as well as S-bearing molecules such as H<sub>2</sub>CS and SO. First, we found that line profiles of CH<sub>3</sub>OH, and SO consists of two components with narrow (<3km/s) and wide (>3km/s) velocity widths, and the wide-velocity components are detected only at the outflow-shocked region, FIR4, as well as the emission of SiO, a typical shock tracer. These facts strongly suggest that the CH<sub>3</sub>OH, SO, and SiO lines surely trace the shocked gas. Second, the rotational temperatures of possible shock tracers are estimated to be as high as 50-150K, suggestive of shock heating. In contrast, the rotational temperatures of dense gas tracers such as H<sub>13</sub>CO<sup>+</sup>, HCN, and HNC are estimated to be ~20K, which can be considered as the temperature of the quiescent gas.

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## Abundant CH<sub>3</sub>OH in the Cold Starless Core TMC-1

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Methanol (CH<sub>3</sub>OH) is generally abundant in star-forming regions [1][2]. It is thought to be produced mainly on grain mantles, and is released into the gas phase by various star-formation activities. Since its abundance is apparently enhanced in the shocked region such as L1157B1 [3][4][5], CH<sub>3</sub>OH is sometimes used as a shock tracer. However, CH<sub>3</sub>OH is moderately abundant even in cold starless cores like Taurus Molecular Cloud-1 (TMC-1) ( $T_k \sim 10$  K), although no heating sources are embedded there. Since evaporation temperature of CH<sub>3</sub>OH is about 100 K, existence of CH<sub>3</sub>OH in TMC-1 is puzzling. While the production pathway in the gas phase is proposed [6], it cannot explain the observed abundance of CH<sub>3</sub>OH in TMC-1.

Recently, we have conducted high velocity-resolution observations of CH<sub>3</sub>OH in TMC-1. We have found that the line shape of CH<sub>3</sub>OH is much different from those of other carbon chain molecules toward TMC-1 (Cyanopolyne Peak; CP), which indicates different distribution of these two species in the core. We have also conducted mapping observations of CH<sub>3</sub>OH ( $J_k = 2_k - 1_k$ ), C<sup>34</sup>S ( $J = 2-1$ ) and C<sup>18</sup>O ( $J = 2-1$ ) in the 150'' $\times$ 150'' area around TMC-1 (CP), and revealed that the distribution of CH<sub>3</sub>OH is anticorrelated with that of C<sup>34</sup>S. This difference would be an important clue to understand the mechanism for production of CH<sub>3</sub>OH in TMC-1.

We are considering two possible mechanisms for desorption of CH<sub>3</sub>OH from grain mantles in starless cores. One is soft shock caused by collisions of small clumps inside the core and/or accretion motions of envelope materials onto the core, whereas the other is desorption by cosmic-ray induced UV. In any case, the distribution of CH<sub>3</sub>OH would not follow the distribution of the dense gas (CS), being consistent with our observation. It therefore seems likely that the molecular composition in the gas phase would significantly be affected by non-thermal desorption processes of grain mantles in starless cores.

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## Developments of Optical Spectrometers as Approaches to Diffuse Interstellar Bands

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The diffuse interstellar bands (DIBs) were first discovered in the optical absorption spectra on stars in 1922. Although several hundreds DIBs were detected already, DIBs still remain the longest standing unsolved problem in spectroscopy. It has not been known that what kind molecules have these absorptions. One of the best approaches to identify DIBs can be the following procedure: 1) a generation of a DIBs candidate molecule in laboratory, 2) measurements of laboratory frequencies of electronic transitions of the molecule, and 3) comparisons between the laboratory frequencies and astronomically observed DIBs spectra.

To be able to solve the DIBs problem, we have been developed a discharge-emission spectrometer. A hollow cathode was used to generate molecular ions in a discharge, since it has been suggested that molecular ions can be probable DIBs candidates. The discharge was produced by a pulsed voltage of 1500V. A wide wavelength range of this spectrometer was covered by a monochromator HORIBA Jobin Yvon iHR320 (the 200-800 nm wavelength range using three gratings having groove densities 1200 and 1800 gr/mm). The dispersed discharge-emission was detected by a photomultiplier and recorded via a lock-in amplifier. Recently the  ${}^2E_2-X^2B_3$  electronic transition of the butatriene cation  $H_2CCCCH_2^+$  was observed in the discharge emission by using 2-butyne  $CH_3CCCH_3$  as shown in Figure 1. The frequency of the electronic transition was measured to be  $20380\text{ cm}^{-1}$ , which make a study of a comparison with the observed DIBs spectrum.

Although the above spectrometer can cover the wide wavelength range, the resolution is insufficient to have an accurate comparison between the laboratory frequencies and astronomically observed DIBs spectra. Since DIBs are absorption, an absorption spectrum in laboratory is better suited for the comparison. To obtain a high-resolution absorption spectrum, a cavity ringdown spectrometer using the same hollow cathode is under development.

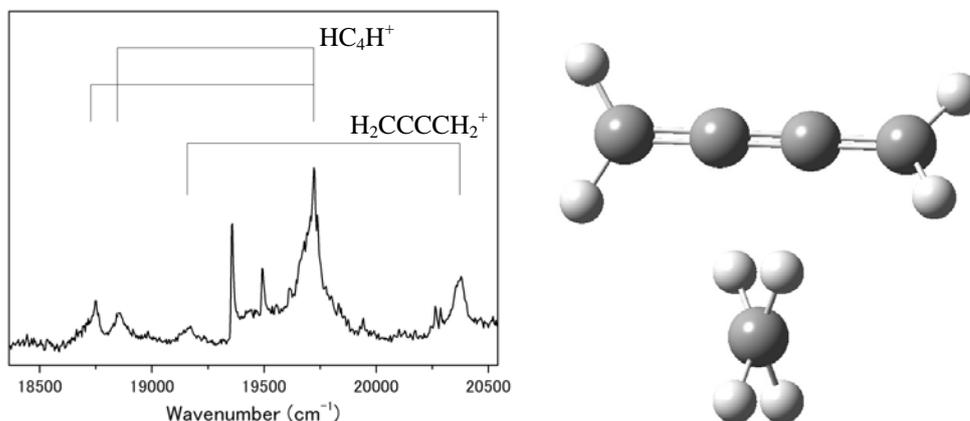


Figure 1: Emission Spectrum of  $H_2CCCCH_2^+$  observed by the discharge-emission spectrometer (left) and the molecular structure of  $H_2CCCCH_2^+$  (right).

## Rotational spectra of methyl formate in the new vibrational excited states

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The methyl formate molecule ( $\text{HCOOCH}_3$ ) is a typical example of the molecule with high spectral density found in interstellar space. So far, many transitions were found in hot cores in massive star-forming regions and recently, were also found in very young low mass star-forming regions. We have also identified in its first and second torsional excited state in Orion KL. [1][2] The observed intensity suggests the possible detection of transition of this molecule in the higher vibrational state. The methyl formate has several low-lying vibrational states. Figure 1 shows the fundamental band below  $500\text{ cm}^{-1}$  as well as the excited state of the  $\text{CH}_3$  torsion (internal rotation).

The microwave spectral data below 200 GHz were taken at the University of Toyama. Additional measurements including the date below and above 200 GHz have also been carried out. All the date was used to search for the excited state with the aid of the computer program developed at Kanazawa University.

We have assigned series of lines in the two new vibrational excited states. The relative energy to the ground state estimated from the spectral intensities was determined. Based on the results, it is possible that one is COC deform or Skeletal torsion, and another is combination band COC deform or skeletal torsion with internal rotation.

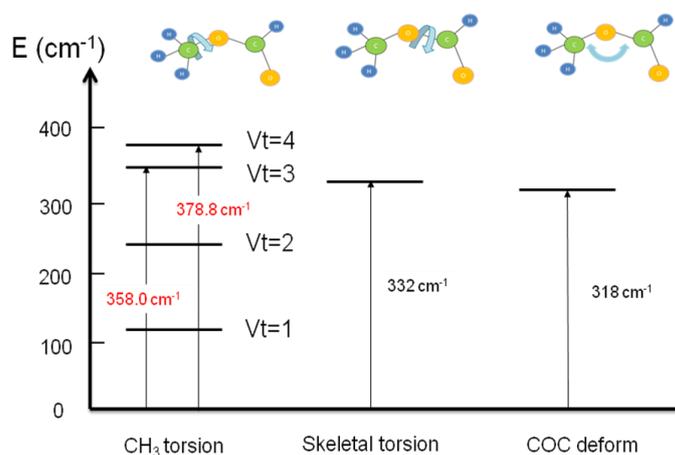


Figure 1: Vibrational energy level of  $\text{HCOOCH}_3$  ( $\sim 500\text{ cm}^{-1}$ ). Red colored energy levels are ab initio MO by Dr. Senent.[3] Black colored energy levels are experiment.[4]

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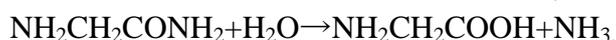
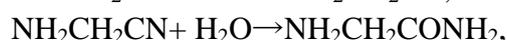
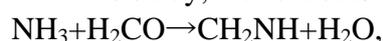
## Sub-millimeter Spectroscopic study for detection of pre-biotic molecules in interstellar space

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Among the biologically important molecules, glycine (NH<sub>2</sub>CH<sub>2</sub>COOH) is the simplest amino acid. Astronomical searches for glycine have continued up to present.<sup>1</sup> But glycine have not detected in interstellar space but for chondrite meteorite. In addition origin of glycine and others amino-acid is yet unknown. In this study, we focusd Strecker synthesis,



one of the famous reaction that produce amino acid. In this synthesis, methylenimine (CH<sub>2</sub>NH, in short MI) and Amino-acetonitrile (NH<sub>2</sub>CH<sub>2</sub>NH in short AAN) are precursors of glycine.<sup>2</sup>

In our experiments, we measured pure rotational spectra of MI, this isotope <sup>13</sup>CH<sub>2</sub>NH and CH<sub>2</sub><sup>15</sup>NH up to 1.2 THz, and AAN up to 1.2 THz to carry out with frequency-modulated sub-millimeter wave spectrometer.

Analysis has been done with Watson's S reduced Hamiltonian. The detailed molecular constants will be reported.

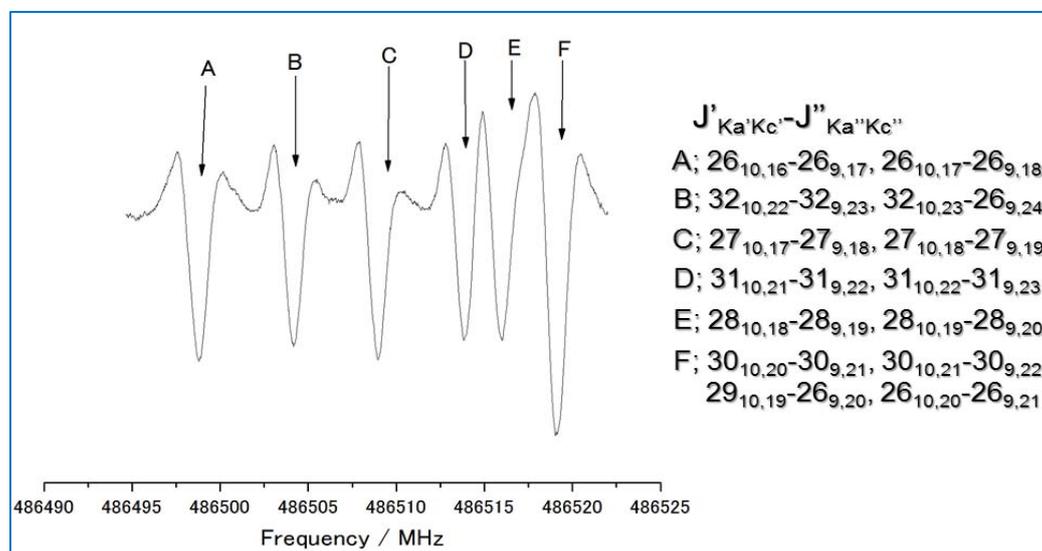


Figure 1: The spectrum of AAN in the 486GHz region.

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## Phosphorous chemistry in the shocked region L1157 B1

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Since shock waves are ubiquitous in interstellar space, a thorough understanding of shock chemistry is important to interpret observed chemical composition. This is particularly true for star-forming regions. For example, outflow gases from protostar bring on shock waves due to collision with surrounding gases.

L1157 dark cloud harbors a low-luminosity Class 0 protostar, which drives a well-collimated molecular outflow. L1157 B1 is a shocked region formed by an interaction between the molecular outflow and ambient gas. Since the B1 position is spatially apart from the protostar, the "pure" shock chemistry can be investigated. Because of this reason, many observational studies are conducted to investigate physical and chemical condition [1] [2] .

Very recently, Yamaguchi et al. (2011) reported detection of PN for the first time in the L1157 B1 and B2 shocked region. The abundance relative to H<sub>2</sub> is estimated to be  $n(\text{PN})/n(\text{H}_2) = (2-6) \times 10^{-10}$  towards B1 and  $(3-7) \times 10^{-10}$  towards B2 [3]. More recently, a subsequent work (Yamaguchi et al. in prep) reported that PO is not detected at shocked region; the upper limit of PO abundance relative to H<sub>2</sub> is  $2.5 \times 10^{-10}$  . Chemistry of P-bearing species has been investigated in the pseudo-time dependent model. For example, Charnley & Millar (1994) investigated P-chemistry in the hot core model, in which they assumed a constant warm temperature (100K-300K) and high density ( $2.0 \times 10^7 \text{ cm}^{-3}$ ), and showed that PN can be produced enough to be observed [4]. But shock chemistry calculations that especially focus on p-bearing species have not been conducted.

In this work, we study the evolution of the P-bearing species in a 1D C-shock model. Temporal variations of physical parameters (density and temperature) are adopted from Jimenez-Serra et al. (2008) [5]. We found that observed abundance of PN can be reproduced in a C-shock model with  $v=20\text{km s}^{-1}$ ,  $n=2.0 \times 10^4 \text{ cm}^{-3}$ , only if the N atom abundance is high ( $n(\text{PN})/n(\text{H}) \sim 10^{-5}$ ) in the pre-shock gas.

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# Can Thermal Instability Grow behind a Shock Wave in HI and Molecular Clouds?

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Thermal instability is an important physical process to determine the structure in the interstellar medium. It is widely known that low and mid-temperature parts of the interstellar medium (ISM) consist of warm and cold neutral medium (WNM and CNM) [1]. Field, Goldsmith & Habing (1969) calculated the thermal equilibrium state. They showed that there are three physical states under the pressure equilibrium: two stable states of CNM and WNM and one unstable state [2].

The thermal instability is considered to be the origin of the tiny scale structures which have been detected HI gas [3] and molecular cloud [4] [5]. Many authors have studied the dynamical condensation (fragmentation) process of the ISM driven by thermal instability in the shocked layer of WNM. Koyama & Inutsuka (2002) show that tiny clumps of CNM are formed as a result of thermal instability in the layer compressed by shock propagation [6]. Recently, Inoue & Inutsuka (2008, 2012) studied the analogous process, including the effect of the magnetic field, and showed the generation of sheetlike HI clouds and molecular cloud [7] [8].

While the thermal instability in the condensation process of WNM to CNM have been studied intensively, its role in CNM and the molecular clouds has not yet been examined. Because the interstellar clouds are known to be always turbulent with supersonic velocity dispersion [9] [10], detailed study of the effect of thermal instability in the shocked cloud must be explored.

Using 1D hydrodynamics simulations with the effects of detailed cooling, heating and chemical processes, we examine thermal stability of shocked gas in HI and molecular clouds. We also estimate the e-folding time of the thermal instability to obtain the degree of perturbation growth in shocked gas. We find that both HI clouds and molecular clouds can be thermally unstable in the cooling layer behind the shock wave. Seed density perturbations in HI cloud can grow  $\exp(5)$ ~150 times larger than the initial state, while perturbations in molecular cloud can grow roughly  $\exp(1)$ ~2.7 for high Mach number shock. These results suggest that, in order to discuss fine structures in the clouds, the isothermal approximation may not be adequate in CNM and molecular cloud.

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# **The influences of disk winds on chemical evolution of protoplanetary disks**

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In the past 20 years, several molecules, molecular ions and radicals have been detected from protoplanetary disks thanks to the improvement of observational facilities. More species will be detected by ALMA which has high sensitivity and spatial resolution. So, theoretical study of chemical structure of protoplanetary disks is required in order to understand detailed chemical and physical structure of the disks from the detected molecular lines.

In this study, we calculate the chemical evolution of protoplanetary disks considering disk winds driven by MRI turbulence and investigate the influences of disk winds on chemical structure of disks. As a result of our calculations, abundances of some molecules increase at the boundary between intermediate and upper layers. It is because molecular hydrogen is transferred into hot layer where molecules such as OH, H<sub>2</sub>O, and then HCN are produced via endothermic gas-phase reactions with H<sub>2</sub>. We also calculate molecular line emission and velocity profile, and discuss which lines are affected by disk winds.

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## From Prestellar to Protostellar Cores: Time Dependence and Deuterium Fractionation

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We investigate the molecular evolution and D/H abundance ratios that develop as star formation proceeds from a dense-cloud core to a protostellar core, by solving a gas-grain reaction network applied to a 1-D radiative hydrodynamic model with infalling fluid parcels. Spatial distributions of gas and ice-mantle species are calculated at the first-core stage, and at times after the birth of a protostar. Gas-phase methanol and methane are more abundant than CO at radii  $r < 100$  AU in the first-core stage, but gradually decrease with time, while abundances of larger organic species increase. The warm-up phase, when complex organic molecules are efficiently formed, is longer-lived for those fluid parcels in-falling at later stages. The formation of unsaturated carbon chains (warm carbon-chain chemistry) is also more effective in later stages;  $C^+$ , which reacts with  $CH_4$  to form carbon chains, increases in abundance as the envelope density decreases.

The large organic molecules and carbon chains are strongly deuterated, mainly due to high D/H ratios in the parent molecules, determined in the cold phase.

We also extend our model to simulate simply the chemistry in circumstellar disks, by suspending the 1-D infall of a fluid parcel at constant disk radii. The species  $CH_3OCH_3$  and  $HCOOCH_3$  increase in abundance in  $10^4$ - $10^5$  yr at the fixed warm temperature; both also have high D/H ratios.

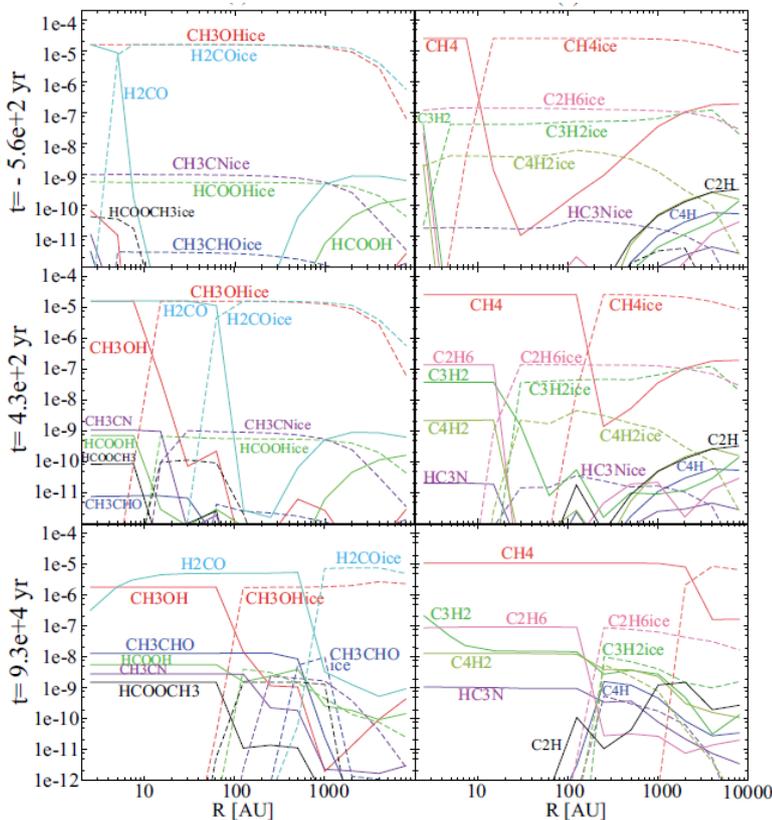


Figure:  
Radial Distribution of complex organic species and carbon chain species at the first core stage ( $t = -5.6 \times 10^2$  yr), and protostellar stage ( $t = 4.3 \times 10^2$  yr, and  $9.3 \times 10^4$  yr).

## Deuterated water in turbulent protoplanetary disks

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Deuterated water observed in the current solar nebula can provide insights into how water has evolved in the primitive solar nebula. So far, D/H ratios in cometary water have been measured in seven comets, six from the Oort Cloud ( $\sim(3-5) \times 10^{-4}$ ; e.g., Mumma et al. 2011, and references therein), one from the Kuiper Belt ( $\sim 1.6 \times 10^{-4}$ ; Hartogh et al. 2011). In all of them, deuterium concentrates by about an order of magnitude relative to the elemental abundance of deuterium in the interstellar medium ( $\sim 1.5 \times 10^{-4}$ ; Linsky 2003). A key question is when this ratio is established during the star and planet formations. Here, we focus on the protoplanetary disk phase.

Deuterium fractionation in protoplanetary disks have been studied numerically (e.g., Aikawa & Herbst 1999). Willacy et al. (2009) investigated deuterium chemistry in inner disks ( $< 30$  AU) considering the radial accretion. They found that the D/H ratio in water ice in the midplane retains their initial ratio ( $\sim 10^{-2}$ , which set by their dense cloud core model) for  $10^6$  yr, since water ice is not destroyed efficiently there. However, we note that turbulent mixing could change the situation drastically. Oxygen is mainly in atomic form in the disk atmosphere, while it is in water ice in the midplane (e.g., Bergin et al. 2007, and references therein). If the turbulence exists, water ice would be transported to the disk atmosphere and destroyed by photoreactions and/or thermal desorption, while atomic oxygen would be transported to the disk midplane and reform water ice. If such destruction and reformation processes occur effectively, the D/H ratio in water ice would be lowered or enhanced depending on the atomic D/H ratio near the disk midplane.

In this presentation, we report the effect of turbulent mixing in the vertical direction on the D/H ratio of water in protoplanetary disks. We solved the rate equations with diffusion terms, which mimic the turbulent mixing, adopting the physical model of a disk surrounding a typical T Tauri star (Nomura et al. 2005, 2007). A collapsing core model is calculated to set the initial molecular abundances of our disk models, in which the D/H ratio in water ice is  $\sim 10^{-2}$ . The D/H ratio in water ice in the midplane does not significantly change for  $10^6$  yr in the case of  $\alpha=10^{-3}$ , while it decreases to  $\sim 10^{-3}$  at  $R=10-30$  AU in the case of  $\alpha=10^{-2}$ . The model ratio remains higher than the cometary ratio. It indicates that in the case of the solar nebula, the D/H ratio in water might be already much less than  $10^{-2}$  in the early phase of the disk.

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# Water formation by OH + H<sub>2</sub> on grain surfaces at 10 K: large isotope effects by quantum tunneling

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Water (H<sub>2</sub>O) is the most abundant solid component in icy grain mantles in molecular clouds. It is widely accepted that grain-surface reactions play a pivotal role for H<sub>2</sub>O formation in those environments. One of the representative pathways is the reaction of hydroxyl radicals (OH) with H<sub>2</sub> molecules;



whose activation barrier is about 2100 K in the gas phase [1]. Due to the large barrier, it is unlikely that reaction (1) thermally occurs on the surface of interstellar grains at as low as 10 K; it should proceed through quantum tunneling. However, it remains unknown whether the tunneling surface reaction really occurs at such low temperatures.

In the present study, we performed laboratory experiments on the formation of H<sub>2</sub>O through quantum tunneling reaction (1) under astrophysically relevant conditions.

When H<sub>2</sub> was codeposited onto a cold (10 K) substrate with OH, which was produced by dissociating H<sub>2</sub>O in a microwave-induced plasma and cooled down to 100 K, the formation of H<sub>2</sub>O was observed in the infrared absorption spectrum of the reaction products.

We next performed similar experiments by using D<sub>2</sub> instead of H<sub>2</sub> in order to measure isotope effects on the reaction. If OH react with D<sub>2</sub>, HDO is formed by the following reaction:



We found that HDO was actually formed by the codeposition of D<sub>2</sub> with OH. However, the efficiency of reaction (2) was about 10% of that of reaction (1) under the same experimental conditions. The relative efficiency of reactions (1) and (2), as well as that of other reactions using OH and H<sub>2</sub> isotopologues (OD, HD, and D<sub>2</sub>) was summarized in Figure 1 where the width of arrows represent the relative efficiency of each reaction. H-atom abstraction from H<sub>2</sub> or HD (thick arrows) was more effective than D-atom abstraction from HD or D<sub>2</sub> (thin arrows). The observed difference in the reaction efficiency can be explained with a difference in the effective mass of each reaction. Therefore, the strong mass-dependence of reactions clearly indicates that reaction (1) proceeds through quantum tunneling at 10 K.

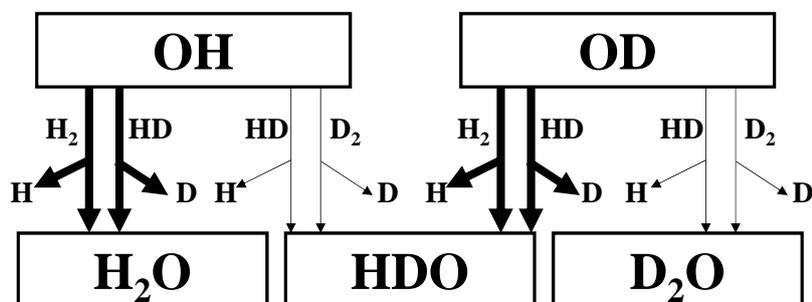


Figure 1: Schematic illustration of reaction efficiency; thick and thin arrows represent effective and less effective reactions, respectively. The relative efficiency is approximated as 1 to 0.1.

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# Deuterium fractionation of methylamine through atomic grain-surface reactions at low temperatures: implication for the possible D/H ratio in molecular clouds

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Interstellar methylamine ( $\text{CH}_3\text{NH}_2$ ) was first found in 1974 toward Sgr B2 and Ori A [1]. This finding is of interest in view of astrobiology because methylamine could be a precursor of amino acid in space [2]. Laboratory studies revealed that methylamine can be formed by various reactions both in the gas phase and the solid phase in molecular clouds (MCs) [3,4]. In either case, it is likely that the  $\text{CH}_3\text{NH}_2$  is retained on icy grains at as low as 10 K and is subjected to various processes on them.

Deuterium (D) fractionation of interstellar molecules is an important issue when considering chemical evolution in MCs. Previous studies revealed that atomic grain-surface reactions play a significant role for the D enrichment of interstellar molecules such as  $\text{CH}_3\text{OH}$  [5] and  $\text{H}_2\text{CO}$  [6]. Although D-substituted methylamine has never been observed, it is reasonable to consider that interstellar methylamine is deuterated to some extent. In the present study, we performed laboratory experiments on the hydrogen (H)-D and D-H substitution reactions of solid methylamine through atomic-surface reactions at low temperatures. Based on the obtained experimental results, we estimated a possible D/H ratio of methylamine brought by atomic-surface reactions in MCs.

When solid  $\text{CH}_3\text{NH}_2$  was exposed to D atoms at 10 K, deuterated methylamine  $\text{CD}_3\text{ND}_2$  was produced. Then we measured the rate of the H-D substitution at the functional group level by using partly deuterated methylamines  $\text{CD}_3\text{NH}_2$  and  $\text{CH}_3\text{ND}_2$ ; the H-D substitution rate of methyl group was about 10 times larger than that of amino group and on the same order with that of methanol [5]. When deuterated methylamine  $\text{CD}_3\text{ND}_2$  was exposed to H atoms at 10 K, hydrogenated methylamine  $\text{CH}_3\text{NH}_2$  was produced. D-H substitution rate of methylamine was also measured at the functional group level: 0.4 for the methyl group and 0.1 for the amino group relative to the H-D substitution rate of methyl group.

Based on the measured H-D and D-H substitution rates of methylamine, we calculated time-variations in the fractional abundances of methylamine isotopologues brought by atomic surface reactions in MCs. Assuming that only  $\text{CH}_3\text{NH}_2$  is present at time  $t = 0$ , atomic  $\text{D}/\text{H} = 0.01$ , and  $n(\text{H}) = 1 \text{ cm}^{-3}$ , about 3% of  $\text{CH}_3\text{NH}_2$  is converted into deuterated methylamines at  $t = 10^6$  years where the typical lifetime of MCs. Among deuterated methylamines,  $\text{CH}_2\text{DNH}_2$  is the most abundant, followed by  $\text{CH}_3\text{NHD}$ . The singly-deuterated methylamines comprise about 97% of total deuterated methylamines.

The present study proposes that deuterated methylamines are possibly present in MCs, although their absolute abundances may not be large. Future astronomical observations with better S/N are highly desired for the detection of deuterated methylamines.

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# The surface diffusion mechanism of hydrogen atom on interstellar ice

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It has been recognized that the abundance of some important molecules, including H<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub>, cannot be explained by pure gas-phase formation, and that surface reactions on dust grains are crucial to explain the production of those molecules. Molecular formation on ASW proceeds via elementary processes of reactants: adsorption, diffusion, and reaction with another adsorbed reactant. Since in cold and dense clouds dust grains are covered with amorphous solid water (ASW), the diffusion of H atoms on ASW is of significant importance for the surface reactions. For the diffusion mechanism of H atom on ASW, quantum tunneling and thermal hopping are often advocated [1]. However, there have been no experimental reports on the diffusion mechanism of H-atom on ASW. Recently, Watanabe et al. (2010) presented the results of a novel type of experiment to shed light on the longstanding dispute about the activation energy of H atom diffusion on ASW [2]. They performed direct detection of H atoms adsorbed on ASW using photostimulated desorption (PSD) and resonance-enhanced multiphoton ionization (REMPI). In the present study, we extended this method to measure the diffusion of deuterium atom on ASW. From the isotope effect of surface diffusion, we discuss the diffusion mechanism of H atom on ASW [3].

The figure shows the time variations of the signal intensities of H and D atoms ( $I_H$  and  $I_D$ ) photodesorbed from ASW at 8 K as a function of the waiting time,  $t$ , after the deposition of atoms. Our another experiment found out that monoatomic desorption from ASW plays only a minor role, and the attenuations of  $I_H$  and  $I_D$  on the ASW surface after atomic deposition are thus caused mainly by recombination of the atoms following diffusion. Both  $I_H$  and  $I_D$  decrease at a similar rate. We derived the activation barriers for the diffusion of H and D atoms to be 22 and 23 meV, respectively. Since the tunneling effect strongly depends on the particle mass, thermal hopping better explains the diffusion mechanism rather than tunneling.

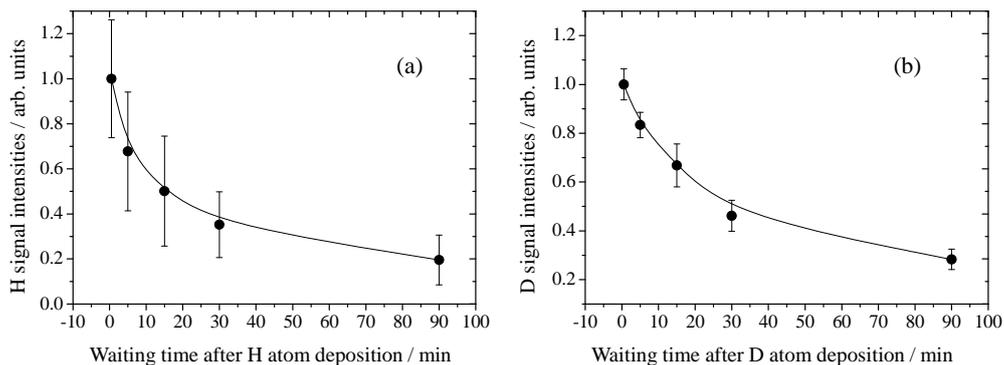


Figure: Attenuation of photodesorption intensities of (a) H atoms and (b) D atoms adsorbed on ASW at 8 K as a function of the waiting time after a deposition time.

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## Photodesorption mechanisms for H<sub>2</sub>O from the 157 nm irradiation of amorphous solid water at 90 K

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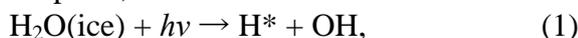
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For grains in the cosmic space, the most important desorption mechanism at the edge of molecular clouds is photodesorption. The desorption mechanisms for H<sub>2</sub>O( $v=0$ ) discussed in our previous papers can be grouped into three types [1]; (A) the one that experiences the initial electronic excitation, (B) expelled as a result of electronic excitation of a neighboring molecule, or (C) formed by the recombination of photofragments arising from different photodissociated molecules. Types (A) and (B) are considered to be direct processes, whereas (C) involves secondary processes. Initially, type (A) and (C) mechanisms will involve high internal energies in the desorbing molecules (due to photoexcitation and recombination, respectively). Both might thus be expected to favor formation of vibrationally excited H<sub>2</sub>O molecules, whereas the type (B) mechanism could well result in desorbed H<sub>2</sub>O( $v=0$ ) molecules.

In the present work, the photodesorption of H<sub>2</sub>O( $v=0$ ) following 157 nm photoexcitation of amorphous solid water, has been observed. In addition, signals of H<sup>+</sup> and OH<sup>+</sup> were detected in the experiments. Measured H<sup>+</sup> and OH<sup>+</sup> signals were deduced to originate from desorbing vibrationally excited water molecules. Two distinct populations were detected, one that appeared promptly and another that grew in relative importance with increasing irradiation time. The former was found to have the same translational temperature as H<sub>2</sub>O( $v=0$ ),  $T_{\text{trans}}=1800$  K, desorbed by the kick-out mechanism (reactions (1) and (2)) [2, 3]. We considered that the H<sup>+</sup> and OH<sup>+</sup> ( $T_{\text{trans}}=1800$  K) component arise by the kick-out of vibrationally excited H<sub>2</sub>O molecules, or by prompt geminate recombination of H and OH photoproducts followed by desorption, or a combination of both mechanisms.



where H\* represents a highly translationally excited H photoproduct with a few eV. The population of H<sub>2</sub>O formed by reaction (3) had a much hotter translational temperature,  $T_{\text{trans}} = 10000$  K. The time evolution of this component suggests that it probably arises from the secondary recombination of photoproducts at the surface. In these experiments we might therefore have observed H<sub>2</sub>O photodesorption resulting from three distinct mechanisms: kick-out, direct recombination, and secondary recombination.

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# Surface abundance change in vacuum ultraviolet photodissociation of CO<sub>2</sub> and H<sub>2</sub>O mixture ices

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The importance of energetic processes caused by vacuum ultraviolet (VUV) photoirradiation is known in the cosmic regions, which can directly induce chemical reactions of the ice mantles. Photoirradiation on pure or mixed ices triggers desorption of atoms, radicals, or molecules and the desorption dynamics of photofragments are known to be sensitive to the adsorption states of the photoirradiated molecules. Therefore, how the surface composition changes after VUV photoirradiation needs to be investigated in order to develop detailed modeling of gas–ice interactions including the reactivity of surface reactions.

In the present work, we have measured time-of-flight spectra and rotationally resolved resonance-enhanced multiphoton ionization (REMPI) spectra of photodesorbed CO species following 157 nm photodissociation of mixed CO<sub>2</sub>/H<sub>2</sub>O (1:4) ice films at 90 K. Two different deposition gas mixtures were used for the mixed ice preparation to investigate CO<sub>2</sub> adsorption structures on H<sub>2</sub>O ice. Hot CO ( $v=0,1$ ,  $T_{\text{trans}}=1600$  K and  $T_{\text{rot}}=800$  K) and cold CO ( $v=0$ ,  $T_{\text{trans}}=90$  K and  $T_{\text{rot}}=150$  K) were observed as photodesorbed products, suggesting that the hot CO comes from CO<sub>2</sub> adsorbed atop the water ice surface, while CO<sub>2</sub> trapped in the porous sites produces the cold CO component due to an energy relaxation process by collisions within the mixed ice en route to the vacuum. Photodesorption of OH and O(<sup>3</sup>P<sub>J</sub>) was also observed, which is predominantly produced from the photodissociation of H<sub>2</sub>O in the mixture ice. Formation of the heterogeneous structures from mixed ice films should depend on photoabsorption cross sections, ice temperatures and photon flux. Since the VUV absorption cross section of CO<sub>2</sub> is smaller than that of H<sub>2</sub>O in the entire VUV wavelength region, CO<sub>2</sub> is less efficiently dissociated than H<sub>2</sub>O. Actually, the CO ( $T_{\text{trans}}=1600$  K) intensity increased with 157 nm irradiation time, while CO ( $T_{\text{trans}}=90$  K) intensity has no appreciable temporal change. These results indicate an increase of the surface abundance of the CO<sub>2</sub> adlayer adsorbed atop the CO<sub>2</sub>/H<sub>2</sub>O mixture ice at 90 K presumably by the preferential H<sub>2</sub>O photodissociation.

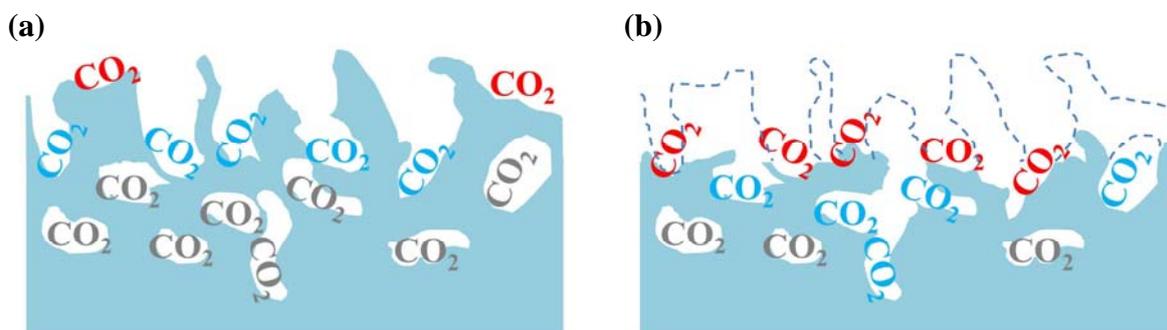


Figure 1: Schematic illustration of the distribution of CO<sub>2</sub> in CO<sub>2</sub>/H<sub>2</sub>O mixture ice, (a) as deposited before irradiation and (b) after prolonged 157 nm irradiation. CO<sub>2</sub> (red) stands for physisorbed CO<sub>2</sub> on the surface, CO<sub>2</sub> (blue) are trapped in the pores and CO<sub>2</sub> (gray) are buried in the bulk phase.

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# Laboratory measurements of spin temperature of water molecules from ice in thermal desorption

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H<sub>2</sub>O contains two protons with nuclear spin of  $I=1/2$ , and two nuclear-spin modifications exist: the ortho ( $I=1$ , triplet, parallel nuclear spin) and the para ( $I=0$ , singlet, antiparallel nuclear spin) with statistical weights  $2I + 1$ . Nuclear-spin temperature ( $T_{\text{spin}}$ ) is defined as the temperature that reproduces a given the ortho-to-para ratio (OPR) if in local thermodynamic equilibrium. The OPR of H<sub>2</sub>O is equal to 3 in statistical equilibrium, which is achieved at temperatures above  $\sim 50$  K.

$T_{\text{spin}}$  of H<sub>2</sub>O molecules is often observed in comet coma and in star forming regions to investigate these molecules' physical and chemical histories. In cometary coma,  $T_{\text{spin}}$  of H<sub>2</sub>O molecules has been derived to be  $\sim 30$  K [1]. These values have been implicated as the temperature of cold grains at molecular condensation or formation in a molecular cloud, or in the solar nebula [2]. However, the real meaning of the observed  $T_{\text{spin}}$  remains a topic of continuing debate.

The present study experimentally measured the  $T_{\text{spin}}$  of H<sub>2</sub>O thermally desorbed from amorphous solid water (ASW) deposited at 8 K. The experiment was performed with the RASCAL apparatus at Inst. of Low Temp. Sci., which consists of a vacuum sample chamber, and a laser system. ASW was prepared on a Al substrate at 8 K by vapor-deposition in the vacuum chamber, and then heated to 150 K to sublime H<sub>2</sub>O. The thermally desorbed H<sub>2</sub>O molecules were analyzed ro-vibrationally by the resonance enhanced multiphoton ionization (REMPI) method [3]. We also produced ASW at 8 K by photolysis of a CH<sub>4</sub>/O<sub>2</sub> mixture (photoproduced ASW) for the idea that  $T_{\text{spin}}$  of H<sub>2</sub>O molecules may relate to formation processes on cold dust grains. Figure 1 shows the REMPI spectrum of desorbed H<sub>2</sub>O for the vapor-deposited ASW. The spectrum was best reproduced by the simulation with  $T_{\text{rot}} = T_{\text{spin}} = 150$  K, where  $T_{\text{rot}}$  represents rotational temperature. Thermally desorbed H<sub>2</sub>O molecules from the both ice samples showed  $T_{\text{spin}}$  almost at the statistical high-temperature limit. These results suggest that the  $T_{\text{spin}}$  of gaseous H<sub>2</sub>O molecules thermally desorbed from ice does not necessarily reflect the surface temperature at which H<sub>2</sub>O molecules condensed or formed. We discuss the possibility of nuclear-spin conversion of H<sub>2</sub>O in water ice [3].

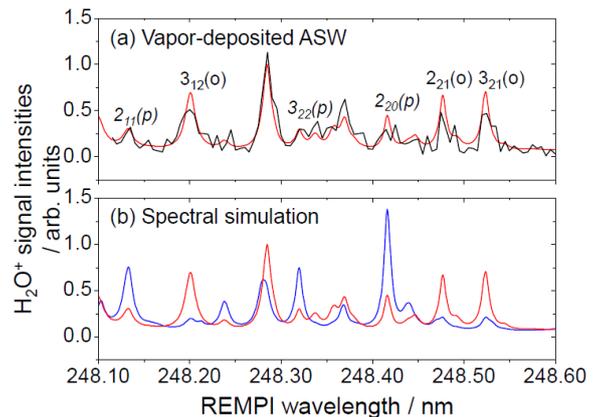


Figure 1. (a) (The black line) 2+1 REMPI spectrum of thermally desorbed H<sub>2</sub>O from vapor-deposited ASW. (The red line) The best-fitting simulations with  $T_{\text{rot}} = T_{\text{spin}} = 150$  K. Indications ( $J_{K_a, K_c}$ ) are rotational assignments in H<sub>2</sub>O. H<sub>2</sub>O molecules with ( $K_a + K_c = \text{odd}$ ) are ortho, while those with ( $K_a + K_c = \text{even}$ ) are para species (*italic transitions*). (b) Reference simulations with  $T_{\text{spin}} = 150$  K (red) and 8 K (blue).  $T_{\text{rot}}$  is fixed at 150 K.

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## Mid-infrared High-resolution Spectrograph for SPICA

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We present the status of the development of mid-infrared high-resolution spectrograph for SPICA, which is a next-generation infrared astronomical mission in space with a cooled 3.0 m telescope [1]. High-resolution spectroscopy in the mid-infrared wavelength range is of strong interest. Since numerous rotational-vibration bands of molecules are located in this wavelength range, spectra of celestial objects and ISMs provide fruitful information on physical/chemical condition of them. However, in ground-based observation, systematic observations have been hampered by the strong atmospheric extinction, which limits the observational wavelength range, and also by the large amount of thermal background, which reduces the sensitivity in most cases. Therefore high-resolution spectroscopy from space has been awaited for investigating the mid-infrared wavelength region, but it has not yet been realized because the size and the weight of instruments for high-resolution spectroscopy are so large and so heavy that it is difficult to launch them. SPICA is a precious opportunity to explore this exciting field. Mid-infrared Camera and Spectrograph (MCS) is proposed for SPICA [2]. As one function of MCS, we have been developing a high-resolution spectrograph (MCS-HRS) [3].

The goal of MCS-HRS is to achieve a spectral resolution ( $\lambda/\Delta\lambda$ ) of 20,000-30,000 in the mid-infrared wavelength. In the latest specification, the wavelength coverage is set to be 12-18  $\mu\text{m}$ , where many organic molecules can be detected but it is hard to access from ground due to the strong atmospheric extinction. The main observational targets are ISMs, proto-planetary disks, and comets. The high-resolution capability of the spectrograph enables not only identifying molecular lines but also kinematic studies in the mid-infrared wavelengths. Observing the compositional distribution in proto-planetary disks provides crucial information to understand the formation process of planets. MCS-HRS can shed light on the material evolution among ISMs - proto-planetary disks - comets (planetesimals), and it also has possibility to find molecules some of which could be bio-maker.

### References

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