

# The Spectral Line Survey in TMC-1 -- Progress of the Data Analysis

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Cold dark interstellar clouds have been extensively studied as the formation sites of low-mass stars and planetary systems since their identification to the interstellar molecular clouds in 1970's. A variety of exotic chemical compounds found in molecular clouds, especially those containing carbon atoms, attracted strong interests in connection with the formation of planets and the origin of life in the universe. Recent radio and IR observations towards comets collected important evidence that comets, 4.6 billion year-old fossil bodies of the proto-solar-system nebula, keep molecular composition similar to that in cold dark clouds. Therefore, the chemical evolution in cold dark clouds is basically important as the initial process of interstellar matter evolution toward the planets, and, ultimately to life.

Chemical reactions in dark clouds are not yet fully understood, and many unknown molecules might be synthesized in dark clouds. It is essential for understanding the chemical reactions in dark clouds, therefore, to make an unbiased frequency survey that can detect all molecular lines, including unpredicted lines of unknown molecules.

Kaifu et al. [1] published a molecular spectral line survey data toward a dark cloud, the cyanopolyne peak of TMC-1, in the frequency range between 8.8 and 50 GHz (see Figure 1), using the 45-m mm-wave telescope of the Nobeyama Radio Observatory<sup>1</sup>. They detected 414 lines from 38 molecules. Most of the molecules are linear carbon chain species and their derivatives, and there are only a few organic species such as CH<sub>3</sub>OH, CH<sub>3</sub>CHO, HCCCHO and CH<sub>2</sub>CHCN. More saturated species, e.g., C<sub>2</sub>H<sub>5</sub>CN and HCOOCH<sub>3</sub>, were not detected.

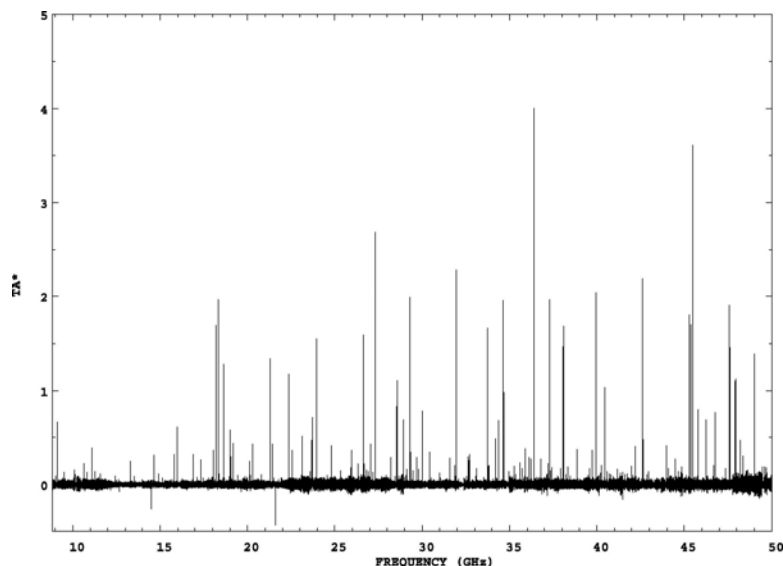


Figure 1: A compressed atlas of the 8.8--50 GHz spectrum toward TMC-1 (cyanopolyne peak).

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<sup>1</sup> Nobeyama Radio Observatory is an open-use facility for mm-wave astronomy, being operated under the National Astronomical Observatory of Japan (NAOJ).

We have made detailed data analyses for the 29 species out of detected 58 species by utilizing peak line temperatures that were obtained through the Gaussian fitting. The detected lines for each molecule were analyzed assuming the LTE condition with the weight of  $1/\sigma^2$  where  $\sigma$  is the rms noise value at each line position. When available, we incorporated weaker hyper fine components in order to avoid the photon trapping effect. Figure 2 shows a comparison between old column density values [2] and present values for several carbon chain species.

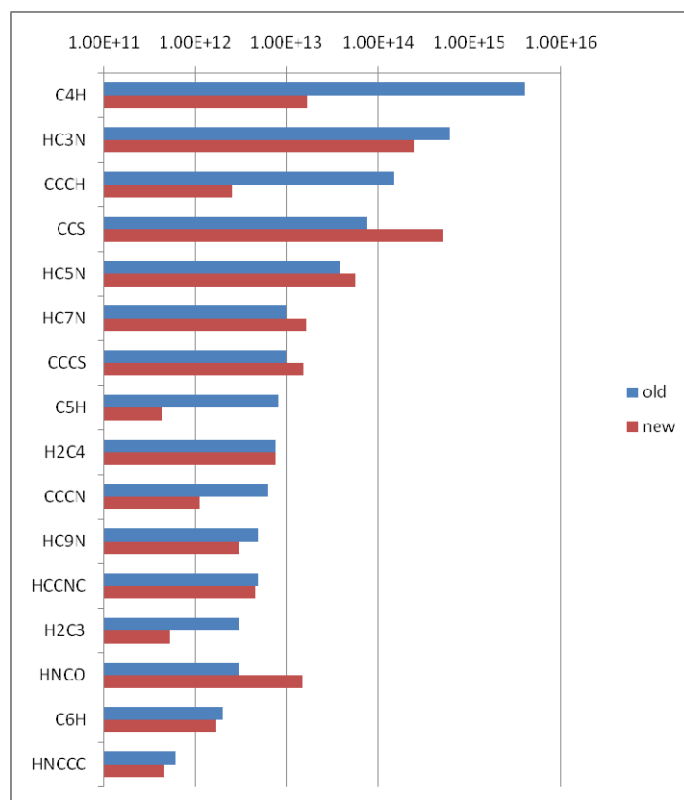


Figure 2: Comparison between old column density values and new values for several carbon chain species.

It is readily seen that the column density of C<sub>4</sub>H has lowered by about two orders of magnitude, which is consistent with the theoretical prediction by [3] on the abundance ratio of C<sub>4</sub>H to C<sub>4</sub>H. The abundances for C<sub>5</sub>H and C<sub>6</sub>H have been reversed, which is consistent with the past reports. For HC<sub>n</sub>N molecules, the old and new values do not change significantly.

We will talk the detailed procedure of the analyses, excitation temperature variation vs. number of carbon atoms, and derived isotope ratios, D/H, <sup>13</sup>C/<sup>12</sup>C, and <sup>15</sup>N/<sup>14</sup>N.

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Study of the L1551 pre-stellar core using the  $C^{18}O(1-0)$  and  $H^{13}CO^+(1-0)$  line emission with the Nobeyama 45 m telescope and Millimeter Array.

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We carried out  $C^{18}O(1-0)$  and  $H^{13}CO^+(1-0)$  line observations of the L1551 pre-stellar core (L1551 MC) with the Nobeyama 45 m telescope and Millimeter Array (NMA). The purpose of this study is to reveal the initial conditions for low-mass star formation. We obtained the  $C^{18}O$  and  $H^{13}CO^+$  maps of the core with the 45 m telescope. The peak position of the  $C^{18}O$  core is shifted by 60" to the center from that of the  $H^{13}CO^+$  core. The radius, mass, and velocity width of the core are 0.1 pc, 1  $M_{\odot}$ , and 0.71 km s<sup>-1</sup>, respectively, in  $C^{18}O$ , and 0.15 pc, 4  $M_{\odot}$ , and 0.47 km s<sup>-1</sup>, respectively, in  $H^{13}CO^+$ . Our model analysis derived the density profiles of  $\rho \sim r^{-1.3}$  and  $r^{-1.4}$  for the  $C^{18}O$  and  $H^{13}CO^+$  cores, respectively, which are flatter than the theoretical prediction of  $r^{-2}$  for a star-forming core (Shu 1977<sup>[1]</sup>; Larson 1969<sup>[2]</sup>; Penston 1969<sup>[3]</sup>). In addition, we found that the  $C^{18}O$  core has a velocity gradient along the NE-SW direction, which can be interpreted as rotation, and that the velocity width of the core increases toward the center. However, the NMA could not detect any compact component within 0.05 pc from the core center in  $C^{18}O$ . These results lead us to the conclusion that the L1551 MC has not yet evolved into a centrally concentrated star-forming core in spite of the age of  $10^{4-5}$  yr (Swift et al. 2005<sup>[4]</sup>). The ALMA can reveal the detailed density and velocity structures of the interesting core.

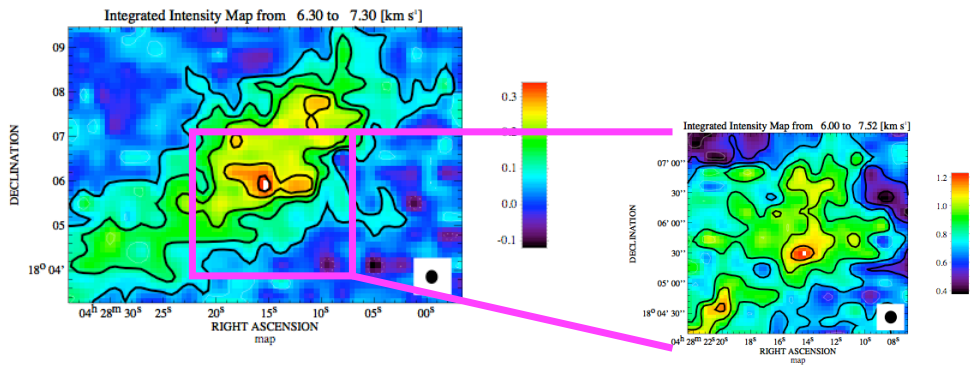


Figure 1: (left) Total integrated intensity map of the  $H^{13}CO^+(1-0)$  emission (color and contours). (right) Total integrated intensity map of the  $C^{18}O(1-0)$  emission (color and contours). The contours with the intervals of  $3\sigma$  level start from the  $3\sigma$  levels, where the  $1\sigma$  noise levels are 0.05K and 0.1K in  $T_A^*$  for  $H^{13}CO^+$  core and  $C^{18}O$  core, respectively.

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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 chemical compositions in representative sources, but also for finding out new observing tools probing interstellar medium and star formation. We started the line surveys toward a few new type of sources with the Nobeyama 45 m telescope. The target sources include the low-mass star forming region L1527, the shocked region of L1157, infrared dark clouds G28, and external galaxies Arp 220, NGC 1068 and NGC 253. Mainly with the new 3 mm receivers installed on the 45 m telescope [1], the frequency range from 84-115 GHz will be surveyed with much higher sensitivity than the previous observations. The total observing time is expected to be about 1000 hours for four years. The results from the survey will be used for detailed studies on chemistry in each source, and will also provide us with useful templates for planning the observing strategy with ALMA. The first year of the line surveys was finished. We report the preliminary results.

L1527 is a very interesting object, because the abundances of carbon-chain molecules are high, though this source is a low-mass star forming region [2]. We detected many lines including high excitation lines of HC<sub>5</sub>N (e.g. J=41-40, upper state energy of 110 K), isotopic species (D, <sup>13</sup>C) of some carbon-chain molecules, and HCO.

In L1157, where interactions between an outflow and ambient clouds are prominent [3, 4], we detected many lines including C<sup>34</sup>S, CH<sub>3</sub>CHO, and HCOOCH<sub>3</sub>. To study shock chemistry and gas-grain interaction, these detections are rather important information. After our observations, we noticed that HCOOCH<sub>3</sub> is independently detected with the IRAM 30m telescope [5].

In G28 three interesting positions called mm1, mm4, and mm9 are selected. Toward mm1 and mm4 line wings were found in HCO<sup>+</sup>, HCN, SiO, CS, and CH<sub>3</sub>OH. These wings indicate outflow activities. In addition, CH<sub>3</sub>CHO is detected only in mm1 and mm4. This molecule is one of the probable grain related species. Therefore CH<sub>3</sub>CHO may be evaporated from grain. Based on these results, mm1 and mm4 are thought to be high-mass protostellar objects.

About galaxies we observed only Arp 220 in the first year. In Arp 220 wide absorption lines of ammonia have been detected [6]. We expected such absorption lines for other molecules, which have low excitation lines at relatively low frequency region like ammonia. We tried to find spectral lines of HNCO (21.98 GHz) and SO (30.00 GHz), but they were not detected at the rms antenna noise temperature of 1.0 and 1.5 mK, respectively.

Many new lines were detected in L1527, L1157, and G28. We hope that these results will become invaluable heritages of molecular line data.

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# Gas and dust of asymptotic giant branch (AGB) stars and planetary nebulae (PNe)

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Recent infrared observations using the Spitzer Space Telescope, the Subaru Telescope and the AKARI provided good opportunities to understand the mass and gas formed in evolved stars. We first present the estimation of the total mass-loss rate from all carbon-rich AGB stars in the Large Magellanic Cloud (LMC). AGB stars are one of the important dust sources in the ISM of the LMC. Gas injection from supernovae is more important in the Bar region, than AGB stars. AGB stars are an important gas contributor in the Disk. We show some of the representative spectra of AGB stars and PNe in the Galaxies in the Local Group, including the LMC, and Galactic Globular Clusters (GC). Their spectra show a wide range and varieties of molecular and dust features. The strength of this molecular band tends to be stronger towards the AGB stars at low metallicity. This can be explained, because at low metallicity, the initial oxygen abundance is low, resulting in chemical processes being more sensitive to carbon synthesized in AGB stars [1]. It appears that the dust composition depends on both the stellar evolution stage and the metallicities of the galaxies. Finally, we show a wide-field-of-view (4'x7') image of the Helix Nebula in the molecular hydrogen lines. The Helix Nebula is one of the closest PNe (219 pc), and detailed studies within the nebula are possible. Molecular hydrogen is found only in association with globules in the nebula. PDR models suggest that these hydrogen molecules were formed during the AGB phase, and they survived over the UV radiation field from the PN central star.

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# Properties of Interstellar PAHs in the Milky Way and in Nearby Galaxies

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The ubiquitous infrared (UIR) bands are a family of emission bands that have been observed ubiquitously in various astrophysical environments including planetary nebulae, reflection nebulae, HII regions (see [1] for a review), general interstellar medium and cirrus clouds (e.g., [2], [3], [4]) not just in our Galaxy but also in external galaxies (e.g., [5], [6]). It is widely accepted that the carriers of these bands contain polycyclic aromatic hydrocarbons (PAHs; [7]) or PAH-like molecular groups (i.e. QCCs; [8]). Indeed, [9] has recently reported that the observed UIR spectra are closely reproduced by a mixture of theoretically calculated infrared spectra of PAHs with different size distribution, charge state and the precise chemical composition of the contributing molecules. However, it still remains uncertain how we could interpret the observed variations in the spectra of UIR bands and how we could understand the evolution of interstellar PAHs. For this purpose, close collaboration among the laboratory experiments as well as the theoretical calculations on the infrared spectra of PAH related materials and the observations of UIR spectra in various environments are indispensable.

AKARI, the Japanese Infrared Satellite, has been playing an important role in this field presenting a number of near- to mid-infrared spectra of ISM in our Galaxy and in nearby galaxies. In this presentation I will introduce some of AKARI's latest observational results and their impacts on the studies of interstellar PAHs.

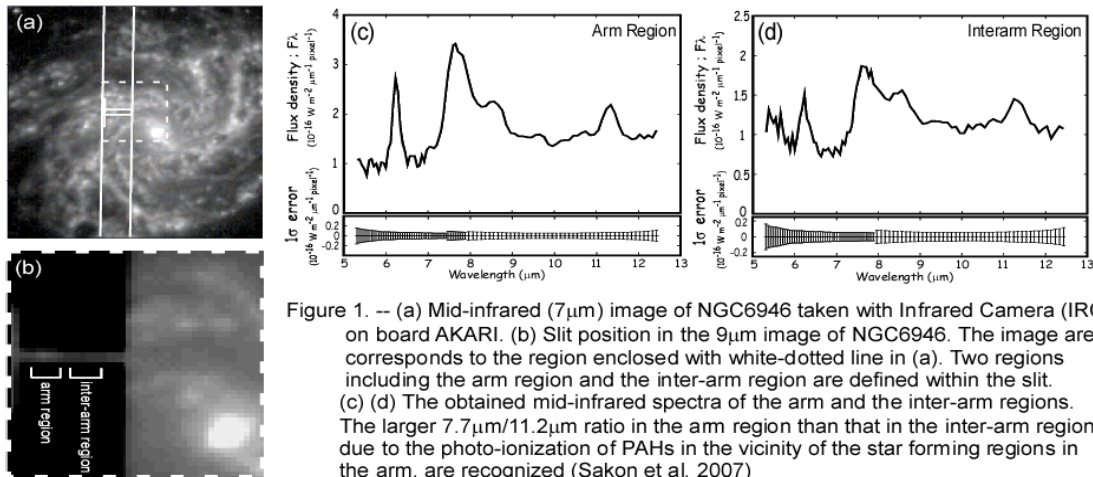


Figure 1. -- (a) Mid-infrared (7 $\mu$ m) image of NGC6946 taken with Infrared Camera (IRC) on board AKARI. (b) Slit position in the 9 $\mu$ m image of NGC6946. The image area corresponds to the region enclosed with white-dotted line in (a). Two regions including the arm region and the inter-arm region are defined within the slit. (c) (d) The obtained mid-infrared spectra of the arm and the inter-arm regions. The larger 7.7 $\mu$ m/11.2 $\mu$ m ratio in the arm region than that in the inter-arm region, due to the photo-ionization of PAHs in the vicinity of the star forming regions in the arm, are recognized (Sakon et al. 2007)

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## How forms observed low-temperature crystalline silicate: Approach from laboratory experiments

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Astronomical observations have shown the existence of abundant silicate grains around evolved stars in the infrared spectra. It has been realized that most of the silicate grains are amorphous phases based on the infrared features. In contrast, characteristic infrared features attributed to Mg-rich crystalline silicates have been reported in limited number of evolved stars with high mass loss rate ( $>10^{-5} M_{\text{sun}}/\text{yr}$ ) [1]. The fraction of the crystalline silicates, particularly forsterite, is typically 10-15 % in the outflows with high mass loss rate of asymptotic giant branch (AGB) stars [2]. During the formation of silicate grains, whether a silicate grain becomes crystalline or amorphous depends sensitively on its formation conditions. To elucidate the crystallization condition of amorphous silicate, several laboratory experiments have been attempted. It has been known that crystalline forsterite grains are formed at a slower cooling rate ( $\sim 700$  K/s: [3]) or by later annealing ( $\sim 1000$  K: [4]) of previously condensed amorphous grains. Crystallization has generally been discussed on the basis of thermal annealing [5]. However, it seems to be unrealistic to find a mechanism of partial annealing occurred only at the stars with high mass loss rate, because the crystallization of silicate is very sensitive in temperature. In addition, some implications of low-temperature crystallization have been reported from the astronomical observation of both young and evolved stars [6-8]. Generally, the temperatures of the crystalline silicate grains astronomically observed are at as low as 100-250 K. In contrast, warmed amorphous silicates in a stationary circumstellar disk were observed [9]. Therefore, it can be considered that the crystallization of silicates may be not affected by thermal heating.

In this situation, I would like to propose that the astronomically observed crystalline forsterite can be formed by direct condensation from the vapor phase of magnesium and silicon oxide. It was found that the crystallinity, which was deduced from the shape of the 10  $\mu\text{m}$  feature, of the circumstellar silicates could be determined by the balance between heat generation by Mg oxidation and heat dissipation due to radiation. In this case, later annealing of the silicate fraction or the use of a warm substrate for condensation of crystalline silicate is unnecessary. In addition, to explain the existence of highly crystalline silicate grains (75% of total silicate) observed in some silicate carbon stars, the possibility of low-temperature crystallization is presented based on electron irradiation on amorphous Mg-silicate grains, because the environment of the envelope is very low in temperature for the crystallization of silicates due to annealing [10].

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# The role of heterogeneous reactions in the origin and evolution of Titan's atmosphere

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Titan, the largest moon of Saturn, has a thick atmosphere composed primarily of nitrogen and methane. More than 10 organic molecules and dense haze layers also have been detected in Titan's atmosphere [1]. The goal of this study is to understand why Titan's atmospheric composition is the current one and how the atmosphere has evolved during the age of solar system. In this study, we focused on the heterogeneous reactions on the surface of organic aerosol, which forms haze layers in Titan's atmosphere. We experimentally investigated the heterogeneous reactions of atomic deuterium with Titan tholin (laboratory analog of Titan's aerosol) in a laboratory and determined the reaction probabilities of the heterogeneous reactions quantitatively [2]. By incorporating the reaction probabilities into a photochemical model of Titan's atmosphere, we evaluated the role of organic haze both in the chemical composition of the atmosphere and the hydrogen budget on Titan [3].

Our results suggest that the heterogeneous reactions significantly reduce the concentrations of atomic hydrogen in the stratosphere and mesosphere. Low concentration of atomic hydrogen enhances the concentrations of unsaturated complex organics and reduces the concentrations of saturated hydrocarbons. These results show that Titan's aerosols act as an efficient sink of atomic hydrogen (Figure 1). Such behavior of aerosol may keep the chemical composition of the Titan's atmosphere to the current one, which is suitable for synthesis of complex organic molecules. Furthermore, our results also suggest that the increase in haze production induces further increase in the haze production in the atmosphere. By taking into account this positive feedback in Titan's atmosphere, we will discuss the role of the heterogeneous reactions in the evolution of the atmosphere-surface system on Titan.

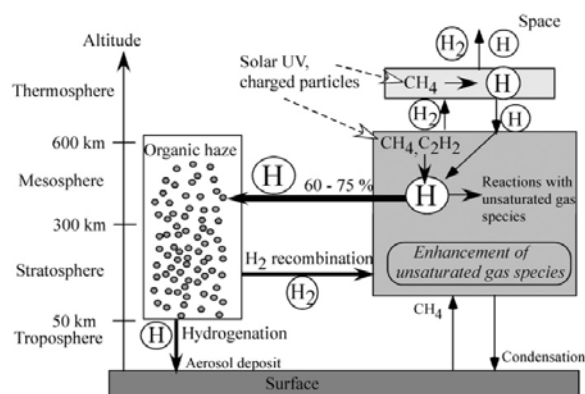


Figure 1: Schematic diagram of the fate of atomic hydrogen in Titan's atmosphere. The organic aerosol acts as a catalyst not only to remove highly reactive atomic hydrogen from the atmosphere but also to enhance the efficient production of higher molecular-weight hydrocarbons in the atmosphere.

## References

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## Reaction Dynamics in the Interstellar Medium - From Molecule Formation in the Gas Phase to Interstellar Grains

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The formation of molecules in extraterrestrial environments has fascinated scientists since the pioneering detection, in 1937-39, of CH, CH<sup>+</sup>, and CN in interstellar space. We now know of at least 120 species, ranging in complexity from diatomics such as molecular hydrogen (H<sub>2</sub>) to polyatomics like the sugar glycolaldehyde (HOCH<sub>2</sub>CHO), benzene (C<sub>6</sub>H<sub>6</sub>), and cyanopentaacetylene (HC<sub>11</sub>N), which have been identified as gas-phase constituents of extraterrestrial environments. Nevertheless, many facets of the question "How do these molecules arise?" remain unanswered or contentious. In searching for answers to this question, we also obtain crucial information relevant to the chemistry of our immediate environment: the rules of chemistry, after all, are universal, even when the conditions are very different.

This talk reviews recent developments on laboratory experiments to untangle how complex (astrobiologically important) molecules are formed in extraterrestrial ices (Solar System Ices, ices on interstellar grains) and in the gas phase (ISM, atmospheres of planets and their moons). The experimental techniques utilized are surface scattering experiments at UHV conditions ( $< 5 \times 10^{-11}$  torr) and crossed molecular beam studies under single collision conditions. Implications to specific Solar System Environments like Kuiper Belt Objects and Saturn's satellite Titan are presented, too.



Figure 1: Images of the crossed molecular beams machine (left) and the surface scattering machine (right) utilized to study bimolecular neutral-neutral reactions in the gas phase and the interaction of ionizing radiation with (icy) surfaces.

## **Experimental Studies of Molecule Formation on Astrophysical Surfaces at Low Temperatures**

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Heterogeneous catalysis on dust grains has been proven to be very important for the chemical enrichment of interstellar clouds through a relevant series of experiments performed by several groups in conditions and on surfaces close to realistic ones.

I will present results relative to species that need surfaces either to be synthesized or to be formed more efficiently than in the gas phase.

Attention will be paid to the mechanisms that might be involved.

# Ice Surface Chemistry: Implication for Molecule Formation on Interstellar Dust Particles

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Icy surfaces of interstellar dust particles are considered to play important roles in molecule formation in space. This presentation will describe our recent investigations of chemistry of ice surfaces with the emphases on the mechanistic features of elementary reactions and the implication for molecular evolution on interstellar grains. The types of reactions include the diffusion of molecules, proton transfer through the hydrogen-bonded network of ice, and simple acid-base reactions. Photoreaction of amine and carbon dioxide on ice surfaces leading to the formation of glycine and its isomers as identified by *in situ* mass spectrometric detection is also presented.

## References

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# Quantum chemical studies of $\text{H} + (\text{H}_2\text{O})_n$ system as model of chemisorption on icy grain

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The reactions of hydrogen atom with various chemical species on icy grain are important processes on the formation of hydrogenated molecules in interstellar medium. It would be interesting to see the behavior of hydrogen atom both on ice surface and inside ice. The interaction between hydrogen atom and amorphous ice can be modeled as  $\text{H} + (\text{H}_2\text{O})_n$  cluster system in order to explore quantum chemically. We have calculated the structures and interaction energies between hydrogen atom and water clusters with the hybrid density functional method. We have used the B3LYP method with 6-311G(d,p) basis functions to optimize the geometries of  $\text{H}\dots(\text{H}_2\text{O})_n$  system for  $n=1\sim 4$ . Table 1 shows the distance between hydrogen atom and oxygen atom of  $\text{H}_2\text{O}$  and the stabilization energies depending on the number of water molecules. All interaction energies are calculated to be small ( $1\sim 2 \text{ kJ mol}^{-1}$ ) and the distance between hydrogen atom and water clusters are shown to be ca.  $2.5 \text{ \AA}$ . This indicates that the interaction between hydrogen atom and water molecule is due to the weak van der Waals attraction. When we look at the dependence of the number of water molecules surrounding to a hydrogen atom, both the binding energies and the distances are found to be nearly the same except the case of water dimer.

If one says that this type of interaction is physisorption, there might be a type of chemisorption between H atom and  $\text{H}_2\text{O}$  molecules. Nevertheless,  $\text{H}_3\text{O}$  radical is energetically high species and spontaneously decompose to  $\text{H} + \text{H}_2\text{O}$ . Since the energy of  $\text{H}_3\text{O}$  molecule ( $69.0 \text{ kJ mol}^{-1}$  relative to  $\text{H} + \text{H}_2\text{O}$ ) is higher than that of the transition state leading to  $\text{OH} + \text{H}_2$  ( $42.0 \text{ kJ mol}^{-1}$ ), the chemical species  $\text{H}_3\text{O}$  cannot exist not only in gas phase but also in solid or liquid phase. The transition states for hydrogen exchange reactions in  $\text{H} + (\text{H}_2\text{O})_n$  clusters are calculated to be also high in energy.

Table 1. The interaction distances and interaction energies between H atom and  $\text{H}_2\text{O}$  clusters.

n	system	H ... O distance ( $\text{\AA}$ )	stabilization energy $\Delta E$ ( $\text{kJ mol}^{-1}$ )
1	$\text{H}_2\text{O}\dots\text{H}$	2.38	0.9
2	$(\text{H}_2\text{O})_2\dots\text{H}$	2.14	2.2
3	$(\text{H}_2\text{O})_3\dots\text{H}$	2.49	1.1
4	$(\text{H}_2\text{O})_4\dots\text{H}$	2.50	0.9

## Negative ions in space

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Existence of negative ions in space has been discussed for a long time. Although 15 positive ions have been known in interstellar space, the first identification of the negative ion  $C_6H^-$  was carried out quite recently(2006).

The late type carbon star IRC+10216 is well known to be one of the richest molecular source. So far more than 53 molecular species were identified in IRC+10216. During spectral line survey observations in the frequency region between 28 and 50 GHz by using the Nobeyama 45-m radio telescope, Kawaguchi et al.[1] found a series of unidentified lines with a spectral pattern of a  $^1\Sigma$  linear molecule. The rotational constant was determined to be 1376.864 MHz. Later, Aoki [2] carried out ab initio calculations to find a candidate to explain the magnitude of the rotational constant and concluded that the  $C_6H^-$  anion is a probable candidate. In 2006, McCarthy et al. [3] succeeded to detect the rotational lines of  $C_6H^-$  by laboratory millimeter wave spectroscopy and Fourier transform microwave (FT MW) spectroscopy and established that the  $C_6H^-$  anion is the carrier of the unidentified species with the rotational constant.

Following to  $C_6H^-$ , the  $C_4H^-$ ,  $C_8H^-$ ,  $C_3N^-$  anions have been detected in IRC+10216 and other sources. The  $C_8H^-$  detection [4] and search for  $C_{10}H^-$  with the Nobeyama 45-m telescope will be presented. Table 1 lists the electron affinities of the  $C_nH$  ( $C_nN$ ) radicals and dipole moments of  $C_nH^-$  ( $C_nN^-$ ), where  $n$ =odd (for  $C_nH$ ) and  $n$ =even (for  $C_nN$ ) chain molecules are not listed because of less abundances.

Table 1. Electron affinity(EA) of  $C_nH(N)$ , dipole moment ( $\mu$ ) of  $C_nH(N)^-$ , and column density( $N$ ) in IRC+10216

$(C_nH)$	n=2	4	6	8	10	$(C_nN)$	1	3	5
EA of $C_nH$	2.96	3.56	3.81	3.97	3.9		3.86	4.6	4.5 (eV)
$\mu$ of $C_nH^-$	3.4	5.9	8.2	10.4	12.7		0.6	3.1	5.2 (Debye)
$N$ of $C_nH$	5000	2980	80	5.5			640	310	$6 (\times 10^{12} \text{ cm}^{-2})$
$N$ of $C_nH^-$	<0.4	0.71	6.9	2.6			<16	1.6	$<1 (\times 10^{12} \text{ cm}^{-2})$
Ratio <sup>a</sup>	<1/12500	1/4200	1/12	1/2			<40	1/194	<1/6

<sup>a</sup>[anion]/[neutral]

We discuss about production reactions related to the observed abundances listed in Table 1 and spatial distributions of negative ions and neutral species in IRC+10216. When we consider star forming region like as Orion KL, above anions are expected to be less because of small abundances of carbon chain molecules. On the other hand, the positive ion  $HCO^+$  is abundant with a column density of  $3 \times 10^{14} \text{ cm}^{-2}$ , so we will discuss about existence form of negative charge in star forming regions.

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## Oxygen isotope anomalies of the Sun and the original environment of the Solar system

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Most stars form in clusters [1] even though our star, the Sun, seems alone at present with the closest stellar neighbor at 1.3 pc. It is not certain, however, whether the Sun formed in a cluster or in isolation. Some memory of the environment where the Sun formed might exist within the remnants of the formation of the Solar System. In this regard, primitive meteorites, interplanetary dust particles, and comets have been considered as the best sources to search for memory of conditions prior to and during formation, since they escaped from significant physical and chemical processing and therefore may preserve some relic of interstellar material. For instance, the inferred presence of short-lived radionuclides, especially  $^{60}\text{Fe}$ , in meteorites [2] suggests that the Sun formed near a massive star, which went through the core collapse of a supernova and provided the radionuclide to the solar nebula [3] or to the proto-solar molecular cloud [4]. This possibility of the Sun formation in proximity to massive stars is also supported by the prominent dearth of objects beyond the semi-major axes of the Kuiper Belt, which might be caused by the dynamical truncation through stellar encounters [5][6] or by the external photoevaporation [7].

If the Sun formed in a cluster, as described above, the ultraviolet radiation field around the proto-Sun would have been enhanced by 4 to 5 orders of magnitude compared to the standard local interstellar radiation field. Therefore, this enhanced radiation environment must have also left some evidences in chemistry affected by photolysis. It has been discovered that oxygen isotopes in calcium aluminum rich inclusions (CAIs) embedded in primitive meteorites had different ratios from those seen in terrestrial rocks [8], where the oxygen isotopic fractionation depends on mass. Recent theories suggest this mass-independent fractionation recorded in meteorites can be understood as a result from the isotopic-selective photodissociation of CO, either in the Solar Nebula [9][10] or parent cloud [11]. The photodissociation of CO is strongly coupled with the strength of the far-ultraviolet (FUV) radiation field as well as the CO column density. The studying of oxygen isotope ratios in the Solar system, therefore, will place strong constraints on its formation environment.

The oxygen isotope composition of the Sun is central to understanding the oxygen isotope evolution of the Solar system as recorded in meteorites. Recent preliminary Genesis results [12] of the direct Solar wind measurements show that the Solar oxygen isotope ratios are similar to the initial bulk values ( $\delta^{18,17}_{\text{SMOW}} = -50$  permil), i.e., isotopically light compared to the Standard Mean Ocean Water (SMOW). However, the Solar wind isotope measurements in lunar metal grains have yielded dramatically different results;  $\delta^{18,17}_{\text{SMOW}} = -50$  permil in one case [13] and  $\delta^{18,17}_{\text{SMOW}} = +50$  permil in the other [14].

Based on the CO self-shielding model in a collapsing low mass star forming cloud, we have showed that the Solar oxygen isotopic anomalies could vary depending on the strength of the surrounding radiation field ( $G_0$ ) when the Sun formed [15]. When constrained by oxygen isotope anomalies measured in meteorites, comets, and the Solar wind (Genesis), our model independently suggests that the Sun formed in the vicinity of massive stars, which is

consistent with other evidences such as short-lived radionuclides and the dynamical properties of planets and Kuiper Belt objects.

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# Observations of deuterium-bearing molecules in star-forming regions

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Despite the low deuterium abundance in the Universe ( $D/H \sim 1.5 \times 10^{-5}$ ), high abundances of deuterated molecules are detected in star-forming regions, with the abundance ratio of the deuterated over the main isotopologues being higher than the cosmic abundance of deuterium by several orders of magnitude. Particularly, the warm dense gas in hot cores around low-mass protostars is enriched in deuterated species, with even high observed abundances of triply-deuterated species such as  $CD_3OH$  ([1], see Figure 1). These deuterated molecules provide valuable tools to probe the physical conditions occurring during star formation, as well as the formation mechanisms of molecules. Deuteration is thought to be driven by the small energy differences between a deuterated species and the normal isotope. Because the temperatures indicated by the fractionation are much lower than the present gas temperatures in hot cores, the observed deuteration is thought to reflect a previous cold phase. Likely these molecules formed during the preceding prestellar core phase -- either in the gas phase or on the grain surface -- and were stored in an ice mantle which evaporated once the YSO heated its environment above the ice sublimation temperature.

In this talk, I will present observations of deuterium-bearing molecules in star forming regions, and illustrate which constraints they bring to the understanding of the formation processes of molecules. I will also underline the interaction with studies performed in the laboratory.

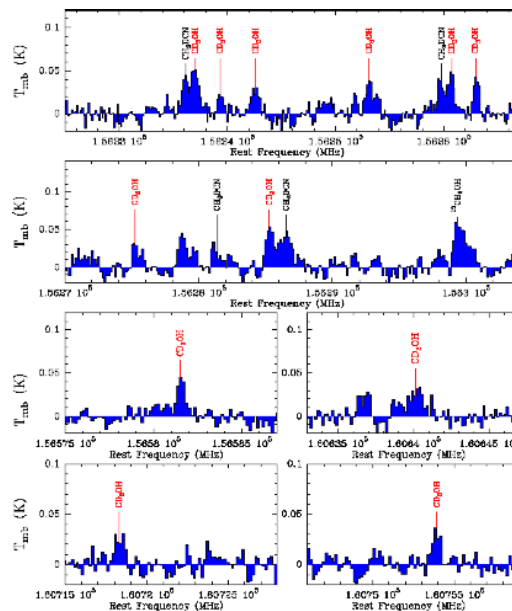


Figure 1: Detection of  $CD_3OH$  towards the low-mass protostar IRAS16293-2422. The abundance ratio  $CD_3OH/CH_3OH$  is 13 orders of magnitude higher than the cosmic  $D/H$  ratio.

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## Molecular Signatures in Massive Star Forming Regions

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Star formation processes not only reshape the physical environment of molecular clouds but also alter the chemical composition in the clouds, such chemical evolution could in turn influence critical physical states of the clouds as well as determine the molecular inventory in the clouds. The chemical signature of different components at various stages of star formation, therefore, is a result of complicated interplay between the chemical processes in gas phase, on grain surfaces and the interactions between gas and grains. Such effect may be particularly important for high-mass star forming regions, since massive star formation process can be very energetic and hence the interactions presumably have more significant impacts, even at very early stages.

Rich molecular complexity has been demonstrated to exist in massive star forming regions. For example, the so-called "hot molecular cores" are characterized by enhanced abundances of complex and highly-saturated organic molecules, which is likely to be resulted from surface reactions and/or UV-radiation, cosmic ray processing during the collapse phase and mantle evaporation after the onset of central massive stars. However, our understanding of the chemical condition for the precursors of high mass stars is still far from complete. What are their unique chemical characteristics? Do they have any molecular signature similar to the cold dark clouds? Or significant chemical evolution has already occurred? In this contribution, I will review recent results from observations of massive star formation regions, with some emphasis over high angular resolution studies with interferometric arrays.

# Evidences of infalling gas onto the circumnuclear ring at the galactic center from SiO and H<sup>13</sup>CO<sup>+</sup> emission lines observation

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The central region of our Galaxy (Sgr A<sup>+</sup>) is the nearest galactic center harboring a massive black hole [1,2]. The environment around Sgr A<sup>+</sup> is a topic of interest to diverse fields. We are interested in gas feeding from giant molecular clouds (GMC) within 10 pc of the Galactic center to the Circumnuclear Ring/Disk (CND), which is presumable "lay-down bay" of infalling gas toward Sgr A<sup>+</sup> [3]. In order to reveal the mechanism, we observed the CND and its surroundings in SiO and H<sup>13</sup>CO<sup>+</sup> lines using Nobeyama Millimeter Array (NMA). We depict the CND clearly in both lines and some molecular streamers to the CND in only SiO line including one new detection. The line intensity ratios at overlapping points of streamers with the CND are higher ( $I(\text{SiO})/I(\text{H}^{13}\text{CO}^+) > 6$ ) than the average of CND (2-4). This is a strong evidence indicating these streamers are connecting to the CND. Some components at the outer region of the CND are also detected in both lines. We also estimate the rotation velocity of the CND as  $110 \pm 10 \text{ km s}^{-1}$  and of just a bit outside from the CND as  $93 \pm 14 \text{ km s}^{-1}$ . The estimation of the rotation velocity in the distance range of 5-10 pc from the Sgr A<sup>+</sup> has a great meaning since there have been few report about the kinematic parameters at just outside of the CND [3,4 and 5].

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## AKARI's view of interstellar matter in galaxies

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We review recent observational results on the interstellar matter in galaxies obtained by the Japanese infrared astronomical satellite AKARI.

AKARI was launched in February 2006 and started observations in May of the same year. AKARI has a 68.5 cm cooled telescope together with two focal plane instruments, which have imaging and spectroscopic capability in the wavelength range 2-180  $\mu\text{m}$ . One of the most important missions of AKARI was to make an all-sky survey in six bands in the mid- and far-infrared, and AKARI also made extensive observations of specific targets in pointed modes. After liquid helium ran out in August 2007, AKARI has been making observations in the near-infrared with mechanical cryocoolers.

AKARI made systematic observations of near-by galaxies. Wide spectral coverage of AKARI enables us to deconvolve dust thermal emission in the far-infrared into two components: warm dust, which traces recent star-formation activity, and cold dust, which traces general interstellar dust. The distribution of hot dust component shows wide variety among observed galaxies, reflecting the difference of recent star-formation activity and distribution of heating sources.

Another important aspect of AKARI observations is its capability of sensitive spectroscopic observations in the near- and mid-infrared. Especially toward heavily obscured galaxies (e.g. most of ultra luminous infrared galaxies), AKARI detected absorption features due to various types of molecules. Observed absorption features show huge variety, reflecting the difference of physical conditions of interstellar matter in various types of galaxies.

Some galaxies show wide CO absorption features around 4.6  $\mu\text{m}$ , which indicates the presence of hot (500-1000 K) molecular gas in these galaxies. These hot clouds could be heated by X-ray radiation from the central activity of the galaxies.

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# The simplest carbon growth mechanism by atomic carbon insertion reactions and the source of DIB

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Carbon growth reactions represent one of the most fundamental chemical processes. The simplest example is the atomic carbon insertion reaction (ACIR). In ACIR, atomic carbon,  $\text{:C}$ , or its precursors,  $\text{:CCO}$  and  $\text{C}_3\text{O}_2$ , jump into the CC bond without cleaving the overall structure. As a result, no side-products are produced from this reaction (Figure 1).

The mechanism of linear-carbon monoxides formation,  $\text{C}_n\text{O}$  ( $n = 2 - 9$ ), which is synthesized in the discharge of  $\text{C}_3\text{O}_2$ , has been investigated based on the detailed analyses of FTMW spectroscopic data [2]. The relative abundances of the  $\text{C}_n\text{O}$  products, determined from their rotational spectrum intensities, agree with those for the  $\text{C}_n\text{O}^+$  ions, which were known to be lengthened by successive mono-carbon insertions [1b]. The active chemicals in the reaction system include only  $\text{:C}$  and  $\text{:CCO}$ . Moreover, since the observed products consist exclusively of  $\text{C}_n\text{O}$ , the reaction occurs via the ACIR mechanism (Figure 2).

Nearly all of the linear-carbon-chain molecules detected in laboratories or in space, which are available on Prof. Okabayashi's homepage [4], can be interpreted by this formation mechanism. The exception is  $(\text{c-H}_2\text{C}_3)=\text{C}=\text{C}$ , which requires isomerization from  $(\text{c-HC}_3)-\text{C}\equiv\text{CH}$ .

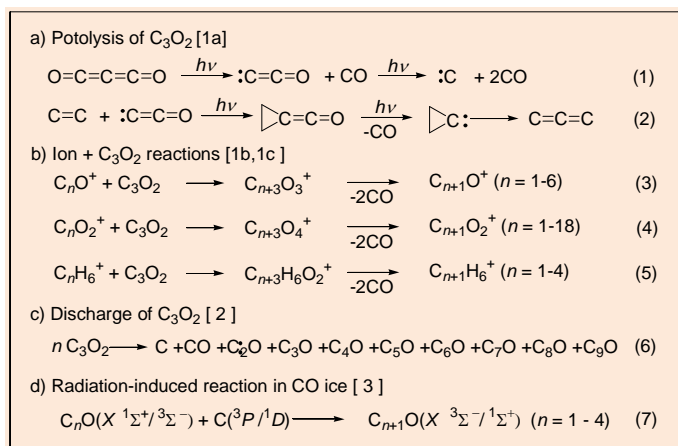


Figure 1: Some linear-carbon-chain growths by atomic-carbon-insertion reactions.

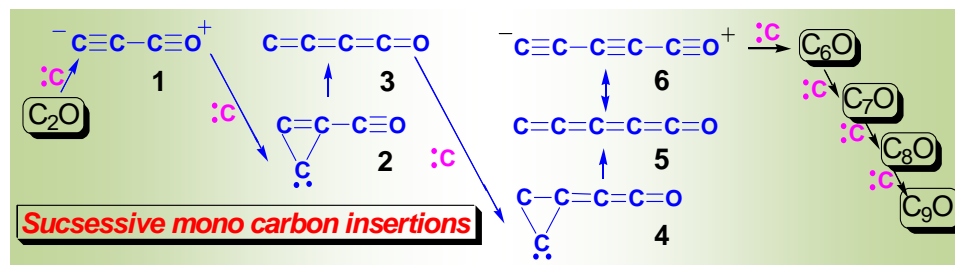


Figure 2: The proposed formation mechanism for  $\text{C}_n\text{O}$  ( $n = 2 - 9$ ) by atomic carbon insertion reactions.

ACIR is simple, as it only requires the presence of  $\text{:C}$  and a CC bond, and efficient due to its low or zero activation energy. Hence, this reaction scheme is applicable to a wide-range of carbon-based processes, in particular, to ultra low temperature or incomplete combustion conditions [5]. It is commonly thought that long carbon chains and atomic carbon primarily exist in a relatively diffuse part of the molecular cloud in space, which suggests that carbon chains are formed by ACIR.

Based on the following evidence, we can also imagine that a huge amount of the atomic carbon inserted clusters form a kind of “amorphous carbon” in interstellar space (reminiscent of the source of DIBs):

1. “Amorphous carbon” can be formed by ACIR, which is the dominant reaction at ultra low temperatures [5b].

2. While all “amorphous carbon” species have distinct structures from each other, their structures may be partially similar.
3. “Amorphous carbon” is black, implying that many absorption features fall in the UV-visible light region.
4. “Amorphous carbon” can withstand bombardment with ultraviolet photons in space.

Previous work has reported that the absorption curves for soots and quenched carbonaceous composites agree well to the absorption curves from interstellar extinction [6].

Presumably, “amorphous carbon” has a highly strained filled interior with many dangling bonds. The possible structure and formation mechanism of “amorphous carbon” will be proposed at the workshop.

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## Ab initio molecular dynamics approach to dissociative recombination reactions

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The dissociative recombination (DR) reaction is a combination of an electron and a positive molecular ion, which is followed by the dissociation into neutral molecules. The DR reaction proceeds via the direct mechanism or the indirect mechanism. In the direct mechanism, the molecular system makes transitions directly from the electronic ground state of cation to the dissociative state of neutral molecule after capturing an electron. In the indirect mechanism, this transition proceeds via Rydberg states. In the interstellar medium, polyatomic ions are produced through ion-molecule reactions, and the DR process is one of the possible ways of neutralizing the ions. Through the DR reactions, polyatomic ions dissociate into different combinations of neutral atoms/molecules, and the study of the branching ratios of the DR reaction will help to understand the chemical evolution in interstellar clouds.

In order to examine the reaction mechanism and dynamics in the DR processes, we have developed an ab initio molecular dynamics (AIMD) program code for excited-state dynamics, including the Tully's surface hopping algorithm for nonadiabatic transitions between adiabatic electronic states. The code uses the adiabatic potential energy, energy gradients, and nonadiabatic coupling terms at the state-averaged complete active space multi-configurational SCF level, evaluated by the quantum chemistry program package, MOLPRO. The code has been applied to DR reactions,  $\text{HCNH}^+ + e^-$  [1,2],  $\text{H}_3\text{O}^+ + e^-$  [3],  $\text{HD}_2\text{O}^+ + e^-$  [4], and  $\text{CH}_3^+ + e^-$  to examine the tendency in the branching ratio of the dissociative products, and to investigate the dynamical processes with nonadiabatic transitions. In the application to  $\text{HCNH}^+ + e^-$  [1], we found that (1) HNC and HCN are generated with almost the same ratio, (2) the products,  $\text{CN} + 2\text{H}$ , are also generated, and (3) the isomerization between HNC and HCN can occur while the HCNH molecule descends through the electronic excited states. In the second application [3], two Rydberg states and three valence states were included in dynamics, the surface hopping was observed in the relatively early stage less than 30 fs in most cases, and the rates of the respective dissociative products are estimated as  $(\text{OH} + 2\text{H}) : (\text{H}_2\text{O} + \text{H}) : (\text{OH} + \text{H}_2) : (\text{O} + \text{H}_2 + \text{H}) = 0.87 : 0.10 : 0.015 : 0.015$ , while the corresponding experimental rates were reported as  $0.60 : 0.25 : 0.14 : 0.013$ . The rate of exothermic products is small compared to the experimental ones, but the order in the ratio is reproduced. In the third application [4], it was shown that the dominant products,  $\text{OD} + \text{D} + \text{H}$ , were generated in 63% of trajectories, while the products,  $\text{OH} + 2\text{D}$ , were generated in only 11% of trajectories, indicating that the release of a light fragment H is favored over the release of a heavy fragment D. This result is in conformity with the observation that there is a larger amount of deuterium substituted species than the non-substituted species in the interstellar space.

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# Atomic density dependence of formation of polycyclic aromatic hydrocarbon by molecular dynamics simulation

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We have been studying the formation and deformation processes of nano-carbon molecules by use of molecular dynamics (MD) simulation. We deal here with the formation of hydrocarbon dust in the interstellar space. The purpose of this study is to make clear the growth of hydrocarbon dust from carbon atoms, hydrogen atoms and their small molecules.

In the MD simulation, the carbon and hydrogen atoms were initially located at random in a simulation box under periodic boundary condition. Chemical interaction between atoms was represented by the modified Brenner reactive empirical bond order potential [1] and temperature was controlled by the Langevin thermostat regarded as background radiation.

As a simulation result, polycyclic aromatic hydrocarbons (PAH) occurred and the following formation process was clarified. First, many carbon chain molecules occurred. Next, long carbon chains made carbon rings with tentacle, which is called “octopus structure”. Finally, the rings and tentacle were knitted into six-membered rings and then they were formed into the PAH like a graphene. In addition, amorphous carbon did not appear.

This MD simulation treated high atomic density and short time scale. However, under the assumption that the collision number of molecules is in proportion to atomic density, this formation process of PAH corresponds to a phenomenon for 300 year on the atomic density of 100 atom/cc. The second point that requires clarification is whether this assumption is valid. To clarify its point, we execute the MD simulations on deferent atomic densities and we compare formation speeds.

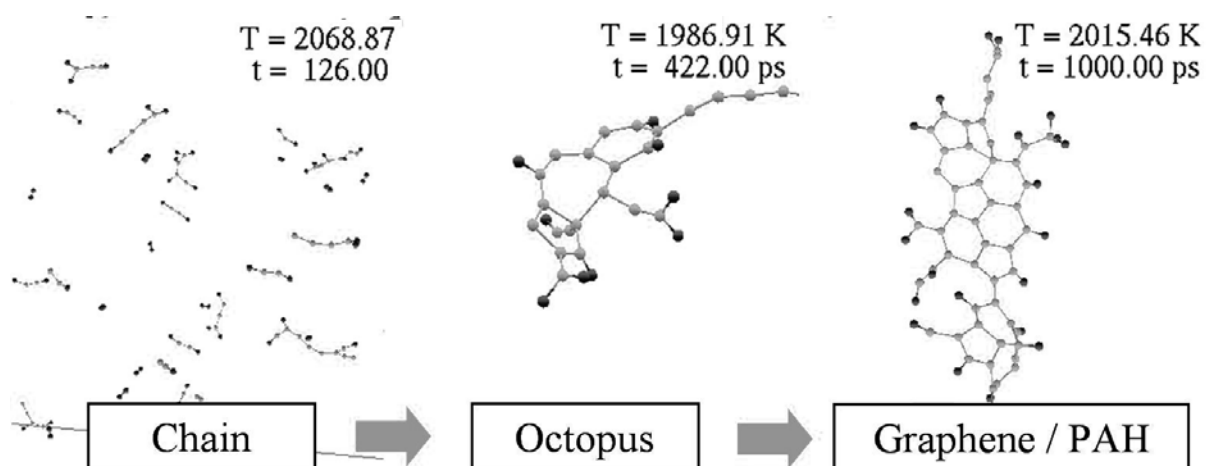


Figure 1: Formation process. The gray and black spheres indicate carbon and hydrogen atoms, respectively.

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# Shocked molecular gas in the foot point of the molecular loop near the Galactic Center

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The Central Molecular Zone (CMZ) of the Galaxy is characterized by high gas kinetic temperature ( $\sim 30\text{-}60\text{K}$ ) and by high gas density ( $\sim 10^4\text{ cm}^{-3}$ ). We found the loop like molecular features 300 pc away from the Galactic Center, which have the same properties of CMZ at the giant molecular cloud (GMC) in their foot point, and suggested that the loops and the GMC are formed by magnetically buoyancy driven by Parker instability [1, 2]. It is expected that there are shock fronts made by the slipping gases along the loop in the foot point. We report the results of molecular line observations by using ASTE, Mopra, NANTEN2 telescopes toward the GMC in the foot point of the loops in order to search for evidence of the shock.

We found more than ten clumps sizes of which 2-3 pc and masses of which  $\sim 1000$  solar masses in the GMC in CO(J=3-2,1-0) [Figure 1]. They show high excited emission in CO (R\_3-2/1-0  $\sim 1.0\text{-}1.5$ ). The shapes of the spectra in these clumps have very broad velocity dispersion (30-40 km/s) and wing like components [Figure 2]. These properties suggest the existence of the shock. High excited CO emissions also support it. On the other hand, the emissions of  $^{13}\text{CO}$  and CI ( $^3\text{P}_1\text{-}^3\text{P}_0$ ) are very weak and almost the same. The emission of CO (J=7-6) was not detected. We have estimated physical parameters in these clumps by using LVG analysis. The results indicate that these regions have low-density ( $10^2\text{-}10^3\text{ cm}^{-3}$ ) and high-temperature ( $>100\text{ K}$ ). Additionally, the model of shocked gas shows the consistent results on temperature and density and indicates the shock velocity of 40-50 km/s [3].

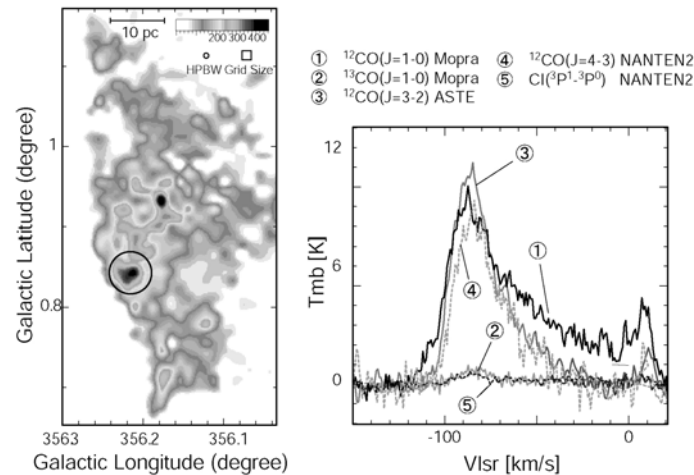


Figure 1(left): The integrated intensity map of the foot point of the Galactic Loop in  $^{12}\text{CO}(J=3-2)$ .

Figure 2(right): The spectra in each line toward the region indicated by circle in Figure 1.

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# Chemical Models of Hot Molecules at Shocks in Outflows

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It is observationally known that outflows are associated with many young stars, and they are thought to originate from accretion disks around the stars. Meanwhile, molecular line observations have shown that some molecules such as CH<sub>3</sub>OH and SiO are very abundant at shocks and/or clumps in outflows.

In this work we have constructed chemical models at shock fronts in outflows by calculating time-dependent gas-phase reactions which are initiated by evaporation of icy mantle molecules on dust grains [1]. We have studied dependences of the chemical structure of O-, N-, and S-bearing molecules at the shocks on different physical conditions to show that a variety of molecular abundance ratios can be obtained, owing to the dependence of dissociation rates on gas temperature and of adsorption rates on dust temperature. Initial condition, that is, physical properties in disks at the upstream of the outflow also affects the abundance ratios. Our results suggest that observations of molecular abundance ratios will trace the physical structure and the chemical processes, especially gas-grain interactions, at shock in outflows.

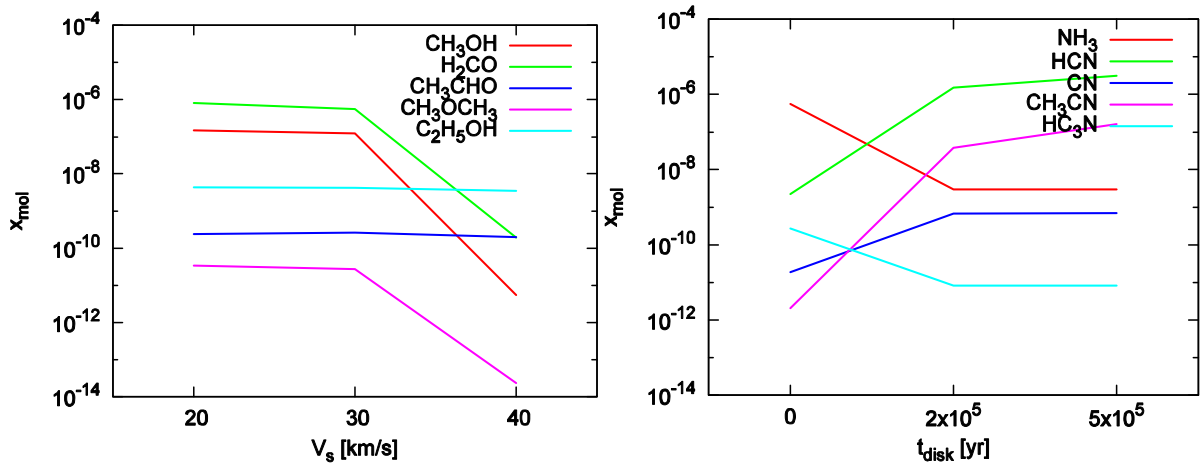


Figure 1: Dependences of the molecular abundances at shock on the shock velocity (the gas temperature) (*left*), and on the time which the molecules spend in the disk after the icy mantle evaporation and before the outflow launching (*right*). Some parent molecules (e.g., CH<sub>3</sub>OH, H<sub>2</sub>CO) and daughter species (e.g., CH<sub>3</sub>OCH<sub>3</sub>) are depleted at strong shock (*left*). Some N-bearing daughter species (e.g., HCN, CH<sub>3</sub>CN) are abundant if they move into the outflow after they spend enough time in the disk (*right*).

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# Oxygen Isotopic Evolution in the Early Solar Nebula: Interpretation of the Small Oxygen Isotopic Variation of Chondrules

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Oxygen isotopic systematics observed in chondritic components provides important clues to elucidate physical and chemical processes occurred in the early solar nebula. Chondrules have O-isotopic composition similar to those of terrestrial materials with small variation. In contrast, CAIs, the oldest minerals formed in the early solar nebula, have anomalously  $^{16}\text{O}$ -rich composition [1]. A plausible explanation for the origin of the systematics is enhancement of  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  concentration in the initially  $^{16}\text{O}$ -rich inner solar nebula [2]. The  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  is produced by isotope-selective photodissociation of CO in the parent molecular cloud and stored as icy mantle on silicate dust in the cold outer part of the nebula. The ice-coated dust particles drift inward due to nebula gas drag [3] and releases water vapor at the hot inner nebula. As a result, the  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  concentrates with time and the mean O-isotopic composition of the inner nebula evolves to be  $^{16}\text{O}$ -poor. This model is consistent with the large variation between CAIs and chondrules, however, not likely to explain the small O-isotopic variation of chondrules because  $\text{H}_2\text{O}$  concentration is expected to be temporally and spatially heterogeneous during chondrule formation.

In this study, we suggest a process which is overlooked in the previous study and possibly explains the small variation of chondrules; i.e., enhancement of silicate dust concentration in the inner nebula. Collision experiment of the nebula dust analogous implies that the typical size of dust particles would be determined by the adhesive properties of them [4]. Because silicate is less sticky than  $\text{H}_2\text{O}$  ice, dust particles would be refined after evaporation of icy mantle. The size of silicate dust is theoretically estimated to be  $\sim$  sub-millimeter, which is interestingly comparable to that of typical chondrules. Such small dust particles are well coupled with the nebula gas motion and hardly drift inward. Thus concentration of silicate dust would also be enhanced almost same degree as that of  $\text{H}_2\text{O}$  in the inner nebula. The most important consequence of this model is that, in case the concentration of  $\text{H}_2\text{O}$  and silicate dust is enhanced  $>\sim 5$  times larger than the solar abundance, the mean O-isotopic composition of the inner nebula is almost determined as the weighted mean of O-isotopic composition of  $\text{H}_2\text{O}$  and silicate in the solar abundance ratio; i.e., independent for their concentration. This suggests that temporal and spatial variation of concentration of  $\text{H}_2\text{O}$  little affects on the mean O-isotopic composition of the inner nebula as long as the enhancement is sufficiently large. Numerical simulation on the evolution of concentration of  $\text{H}_2\text{O}$  and silicate dust using typical properties of observed protoplanetary disks confirms that such large enhancement is sustained during chondrule formation in the inner nebula. Thus, the small O-isotopic variation of chondrules would be reproduced in our model.

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# Effects of Radionuclides on the Ionization State of Dense Cloud Cores and Protoplanetary Disks

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We reinvestigate the ionization rates by radionuclides with the abundances in the primitive solar nebula by adopting the revised data on nuclides, extending the decay processes, and surveying radionuclides more extensively. Although the ionization rates by  $^{232}\text{Th}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$  have become at least 10 times the previous ones, the total ionization rate by the long-lived radionuclides,  $1.4 \times 10^{-22}\text{s}^{-1}$  per hydrogen molecule, is still mostly contributed by  $^{40}\text{K}$ . Among the short-lived radionuclides which are extinct in the present solar system,  $^{26}\text{Al}$  is the dominant ionization source with the rate  $(7 - 10) \times 10^{-19}\text{s}^{-1}$ , overwhelming the long-lived nuclides. With the average interstellar abundance of  $^{26}\text{Al}$  estimated from  $\gamma$ -ray observation of the galactic plane, the ionization rate is 8 times smaller than this. In addition,  $^{60}\text{Fe}$  and  $^{36}\text{Cl}$ , whose ionization rates with the abundances in the primitive solar nebula are at least 10 times smaller than that of  $^{26}\text{Al}$ , can be more efficient than the long-lived nuclides. In protoplanetary disks the ionization rate by radionuclides depends sensitive on the growth and sedimentation of dust particles. Ionization by radionuclides is quite inefficient when the mean dust size is greater than about 1 cm. Using these ionization rates we investigate the ionization state for some configurations of the clouds. We find that in dynamically collapsing very dense cloud cores the short-lived radionuclides are more efficient ionization source than cosmic rays when the mean pressure  $n(\text{H}_2) T \gtrsim 1 \times 10^{14}\text{cm}^{-3}\text{K}$ . We improve the attenuation law of cosmic rays in geometrically thin disks. Using this law we find that the dead zones in protoplanetary disks are significantly larger than those obtained in the previous work.

**Development of the Mid-Infrared High Dispersion Spectrograph (IRHS)**  
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High-dispersion infrared observations are useful for the definite identification of molecular species in the interstellar medium (ISM) by their vibration-rotation transitions. According to radio wavelength observations, molecular transitions in the ISM are Doppler-broadened, with line widths of 2~20 km/s in typical high-mass star forming regions and circumstellar envelopes of late type stars. Due to these broadenings, the wavelength resolving power  $R = \lambda / \Delta \lambda = 15,000 \sim 150,000$  is required for sensitive detection of the spectra. In order to achieve such a high resolution in infrared region, Fourier transform spectroscopy (FTS) has usually been employed. In the mid-infrared region (8~13  $\mu$  m), however, the dominant noise source is the background blackbody radiation, so multiplex property of FTS is no longer advantageous toward fainter astronomical sources.

Recently, we have developed the “mid-InfraRed High dispersion Spectrograph” (IRHS), a cryogenic échelle spectrometer designed for Nasmyth focus stage of NAOJ Subaru 8.2m telescope, which operates at 8-13  $\mu$  m in wavelength with the resolving power  $\lambda / \Delta \lambda$  of  $>50,000$  at 10  $\mu$  m. To reduce thermal radiation of the instrument, all optics of IRHS is arranged on the cold optical base plate (~30K) of the cryostat with the diameter of 80cm. In order to achieve high dispersion, broad bandwidth, and high sensitivity, two key devices are employed: a single crystal germanium immersion echelle grating (30×30×72mm) and a Si:As IBC (Impurity Band Conductor) focal plane array (FPA) detector (412×512 pixels, unit pixel size 30  $\mu$  m) operated at 5 K[1]. The most important key device, germanium immersion échelle grating for collimated beam size of 28mm $\phi$  was fabricated by utilizing ultra precision micro-grinding method coupled with “ELectrolytic In-process Dressing” (ELID) technique[2]. The immersion grating has 600  $\mu$  m groove spacing with a 68.75° blaze angle. It is used in very high order, ranging from 332 at 13.5  $\mu$  m to 597 at 7.5  $\mu$  m. In order to separate the échelle orders by ~10 pixels on the Si:As array detector, the cross-disperser wheel employs two first-order echelette gratings: a 100 grooves/mm with a 26.7° blaze angle for short wavelength (7.5–10  $\mu$  m) and a 61.97 grooves/mm with a 18.1° blaze angle for long (10–13.5  $\mu$  m). The spectral coverage is typically  $\lambda / 15$ , which includes 32–56 échelle orders, depending on wavelength. Eight cross-disperser position angles give full continuous coverage throughout 7.5–13.5  $\mu$  m.

The optics on the spectrometer was aligned by using an attenuated CO<sub>2</sub> laser as a light source. In the alignment procedures at room temperature condition, an infrared bolometer camera was replaced with the Si:As IBC FPA detector. Since the CO<sub>2</sub> laser was operated in multi-mode oscillation, simultaneous observation by using the FT-IR spectrometer (BioRad FTS-6000) was necessary to assign the laser transitions. After the alignment, placing Si:As IBC array back to the original position, we examined the sensitivity tests of IRHS by recording the blackbody radiation around the 10.6  $\mu$  m wavelength region at the room temperature (~300 K). It took approximately 3 seconds to saturate the Si:As IBC detector, which is well compared with our design specification and the full-well capacity of the detector. For the check of the wavelength resolution, we observed the spacially diffracted light from the CO<sub>2</sub> laser source by the #3000 sandpaper. Figure 1 shows the échelle image thus obtained of IRHS in the region of 904 – 967 cm<sup>-1</sup> (10.3-11.1  $\mu$  m in wavelength). The HWHM linewidth for the most faintly observed P(20) laser transition to 0.018 cm<sup>-1</sup>, assuming that one pixel

corresponds to  $0.0052 \text{ cm}^{-1}$ . The currently derived resolving power,  $\sim 50,000$ , is in an excellent agreement with a design specification of our spectrograph.

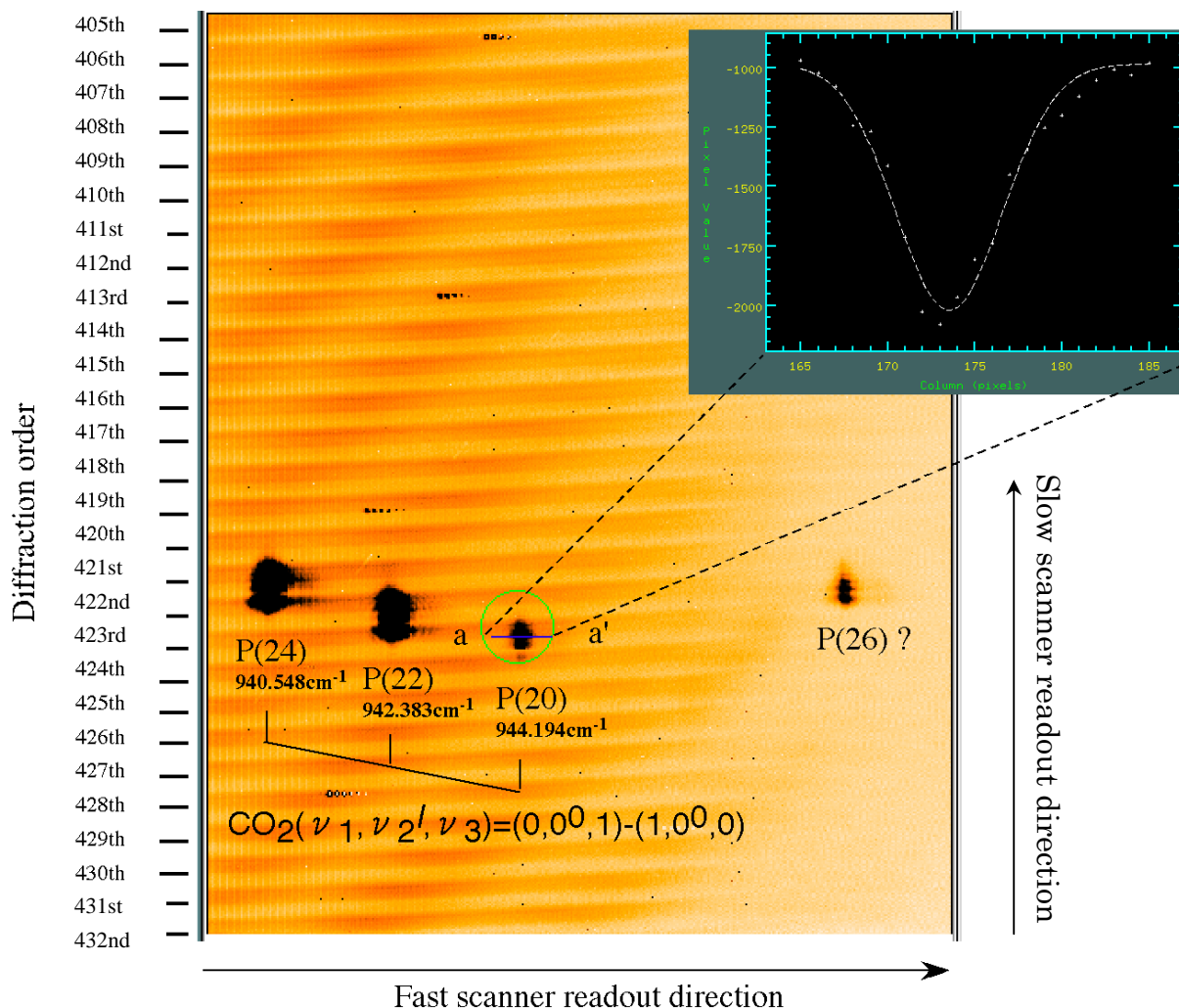


Figure 1: The first échelle image of IRHS for the the  $\text{CO}_2$  laser, taken with Si:As IBC  $512 \times 412$  FPA detector cooled to 5.7K. The exposure time for each pixel is uniformly 0.17 second. The abscissa for the image (412 pixels) represents direction for the fast scanner readout of the detector. The ordinate for the image (512 pixels) represents the direction for slow scanner readout, and that for dispersion for the cross-disperser. Diffraction orders for the Ge immersion grating separated by the cross-disperser are also shown. The assignments for the dark spots for the  $\text{CO}_2$  laser are shown on the image. The background stripes are due to the thermal emission on the room temperature. Note that the laser spots except for P(20) and probably P(26) are heavily saturated and the spot sizes for the laser lines are significantly larger than the intrinsic resolution of the spectrograph, since the laser power during the measurement is still very high.

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## Laboratory measurement of methyl formate ( $\text{HCOO}^{13}\text{CH}_3$ )

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The methyl formate molecule is one of the most known interstellar weeds. The figure 1 shows the structure of methyl foamte. In most cases, saturated organic molecules like methyl formate have methyl group internal rotation which is equivalent to the vibrational mode of torsion. The interaction between the rotation and the internal rotations causes the splitting of the spectra. In addition, since the vibrational frequency of the torsion is usually low and vibrationally excited states are populated even at the room temperature, a great number of lines are observed but many lines remain unassigned. The progress of the laboratory measurement could help assignment of the astronomical detection. Recently unidentified lines from Orion KL were assigned to this molecule in its torsionally excited state [1] based on the previous microwave study.[2]

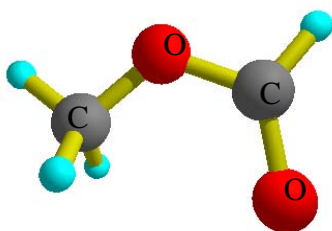


Fig. 1 The structure of methyl formate

Recently the production scheme of CCS was clarified using the observed abundance ratio of isotopomers. It is quite indispensable to have rest frequencies of the isotopomers. Therefore we report the current status of the microwave study on the isotopomer  $\text{HCOO}^{13}\text{CH}_3$  anticipating for future detection. The first microwave study on this isotopomer was carried out by Curl.[3]

The experiment was carried out with our conventional source modulation microwave spectrometer. The microwave radiation from the synthesizer is multiplied and detected with the InSb bolometer. The  $^{13}\text{C}$  isotopomer was synthesized by the reaction of  $\text{HCOOH}$  and  $^{13}\text{CH}_3\text{OH}$ . The observation of spectra from 75 GHz without gap is under way. The preliminary analysis will be given

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## Laboratory FIR Spectroscopy of $\text{OD}^-$ , $\text{N}_2\text{H}^+$ , $\text{H}_2\text{D}^+$

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Rotational spectra of molecular ions which are important in interstellar chemistry are studied with tunable far-infrared spectrometer. Frequency measurements of the rotational lines of  $\text{OD}^-$ ,  $\text{N}_2\text{H}^+$ , and  $\text{H}_2\text{D}^+$  in 1-5 THz region are reported.

As for  $\text{OD}^-$ , the fundamental band transitions were studied by Rehfuß et. al. in 1986 [1], and low- $J$  rotational lines  $\text{R}(J)$  ( $J=1,2$ ) were reported by Cazzoli et.al. [2,3]. We observed the lines  $\text{R}(J)$  ( $J=1-2,4,5,7$ ) (Fig.1). This work is an extension of our previous work of  $\text{OH}^-$  [4]. The molecular constants and the isotope-independent Dunham parameters were obtained.

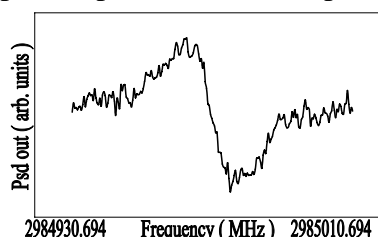


Figure 1: Typical trace of  $J = 5 \leftarrow 4$  transition of  $^{16}\text{OD}^-$ .

The molecular cation  $\text{H}_2\text{D}^+$  and  $\text{D}_2\text{H}^+$  are the isotopomers of  $\text{H}_3^+$ . Submillimeter-wave spectra of  $\text{H}_2\text{D}^+$  and  $\text{D}_2\text{H}^+$  were studied by Amano and Hirao in 2005 [5]. We have observed several lines of  $\text{H}_2\text{D}^+$  such as  $2_{11}-1_{10}$ ,  $3_{13}-2_{12}$ ,  $2_{02}-1_{01}$ , and  $2_{12}-1_{11}$  (Fig.2). Among them, the detection of  $2_{12}-1_{11}$  line in space has recently been reported. Our measured frequency will be useful to analyze this observation.

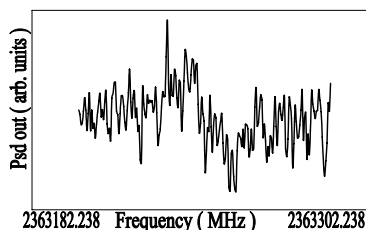


Figure 2:  $J = 2_{12} \leftarrow 1_{11}$  transition of  $\text{H}_2\text{D}^+$ .

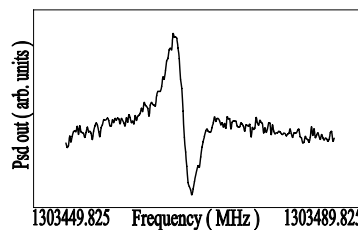


Figure 3:  $J = 14 \leftarrow 13$  transition of  $\text{N}_2\text{H}^+$ .

An extended-negative discharge glow discharge cell was applied to observe some of the molecular cations. Rotational lines of  $\text{N}_2\text{H}^+$ ,  $\text{R}(J)$  ( $J=13,15,20$ ) were measured to confirm the ability of this type of discharge cell (Fig.3).

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# Comparing Cloud Properties from Chemical Compositions of Cores

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The chemical characteristics within dense cloud cores can reveal their evolution stage. Because they have different production chemistries, the column densities of NH<sub>3</sub>, CCS can reveal the chemical characteristics in dense cores. So, N(CCS)/N(NH<sub>3</sub>) is a good indicator of chemical evolution [1].

We observed CCS J<sub>N</sub>=2<sub>1</sub>-1<sub>0</sub>, NH<sub>3</sub> (J, K) = (1, 1), (2, 2) lines toward molecular cores in the Taurus Cloud Complex with the Hokkaido University Tomakomai 11 m Telescope.

Assuming LTE and T<sub>k</sub>=10 K, we estimated column densities from our results. Figure 1 is a distribution of column densities of CCS and NH<sub>3</sub>. Comparing this result with results of other clouds (e.g. the Perseus Cloud Complex [2], the Pipe Nebula [3]), we can compare properties of these clouds from chemical compositions of cores. For example, from low column density of NH<sub>3</sub> in cores, the Pipe Nebula seems to be younger than the Taurus Cloud Complex.

Additionally, we found that N(CCS)/N(NH<sub>3</sub>(1, 1)) of our samples are lower in higher n(H<sub>2</sub>) from H<sup>13</sup>CO<sup>+</sup> J=1-0 line observation [4]. So, we can say chemical evolution of cores is consistent with physical evolution of cores.

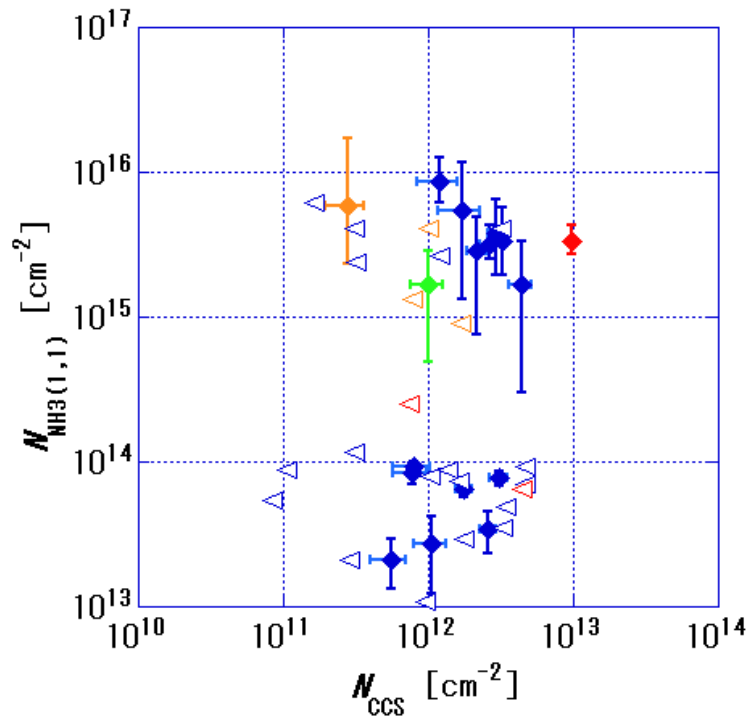


Figure 1: N(CCS) and N(NH<sub>3</sub>(1, 1)) of Cores. Blue symbols show starless cores, orange and red symbols show cores with stars, a green symbol shows an accreting core. Open triangles show upper limit of N(CCS).

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# Water ice absorption map of Pipe Nebula

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Interstellar water ice is one of important materials for interstellar chemistry. Water ice has been observationally detected as an infrared absorption band at 3.07  $\mu\text{m}$  in dark clouds. The results of past observations show that the optical depth of water ice absorption ( $\tau_{\text{ice}}$ ) is quantitatively related to visual extinction ( $A_V$ ) as  $\tau_{\text{ice}} \sim 0$  for  $A_V < A_{\text{th}}$  and  $\tau_{\text{ice}} = q (A_V - A_{\text{th}})$  for  $A_V > A_{\text{th}}$ , where  $q$  is a constant and  $A_{\text{th}}$  is the threshold extinction which depends on the cloud ([1],[2],[3],[4],[5]).

The observations of water ice absorption require background stars at the opposite side of dark clouds. This fact makes it difficult to obtain the continuous spatial distribution of water ice. We employ an unprecedented method to obtain a water ice absorption map by utilizing Galactic bulge stars as diffuse background light. The target dark cloud is Pipe Nebula which is in the direction toward the bulge and at the distance of 130-160 pc from the earth ([6]). Analyzed data were obtained with the Near-Infrared Spectrometer (NIRS) in the Infrared Telescope in Space (IRTS) ([7]), which was optimized for observations of diffuse light. The IRTS observation covered about half area of Pipe nebula.

The result of the detailed analysis shows that water ice absorption at Pipe nebula follows the  $A_V$ - $\tau_{\text{ice}}$  relation which mentioned above, i.e.,  $\tau_{\text{ice}}$  is under detection at  $A_V < A_{\text{th}}$  and  $\tau_{\text{ice}}$  is linearly correlated with the extinction at  $A_V > A_{\text{th}}$ . The water ice map is compared with CO emission maps obtained with NANTEN telescope ([8]). The result shows that the spatial distribution of water ice is correlated with the dense part of molecular cloud. The relation of  $\tau_{\text{ice}}$  with the strength of  $^{12}\text{CO}$  and  $^{13}\text{CO}$  emission shows the “threshold” effect similar to the  $A_V$ - $\tau_{\text{ice}}$  relation. We discuss quantitative relations and properties of water ice in Pipe nebula.

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## AKARI Observation of Interstellar Ice

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In molecular clouds, a significant amount of Oxygen, Carbon and Nitrogen is in the form of molecule in ice mantle, such as H<sub>2</sub>O, CO, CO<sub>2</sub>, NH<sub>3</sub> and CH<sub>3</sub>OH. These icy materials are formed by adsorption of gas-phase molecules onto grain surfaces and/or grain-surface reactions of the adsorbed species (e.g. [1]). Molecular evolution in the gas phase and ice mantle depends on the physical conditions such as temperature, density, and UV intensity. In order to understand the chemical processes of interstellar matter, it is important to observe the composition of gas and ice in various conditions. Composition of ice has been investigated by the absorption feature in the infrared. Spatial distribution of ice composition and its dependence on physical conditions are less constrained than the gas-phase molecules, because there are only a limited number of bright light sources behind or within the molecular clouds. In addition, some important bands cannot be observed from the ground.

We are observing near-infrared (2.5-5micron) spectrum of background stars using *AKARI* satellite. Compared with the ground-based telescopes and *Spitzer Space Telescope*, *AKARI* is unique in enabling us to observe the full NIR wavelength region towards faint background stars with < 14 mag at K band.

We will present preliminary results of our data analysis: spectrum of several background stars behind Taurus molecular clouds and determination of spectrum type and visual extinction (i.e. the continuum spectrum) of each star.

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## AKARI observation of ice in protoplanetary disks

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In outer region ( $r > \text{several AU}$ ) of protoplanetary disks, a significant amount of Carbon, Nitrogen and Oxygen exists in the form of molecular ice such as  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{NH}_3$  on the grain surface. These ices are raw material of comets, and would provide volatiles to form the atmosphere of terrestrial planets. Observing the ice in protoplanetary disks along evolutionary sequence (i.e. from Class 0 to Class II), we can investigate the composition and abundance of ice, and reveal chemical processes in planetary system formation.

We have carried out near-infrared (NIR) spectroscopic observation of protoplanetary disks using *AKARI* satellite. The NIR wavelength region (2.5-5 micron) contains absorption features of ices such as  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$ . While ground-based telescopes and *Spitzer Space Telescope* have already detected ices in disks [1][2][3], *AKARI* is a unique telescope which enables us to observe the full NIR wavelength region towards low-mass YSOs. We selected several edge-on disks around Class I-Class II YSOs, and detected several ice absorption bands towards Class I source IRAS04302+2247 and IRAS04368+2557(L1527) in Taurus star forming region (Fig1). We derive the ice composition in these objects by comparing the absorption feature with laboratory data (e.g. [4])

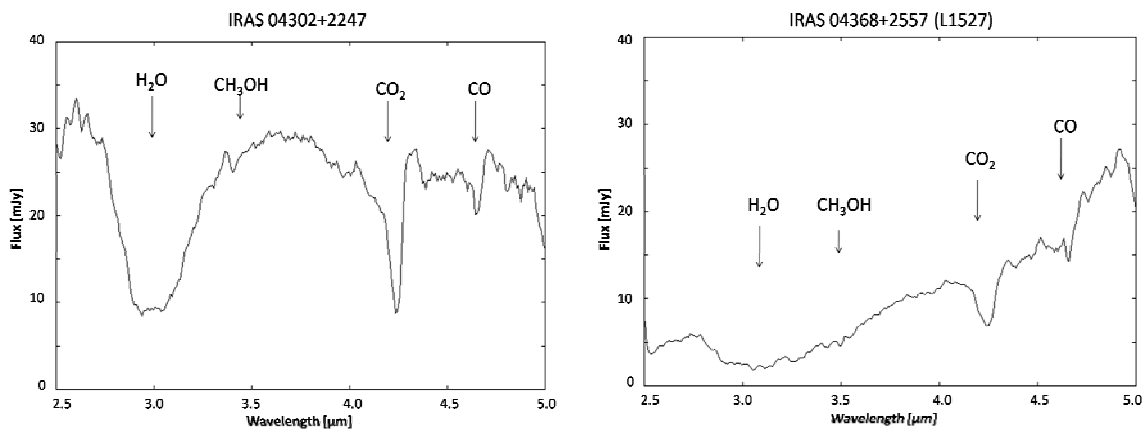


Fig 1 : Our sample of AKARI spectra. This plot is Flux[mJy] vs wavelength [ $\mu\text{m}$ ].

Left is IRAS04302+2247, right is IRAS04368+2557 (L1527). Especially, a deep  $\text{H}_2\text{O}$  and  $\text{CO}_2$  ice absorption is seen in these spectra.

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## Molecular Evolution in Star-Forming Cores: From Prestellar Cores to Protostellar Cores

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We investigate the molecular abundances in protostellar cores by solving the gas-grain chemical reaction network[1]. As a physical model of the core, we adopt a result of one-dimensional radiation-hydrodynamics calculation, which follows the contraction of an initially hydrostatic prestellar core to form a protostellar core. Temporal variation of molecular abundances is solved in multiple infalling shells, which enable us to investigate the spatial distribution of molecules in the evolving core. The shells pass through the warm region of  $T=10-100$  K in several  $10^4$  yr and falls onto the central star in  $\sim 100$  yr after they enter the region of  $T > 100$  K. We found that the complex organic species such as  $\text{HCOOCH}_3$  are formed mainly via grain-surface reactions at  $T \sim 20-40$  K, and then sublimated to the gas phase when the shell temperature reaches their sublimation temperatures ( $T \geq 100$  K). Carbon-chain species are re-generated from sublimated  $\text{CH}_4$  via gas-phase and grain-surface reactions [1][2].  $\text{HCO}_2^+$ , which is recently detected towards L1527[3], are abundant at  $r=100-2000$  AU, and its column density reaches  $10^{11} \text{ cm}^{-2}$  in our model[1]. If a core is isolated and irradiated by interstellar UV radiation, photo-dissociation of water ice could produce higher abundance of  $\text{CO}_2$ , while complex species become less abundant, compared with the case of embedded core in ambient clouds.

We are now extending the above model to multiply-deuterated species. Preliminary results would be reported on the deuterated species.

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# Structural effects of icy grain surfaces in CO hydrogenation at a low temperature

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The successive hydrogenation of CO ( $\text{CO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH}$ ) on the icy grain surface has been perceived as an effective process for the formation of  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  in molecular clouds [1]. That process on amorphous solid water (ASW) has been investigated extensively from several points of view (the dependences of temperature [1,2], ice compositions [3,4]). In the present study, we focus on the structural effects of the ice surface on the hydrogenation of CO at a low temperature, while the reactivity was compared between ASW and crystalline ice (CI) surface.

The top and bottom panels in Figure 1 shows the IR absorption spectra of the initial samples with the same amounts of CO deposited at 15 K and the variation in the absorption spectra of these samples during exposure to hydrogen atoms, respectively. The formation of  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  with decreasing of CO was observed in both samples. The hydrogenation reaction on ASW was found to be much faster than that on CI. The higher reactivity on ASW is attributed to the enhancement of the number density of adsorbed hydrogen atoms due to larger surface area of ASW compared to CI.

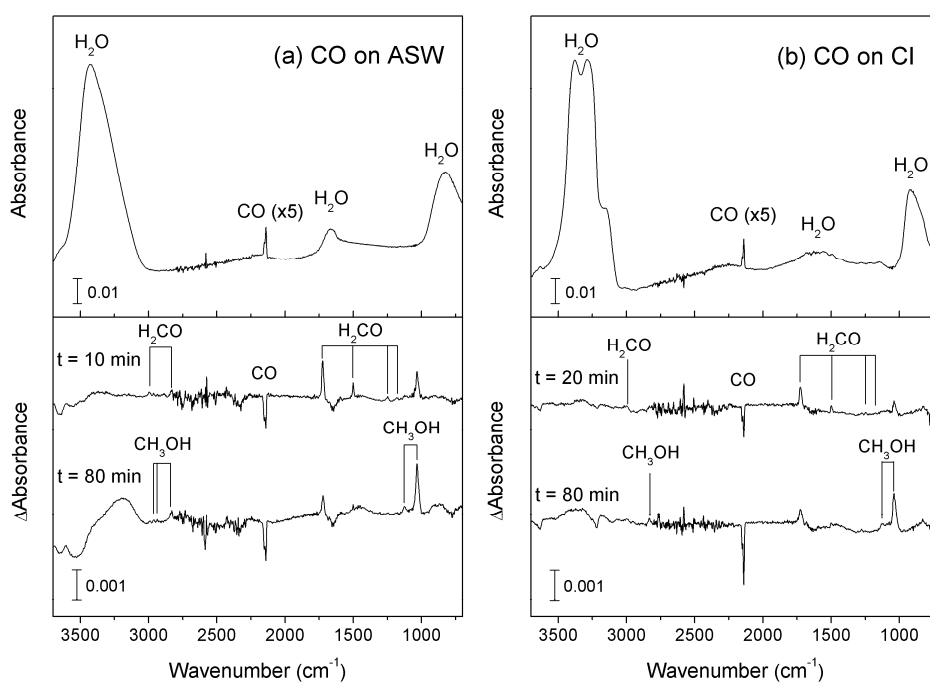


Figure 1: Initial IR adsorption spectra (top) and variations in the absorption spectra (bottom) with H atom exposure for (a) CO on ASW and (b) CO on CI at 15 K, respectively. Peaks below and above the base line represent a decrease and increase in the absorbance, respectively.

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# H-D substitution reactions of formaldehyde on icy grain surfaces at low temperatures

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The high gas-phase abundance of deuterated molecules,  $\text{H}_2\text{CO}-d_{1,2}$  and  $\text{CH}_3\text{OH}-d_{1-3}$ , have been observed in molecular clouds [1-3] and comet [4]. This deuterium fractionation in interstellar molecules has been an interesting topic in interstellar chemistry. Although several studies on the fractionation mechanism have been carried out by using pure gas phase models, it is difficult to explain the deuterium fractionations of formaldehyde and methanol especially in multiply deuterated molecules. Recently, our group revealed the validity of surface reactions in the formation of multiply deuterated methanol [5]. We believe that the surface reaction on interstellar ice is a key process not only for the production of  $\text{H}_2\text{CO}$  and  $\text{CH}_3\text{OH}$  but also for that of  $\text{H}_2\text{CO}-d_{1,2}$  and  $\text{CH}_3\text{OH}-d_{1-3}$ . In this study, the formation of deuterated formaldehyde on amorphous solid water (ASW) surface was investigated experimentally.

Experiments were performed by the exposure of  $\text{H}_2\text{CO}$  and  $\text{D}_2\text{CO}$  on ASW to D and H atoms at low temperatures, respectively. Figure 1 shows the infrared (IR) absorption spectra of initial samples (*top*) and variations in IR absorption spectra (*bottom*) for (a) D atom exposure of  $\text{H}_2\text{CO}$  on ASW and (b) H atom exposure of  $\text{D}_2\text{CO}$  at 15 K, respectively. For D +  $\text{H}_2\text{CO}$ ,  $\text{H}_2\text{CO}$  was converted to HDCO and  $\text{D}_2\text{CO}$  by the H-D substitution reactions. The addition reactions (formation of deuterated methanol) were minor routes. On the other hand, for H +  $\text{D}_2\text{CO}$ , the substitution reactions to produce HDCO and  $\text{H}_2\text{CO}$  as well as the addition reactions proceeded. We discuss formation processes for the deuterated formaldehyde on ASW surface in the environment of molecular clouds.

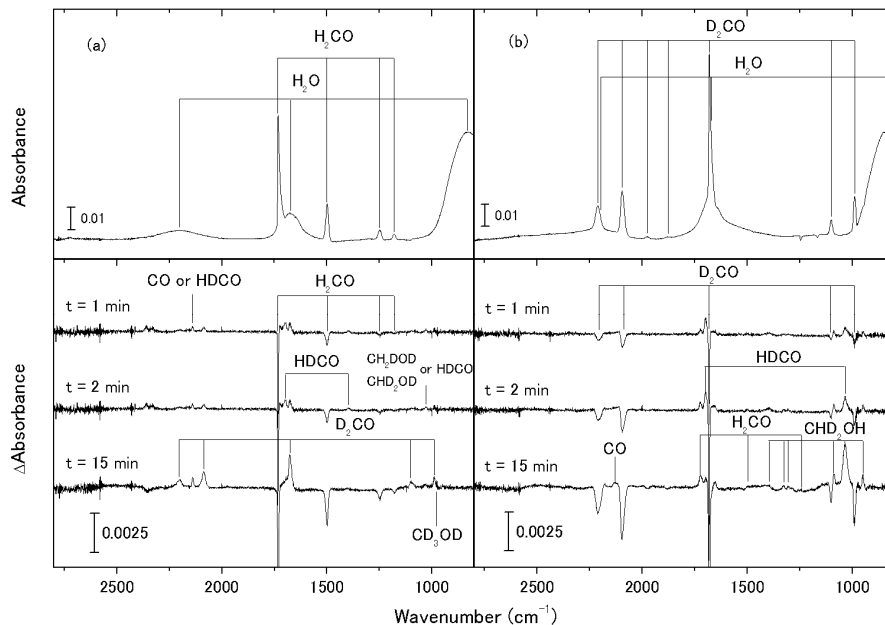


Figure 1: Initial IR spectra (*top*) and variations in the IR spectra (*bottom*) for (a) D atom exposure of  $\text{H}_2\text{CO}$  on ASW and (b) H atom exposure of  $\text{D}_2\text{CO}$  at 15 K, respectively.

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## Effective rate constants for H-D substitution reactions in methanol on the surface at 10 K

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Recent astronomical observations have discovered extreme deuterium enrichment in interstellar formaldehyde and methanol [1-3]. The abundances of these deuterated molecules are up to 4 orders of magnitude higher than the cosmic D/H ratio of  $1.5 \times 10^{-5}$ . For methanol molecules, even doubly and triply deuterated isotopologues have been detected in the vicinity of low-mass protostars [2,3]. Deuterium fractionation in interstellar molecules has long been a topic of interest in interstellar chemistry, and the fractionation processes in molecular clouds have attracted attention from both astronomers and earth and planetary scientists as a potential explanation for the high D fractionations observed in our solar system. Since pure gas phase chemistry hardly reproduces the deuteration level of formaldehyde and methanol observed, the evaluation of the role of grain surface chemistry in the deuterium fractionation was desirable. For methanol, we recently demonstrated that the H-D substitution reactions in methanol proceed efficiently on the ice surface at 10 K, and that the surface substitution reaction is a key for the deuterium enrichment in molecular clouds [4, 5]. However, the reaction rates of the surface substitution remained to be determined.

To obtain the reaction rates of H-D substitution in (deuterated) methanol on the cryogenic surfaces, solid  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{DOH}$ , and  $\text{CHD}_2\text{OH}$  were exposed to D atoms at 10 K. Deuteration levels increased in methyl group in all cases. The pseudo-first-order rates for the reactions  $\text{CH}_3\text{OH} + \text{D} \rightarrow \text{CH}_2\text{OH} + \text{HD}$ ,  $\text{CH}_2\text{DOH} + \text{D} \rightarrow \text{CHDOH} + \text{HD}$ , and  $\text{CHD}_2\text{OH} + \text{D} \rightarrow \text{CD}_2\text{OH} + \text{HD}$  were estimated. The ratios of the reaction rates of the second and third reactions to the first reaction were  $0.69 \pm 0.11$  and  $0.52 \pm 0.14$ , respectively [6]. The difference in reaction rates is thought to be due to a secondary kinetic isotope effect on the H-abstraction reaction from the methyl side by D atoms.

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## Laboratory simulation of competition between hydrogenation and photolysis in the chemical evolution of H<sub>2</sub>O-CO ice mixtures

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Photolysis and hydrogenation of ice dust are important processes of chemical evolution in molecular clouds. Photolysis has been studied experimentally by many researchers using astrophysically-relevant ice-mixture and found to yield various molecules [e.g. 1,2]. Hydrogenation has been first proposed theoretically since 1980s [3] as a main formation route of formaldehyde and methanol from a primordial CO molecule on ice dust. Recently, the series of our experiments [4] have confirmed that this process efficiently proceeds due to tunneling effect under the condition of quiescent molecular cloud where the temperature is as low as 10 K. Experiments of photolysis and hydrogenation were performed separately by different groups with their own experimental conditions. In addition, kinetic data such as rate constants obtained are still not enough. It is very difficult not only to measure those data for surface reactions but also to construct the models because reactions strongly depend on the surface composition and morphology. Therefore, the relative importance of photolysis and hydrogenation in molecular clouds was not examined. To do so, the simulation experiments for those processes under well controlled conditions were very desirable.

In the present study, photolysis and hydrogenation of H<sub>2</sub>O-CO binary ice mixtures (as the analogues of the most primordial ice composition) at 10–50 K are investigated in order to quantitatively evaluate their relative importance in the chemical evolution of interstellar dust icy mantles [5]. The dominant product of photolysis was CO<sub>2</sub>, with lower yields of formaldehyde, methanol, and formic acid, while only formaldehyde and methanol were obtained by hydrogenation reactions. Hydrogenation has higher formation efficiencies and yields of formaldehyde and methanol than photolysis. However, the contribution of photolysis should not be negligible for the formation of these molecules in molecular clouds, in contrast to the previously reported results [2]. The simultaneous irradiation of binary ice mixtures with hydrogen atoms and UV photons resulted in relative abundances of CO<sub>2</sub>, formaldehyde, methanol, and formic acid that are consistent with the observed abundances. Our results show that the composition and structure of ice are crucial in the chemical evolution of ice mantles, as much as the temperature and the type of irradiation.

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## Catalytic effect of amorphous solid water on surface reactions of hydrogen atoms at very low temperatures

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The role of amorphous solid water (ASW) in surface reactions of hydrogen atoms with molecules was investigated. In the series of our experiments on hydrogenation (deuteration) of CO and O<sub>2</sub> molecules [1-3], and H-D substitution in methanol [4], the comparison of reactivities was made between on the surfaces of pure solid reactant molecules (i.e., pure solid CO, O<sub>2</sub>, and methanol) and ASW. It was found that the effective reaction rates are enhanced on the surface of ASW at relatively higher temperatures. This catalytic effect of ASW would be due to the higher adsorption energy of hydrogen atom for ASW than the surface of pure reactant solids and/or the modification of potential energy surfaces by water molecules.

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# Formation of H<sub>2</sub>O by the H-addition to solid O<sub>2</sub> on amorphous D<sub>2</sub>O ice

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## INTRODUCTION

Water is the most abundant solid material in space, and has been observed in various astrophysical environments, e.g., interstellar clouds. Nevertheless, the formation mechanism(s) of water in interstellar clouds still remains understood. Since the formation of water molecules in the gas phase is revealed to be difficult to explain the observed abundance in molecular clouds, it has been suggested that they could be synthesized by atomic reactions of H and O on inorganic grains [1]. Recent studies have demonstrated that water (H<sub>2</sub>O) and its oxygenated molecule, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), were formed after hydrogen atom (H) exposure to pure solid oxygen molecules (O<sub>2</sub>) on a metal substrate at 10-28K [2,3].

It has been reported that the presence of an amorphous water ice enhances the reaction rate and raises the reactive temperature for H-addition reaction to CO [4]. So in this study, we conducted H-addition reactions to O<sub>2</sub> on amorphous D<sub>2</sub>O ice, and compare the results with those using pure solid O<sub>2</sub>.

## EXPERIMENTAL

D<sub>2</sub>O with an ~30 monolayer (ML) was deposited onto an aluminum substrate at 10K under ultra high vacuum conditions (~10<sup>-10</sup> Torr), followed by a deposition of ~3 ML O<sub>2</sub> onto the D<sub>2</sub>O ice. After the deposition, the aluminum substrate was heated to up to 40K and exposed to H atoms (100K) produced by a microwave-induced plasma. Products (H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>) were monitored in situ by FTIR. As a counterpart experiment, pure ~10 ML O<sub>2</sub> was exposed to H atoms at 10-23K.

## RESULTS AND DISCUSSION

As the time of H-exposure to solid O<sub>2</sub> increases, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O were formed (e.g. at 20K, Figure 1), being consistent with previous studies using pure O<sub>2</sub> [2,3]. However, it should be noted that the hydrogenation occurs even at 40K, unlike pure O<sub>2</sub> experiments [3]. This is probably due to the higher sticking coefficients of O<sub>2</sub> molecules to an amorphous D<sub>2</sub>O ice compared to those to aluminum substrate. Both temperature dependence and effect of amorphous ice for the reaction rate will also be discussed in this presentation.

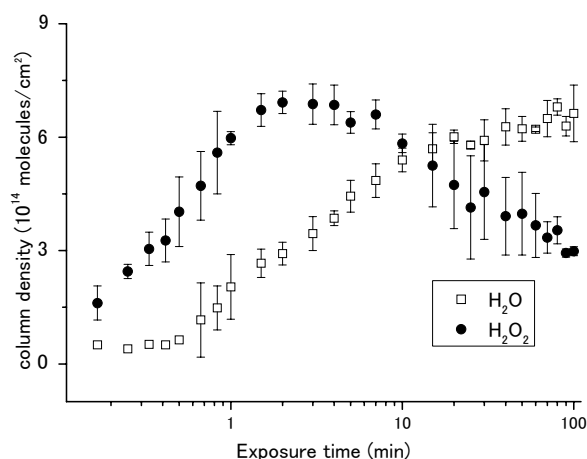


Figure 1 Variations in column density of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> at 20K on amorphous D<sub>2</sub>O ice.

## References

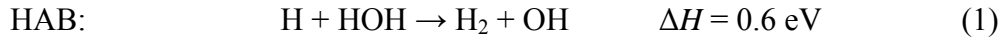
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# Energy partitioning in H<sub>2</sub> formation by photolysis of amorphous water ice

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In molecular clouds at temperatures below approximately 130 K, dust grains are covered with amorphous water ice mantles and thus photolysis of water ice plays an important role in grain chemistry. The formation of H<sub>2</sub> from water ice is a process of fundamental importance in molecular clouds and the outer solar system. H<sub>2</sub> formation from hot H atoms produced by photolysis of water ice involves two distinct mechanisms: endothermic hydrogen abstraction (HAB) and highly exothermic hydrogen recombination (HR).



Since these routes result in very different rovibrational distributions of the H<sub>2</sub> product, measurements of the H<sub>2</sub> state distributions point directly to the respective formation mechanism.

Formation of H<sub>2</sub> molecules from amorphous solid water has been investigated at 100 K using pulsed 157 nm laser radiation. We report the simultaneous measurement of kinetic and rovibrational energy distributions of the H<sub>2</sub> photoproduct. Two distinct mechanisms can be identified as shown in reaction (1) and (2): Endothermic abstraction of a hydrogen atom from H<sub>2</sub>O by a photolytically produced H-atom yields vibrationally cold H<sub>2</sub> products, whereas exothermic recombination of two H-atom photoproducts yields H<sub>2</sub> molecules with a highly excited vibrational distribution, non-Boltzmann rotational population distributions, and kinetic energies that decrease according to their depth of formation beneath the ice-vacuum interface.

Table 1: Energy partitioning and relative population distribution in H<sub>2</sub> from the photolysis of amorphous water ice at 100 K. The tabulated data show the relative populations of products with  $\nu = 2, 3$  and 4, and their variation with  $J$ . HAB and HR denote endothermic hydrogen abstraction and highly exothermic hydrogen recombination, respectively.

H <sub>2</sub> ( $\nu$ )	Relative vibrational population	Vibrational energy (eV)	Translational energy (eV)	Rotational energy (eV)	Energy absorbed by ice (eV)	Dominant Mechanism
0	-	0	0.028	0.013	-	HAB
2	0.58	1.00 (22%)	0.032(0.7%)	0.65(14%)	2.82(63%)	HR
3	1	1.48(33%)	0.028(0.6%)	0.54(12%)	2.45(54%)	HR
4	1.34	1.88(42%)	0.044(0.1%)	0.33(7%)	2.25(50%)	HR

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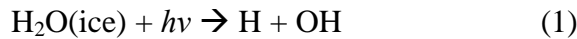
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# Direct observation of OH formation in the photolysis of amorphous water

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Many interstellar dust grains are coated with an ice mantle, a major component of which is amorphous solid water (ASW) that is constantly exposed to photon, magnetospheric ions, the solar wind and cosmic rays. When water ice is exposed to vacuum-ultraviolet radiation, the hydrogen-oxygen bond breaks followed by formation of OH, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and so on.



Tappe et al. [1] have reported the detection of rotationally excited OH by analyzing a 5-7 μm infrared spectrum obtained with *Spitzer Space Telescope* toward the southeastern lobe of the young protostellar out flow HH 211. The origin of the highly excited emission is most likely the photodissociation of H<sub>2</sub>O by the UV radiation generated in the terminal outflow shock of HH 211.

Previous experiments on the photolysis of an amorphous ice focused on species formed on/in ice, and did not investigate atoms and molecules released into the vacuum. Here we have investigated OH radical desorption following 157 nm photodissociation of amorphous solid water at 90 K. Ro-vibrational excited OH(v=0 and 1) radicals are directly detected with the resonance-enhanced multiphoton ionization technique. In addition, we discussed OH radical desorption from photodissociation of H<sub>2</sub>O<sub>2</sub> formed with 157 nm irradiation on ice as the secondary process.

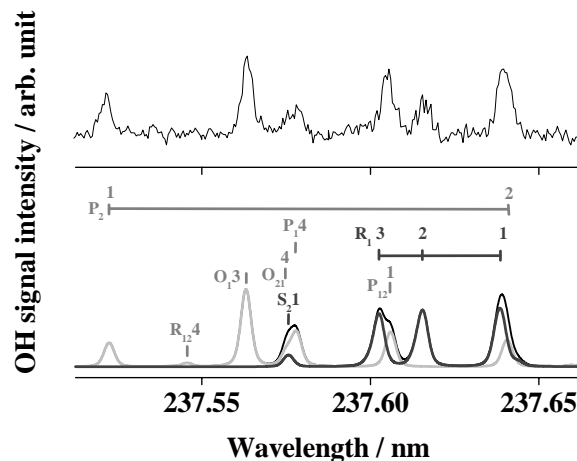


Figure 1: (upper) REMPI spectrum of OH(D<sup>2</sup>Σ<sup>-</sup>, v'=1 - X<sup>2</sup>, v''=0) and OH(3<sup>2</sup>Σ<sup>-</sup>, v'=0 - X<sup>2</sup>, v''=1), and (lower) Calculated spectra of OH(D<sup>2</sup>Σ<sup>-</sup>, v'=1 - X<sup>2</sup>, v''=0) (pale gray line) and OH(3<sup>2</sup>Σ<sup>-</sup>, v'=0 - X<sup>2</sup>, v''=1) (dark grey line).

## Reference

- [1] Tappe, A.; Lada, C. J.; Black, J. H.; and Muench, A. A., *Astrophys. J.* **680**, L117 (2008)

# Translational and internal states of hydrogen molecules produced from the vacuum ultraviolet photodissociation of amorphous solid methanol

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Within water rich interstellar ices, methanol is typically observed and is often the most abundant molecule after water. Because its abundance in some grain mantles varies between 0.05 and 0.50 relative to water, photolysis of methanol could be an appreciable source of the interstellar H<sub>2</sub> molecules.

	$\Delta H$ (kcal/mol)	$E_a$ (kcal/mol)	
CH <sub>3</sub> OH + $h\nu$ → CH <sub>3</sub> O· + H	104	-	(1)
→ CH <sub>2</sub> (·)OH + H	92	-	(2)
→ CH(·)OH + H <sub>2</sub>	71	-	(3)
→ CH <sub>2</sub> (·)O· + H <sub>2</sub>	19	-	(4)
H + H → H <sub>2</sub>	-104	0	(5)
H + CH <sub>3</sub> OH → CH <sub>2</sub> (·)OH + H <sub>2</sub>	-8	9	(6)
H + CH <sub>3</sub> OH → CH <sub>3</sub> O· + H <sub>2</sub>	1	14	(7)

We have investigated the mechanisms and dynamics of H<sub>2</sub>( $\nu=0-5$ ) production from the 157 nm (181 kcal/mol) photodissociation of amorphous solid methanol at 90 K with the resonance-enhanced multiphoton ionization technique. The hydrogen abstraction mechanism from methanol parent molecule by the photolytically produced hydrogen atom, reactions (6) and (7), yields translationally and internally cold H<sub>2</sub>( $\nu=0$  and 1) products. The molecular elimination processes, reactions (3) and (4), are the major sources of H<sub>2</sub>( $\nu=2-5$ ) products while the contribution of the hydrogen recombination mechanism, reaction (5), is minor.

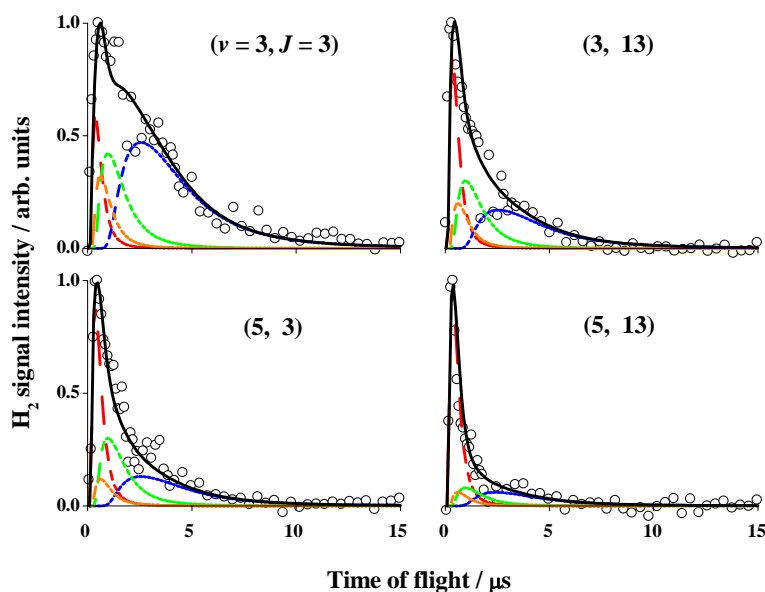


Figure 1: Time-of-flight spectra of H<sub>2</sub>( $\nu=3$ ,  $J=3$ , 13) and H<sub>2</sub>( $\nu=5$ ,  $J=3$ , 13). These spectra are composed of four Maxwell-Boltzmann distributions with  $T_{\text{trans}} = 5000, 1800, 700$  and 100 K.