

Complex organic chemistry in star-forming regions

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Complex organic molecules may play a key role in the emergence of life. They are detected in various astrophysical environments (e.g., low- and high-mass star-forming regions, prestellar cores, outflows, comets). In particular, they are found to be highly abundant in the warm inner regions of protostars, where planets are expected to form. These molecules may survive during the star formation process and be incorporated into asteroids and comets, which could deliver them to planetary embryos through impacts.

The formation mechanisms of complex organic molecules are however debated. Observations and chemical modelling are helpful to constrain how these species form. In particular, measurements of isotopic fractionation (especially deuteration) and relative abundance ratios of isomers or related species can help to distinguish between different routes. The detection of less abundant isotopologues and isomers can, however, be difficult. With the Atacama Large (Sub-)Millimeter Array (ALMA), it is now possible to detect them. The Protostellar Interferometric Line Survey (PILS) is a large spectral survey of the solar-type protostar IRAS 16293-2422 carried out with ALMA [1]. In the framework of this program, the deuterated forms of formamide (NH₂CHO) and glycolaldehyde (CH₂OHCHO) were detected for the first time [1,2]. Ethylene oxide (C₂H₄O) and propanal (CH₃CH₂CHO), the isomers of acetaldehyde (CH₃CHO) and acetone (CH₃COCH₃) respectively, were also found for the first time towards a low-mass protostar [3]. In the first part of this talk, I will present the results of these recent studies and I will discuss the possible formation pathways of these species.

In the second part, I will show the results obtained with the gas-grain chemical code UCL Chem to constrain the formation pathways of a few complex O-bearing species (e.g., glycolaldehyde, ethylene glycol, methyl formate) detected in various star-forming regions [4].

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Exploring Molecular-Cloud formation with OH 18 cm transition

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Recently, we found that the OH 18 cm transition can be used as an excellent thermometer of the molecular gas in a wide range of the H₂ density from 10² -10⁷ cm⁻² ([1] Ebisawa et al. 2015). The OH 18 cm transition consists of the four hyperfine components, and their relative intensities are sensitive to the gas kinetic temperature. For instance, we found a clear absorption feature of the 1612 MHz line against the cosmic microwave background (CMB) toward the translucent cloud eastward of Heiles Cloud 2 (HCL2). By using the statistical equilibrium analysis, we determined the gas kinetic temperature to be 53-60 K in this source, which is apparently higher than that of dense cores. This method was also applied to the dark molecular cloud L134N and the photodissociation region of the rho-Ophiuchi molecular cloud, and the existence of the warm molecular gas surrounding the dense cores were revealed. All these results suggest that the OH 18 cm transition traces a new class of warm molecular gas, which is possibly related to the formation processes of molecular clouds.

Then, we applied this technique to the outstanding straight structure in the northern part of HCL2 to explore its origin (Figure 1 left). Interestingly, we detected the 1720 MHz line in absorption toward the straight structure (Figure 1 right). According to our statistical equilibrium analysis, the 1720 MHz line absorption traces a dense and cold ($T_k < 30$ K) part of the cloud surrounded by a warm envelope gas. Combined analyses of OH, ¹³CO and C¹⁸O suggest that the straight structure would be formed by compression of a warm envelope gas extending to the southwestern part of HCL2. These results demonstrate that the OH 18 cm transition can be used to study molecular-cloud formation.

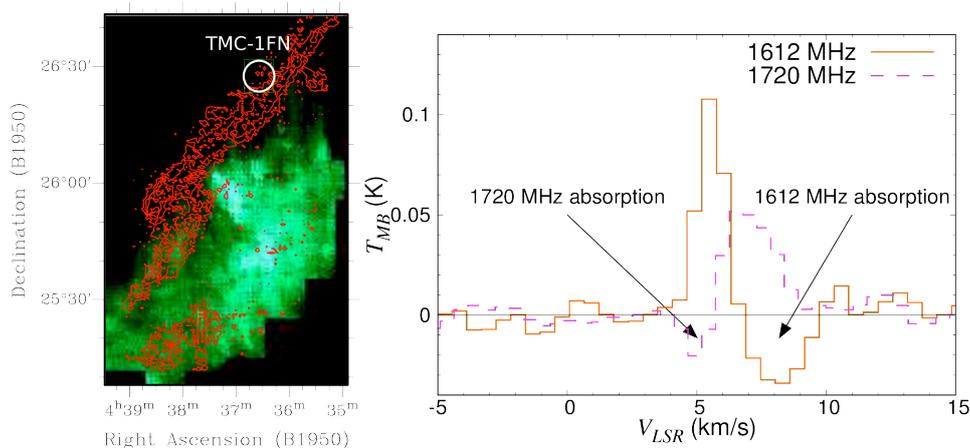


Figure 1: (left) The integrated intensity map of ¹³CO ($J=1-0$) (color) and C¹⁸O ($J=1-0$) (contours) in HCL2. (right) Spectra of the OH 18 cm transition observed toward TMC-1FN (white circle in the left panel).

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Deuterium Fractionation in the Earliest Stages of High-Mass Star Formation

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High-mass stars release a huge amount of energy to interstellar space by outflows, UV radiation, stellar winds and supernovae, so that high-mass stars play important roles in evolution of galaxies. Understanding high-mass star formation is one of the most important issues for astronomy. For the purpose, it is crucial to understand the initial conditions, because expected initial conditions are different among the current proposed models of high-mass star formation (turbulent core accretion model and competitive accretion model). To investigate the initial conditions of high-mass star formation, we focus on the deuterium fractionation of molecules.

Recently, we conducted a molecular line survey, including DNC $J=1-0$ and $\text{HN}^{13}\text{C } J=1-0$, toward the candidates of high-mass starless clumps, which were recently identified by Herschel observations (Traficante et al. 2015), by using the Nobeyama Radio Observatory 45 m telescope. Then, we found that there is diversity of DNC/HNC ratio among the observed sources, although the temperature of the sources is as low as about 10 K. By comparing the observational results with the chemical model calculation results, we suggest that the diversity of DNC/HNC ratio could be due to the diversity of the formation timescale of dense cores.

In addition, we investigate how the chemical composition of hot cores depends on the initial physical conditions. We compared the chemical composition of the hot core in the Infrared dark cloud G34.43+00.24 MM3 (T. Sakai et al. 2013) with that of the other hot cores. Then, we found that the $\text{D}_2\text{CO}/\text{CH}_3\text{OH}$ abundance ratio of the G34.43+00.24 MM3 hot core is higher than that of the Orion KL hot core. We suggest that the difference in $\text{D}_2\text{CO}/\text{CH}_3\text{OH}$ ratio is due to the difference in the initial conditions (i.e. timescale of cold starless phase). We also discuss how the abundances of complex organic molecules in hot cores depend on the initial physical conditions.

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Formation and isotope fractionation of interstellar ices, and their delivery to a forming disk

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The level of isotope fractionation in molecules provides insights into their formation environments and how they formed [e.g., 1, 2]. In this presentation, we present results from a series of astrochemical simulations from molecular clouds to forming circumstellar disks, considering isotope fractionation mechanisms and a layered ice structure [3, 4, 5]. Our main focus is placed on deuterium fractionation, while, if time allows, we will also discuss nitrogen isotope fractionation. In our models, icy molecules are mostly formed in the prestellar stages, and they are delivered to a disk or (partly) destroyed en route into the disk via thermal and stellar UV processing. The processing modifies the level of isotope fractionation in icy molecules. The numerical results are compared with observational studies of objects at various evolutionary stages.

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Dynamic assembly of cometary ices in protoplanetary disk midplanes

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Protoplanetary disk midplanes harbor the largest reservoir of icy dust grains that will be incorporated into planetary embryos and comets. The chemical content of these midplane ices originates in the prestellar phase and is shaped during the dynamic transport towards the disk upon the onset of collapse, as shown by means of a sophisticated physicochemical model [1, 2]. In this talk, results for two protoplanetary disks, one grown predominantly via viscous spreading and another via pure infall, will be shown. The models predict that the amount of CO₂ can increase during infall via the grain-surface reaction of OH with CO, which is enhanced by photodissociation of H₂O ice. Complex organic ices can be produced at abundances as high as a few % of H₂O ice at large disk radii (R > 30 AU) at the expense of CH₃OH ice, meaning that current Class II disc models may be underestimating the complex organic content. These simulations immediately imply that planet population synthesis models may underestimate the amount of CO₂ and overestimate CH₃OH ices in planetesimals by disregarding chemical processing between the cloud and disk phases. The model results are used to derive the C/O and C/N ratios as a function of radius in midplanes of embedded disks and are predicted to differ between the gas and solid phases. The two ice ratios show little variation beyond the inner 10 AU and both are nearly solar in the case of pure infall (Fig. 1), but both are sub-solar when viscous spreading dominates. These models highlight the importance of dynamics and chemistry in the embedded phase of star and planet formation for the chemical budget of comets and planetary building blocks.

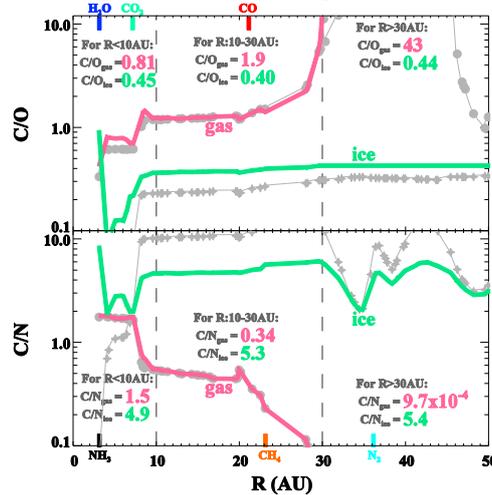


Figure 1: The midplane C/O and C/N ratios as a function of disc radius (R) in the gaseous (coral colored lines) and solid (turquoise colored lines) phases at the end of the simulation (2.46×10^5 yr after the onset of collapse) for the infall-dominated disk. The locations of some snowlines are marked. The grey curves with dots and stars are the ratios in the gaseous and solid phases, respectively, as calculated with abundances of simple volatiles only (namely H₂O, CO, CO₂, CH₃OH, CH₄, N₂ and NH₃ only).

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How to measure snowlines and C/O ratio distributions in protoplanetary disks using infrared spectroscopic observations

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Protoplanetary disks are active environment for the creation of simple molecules (e.g., H₂O, CO, CO₂, HCN) and complex organic molecules (COMs). The emission lines of these simple molecules from disks are detected by the infrared spectroscopic observations using Spitzer space telescope and large ground-based telescopes like VLT, Keck (e.g., [1])

Since protoplanetary disks rotate with Keplerian velocity, the emissions from disks have characteristic profiles due to doppler shift. Analyzing the profiles of lines, we will obtain the information on the distance from the central star of the line emitting regions. We have calculated the chemical structure of protoplanetary disks and H₂O line profiles, and have proposed the method to locate the position of the H₂O snowline in the disk midplane using high-dispersion spectroscopic observations. We have found that the H₂O lines with small Einstein A coefficients and relatively high upper state energies are dominated by emission from the disk region inside the H₂O snowline, and thus their profiles potentially contain information which can be used to locate the position of the H₂O snowline.[2][3].

It is thought that difference in snowlines of oxygen- and carbon-bearing molecules, such as H₂O, CO, CO₂, HCN, will result in systematic variations in the C/O ratio both in the gas and ice [4] [5]. In addition, the C/O ratio of atmosphere of some exoplanets (e.g., Hot Jupiter) were estimated by recent studies [6]. Therefore, the planet forming regions could be confined through comparing the radial distributions of C/O ratio in disks and those of planetary atmospheres.

In this study, we developed our calculations of disk chemical structures, and investigated the abundance distributions of simple molecules. We then calculated various line profiles of simple molecules from disks. We found that through investigating the profiles of various molecular lines with various Einstein A coefficients and upper state energies, we can confine C/O ratio distributions in disks. For example, HCN lines from a Herbig Ae disk in 14 μ m band reflect gas distributions of the outer disk. In contrast, HCN lines in 3 μ m bands reflect those of the inner disk surface. We also discuss the possibility to measure such molecular lines with future near- and mid-infrared spectroscopic observations.

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CO observations toward debris disk candidates with ALMA/ASTE

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From the recent survey of gaseous debris disks, 10 debris disks with gas have been discovered. Our aim is to understand the origin of the gas in debris disk; (1) primordial: the remnant gas of protoplanetary disks[1], and (2) secondary: sublimation of dust grains[2].

We present the results of CO(2–1) and CO(3–2) observations toward debris disk candidates made with ALMA and ASTE. We search for CO gas in debris disk candidates identified by AKARI[3]. In addition, we analyzed ALMA archival data of CO line emission of debris disk candidates. Comparing physical properties and velocity structures of CO emission in our sample with the famous debris disk of Beta Pic[4], we discussed the origin of origin of the gas in debris disk.

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Precise determination of the isotopic ratios of HC₃N in the massive star-forming region Sgr B2(M)

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Isotopic ratio is a critical parameter in understanding galactic chemical evolution. In particular, ¹³C isotopic ratio of an organic molecule reflects its formation mechanism. In the present study, we observed the simplest cyanopolyne HC₃N and its isotopomers in the massive star-forming region Sgr B2(M) with Nobeyama 45 m radio telescope. Fig. 1 shows the observed peaks of the $J = 10-9$ transition. The column density and the rotational temperature of HC₃N were determined to be $1.6 \times 10^{15} \text{ cm}^{-2}$ and 163 K, respectively. The ratios of the column densities for the ¹³C isotopomers were derived to be [H¹³CCCN]:[HC¹³CCN]:[HCC¹³CN] = 1:04(4):1.01(4), where the rotational temperature was fixed to that of HC₃N. The ratios are almost the same. It is considered that the ¹³C isotope exchange reactions do not contribute to make slight difference between the column densities of the three ¹³C isotopomers in the relatively warm region Sgr B2(M). Therefore, we concluded that there is no isotopic fractionation for the specific carbon atoms in HC₃N. We also observed the transitions in the vibrational excited states of HC₃N. The rotational temperature of 352 K determined was obviously different from that of the vibrational ground state.

In addition, we observed the peak of the $J = 10-9$ transition of HC₃¹⁵N as shown in Fig. 1. The ¹⁴N/¹⁵N ratio was tentatively determined to be ~99 in Sgr B2(M), which agrees with that estimated by Adande *et al* (123.8 ± 37.1) [1]. It is considered that this ratio reflects difference of nucleosynthesis processes between ¹⁴N and ¹⁵N atoms.

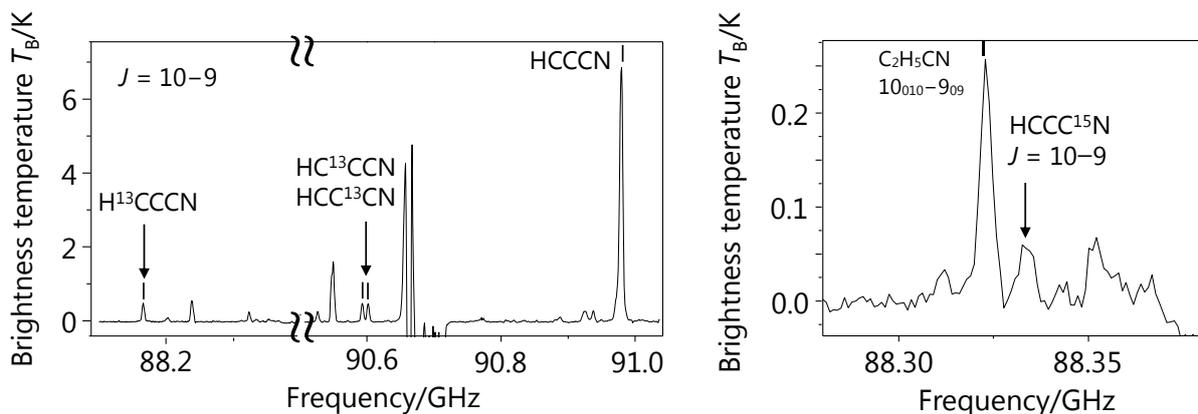


Figure 1: The $J = 10-9$ transitions of HC₃N observed toward Sgr B2(M) with Nobeyama radio telescope. Left panel: the lines of HCCCN, H¹³CCCN, HC¹³CCN and HCC¹³CN. Right panel: the line of HCCC¹⁵N.

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A survey of near-infrared diffuse interstellar bands

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Diffuse interstellar bands (DIBs) are ubiquitous absorption lines in the spectra of the reddened stars, which originate from foreground interstellar clouds. Although the carriers of most DIBs have not been successfully identified yet, they are considered to arise from the gas-phase carbonaceous molecules, such as fullerenes, polycyclic aromatic hydrocarbons (PAHs) and carbon-chain molecules [1]. The observational studies of DIBs may play an important role toward the understanding of the properties and chemistry of large organic molecules in interstellar medium.

To identify their carriers and investigate their interstellar properties, we are conducting the first comprehensive survey of the DIBs in near-infrared (NIR) wavelength range, where the ionized large molecules, such as PAHs and fullerenes, are considered to have absorption bands. The data have been collected with the NIR high-resolution ($R=28,000$) spectrograph WINERED, which offers a high sensitivity in the wavelength coverage of 0.91-1.36 micron. We successfully found a number of new NIR DIBs, some of which are detected at the wavelengths close to the peaks of the absorption bands of PAH cations [2]. In addition, the high transmittance of the NIR wavelength range enables us to explore the environmental dependence of the DIB carriers in the dusty environment [3]. We will present some results obtained in this survey and future prospects.

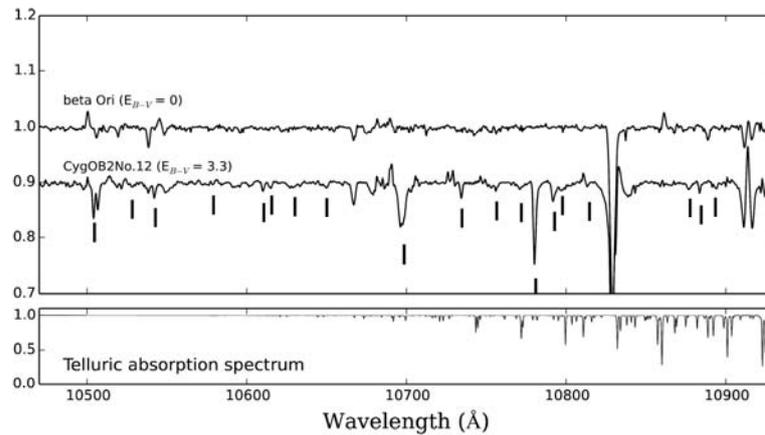


Figure 1: Upper panel: The spectra obtained with WINERED. The DIBs (thick lines) are detected only in the reddened object (lower spectrum). Lower panel: The model spectrum of telluric absorption lines.

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Grain Surface Pathways to Complex Organic Molecule Formation

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Complex organic molecules (COMs) have been identified in a number of distinct interstellar environments, characterized by radically different physical conditions, e.g., hot cores of low- and high-mass protostars as well as cold dense molecular clouds [1]. Although gas-phase COM formation channels may be particularly important in hot cores, they cannot fully explain the presence of complex species in cold regions. Recent laboratory studies showed that COMs form effectively at low temperatures (10-30 K) in the solid state, i.e., on icy grains, typically following a non-energetic (atom-addition) or energetic (X-rays, VUV photons, ions, and electrons) trigger. So far, such studies have been mostly performed for one of the two processes. For decades, surface complex molecule formation has been thought to be induced largely by energetic processing. Very recently, my co-workers and I gave the first laboratory evidence that the building blocks of sugars, fats, and proteins can be formed through non-energetic surface reactions under dark molecular cloud conditions [2, 3]. During my talk, I will review the most recent laboratory work carried out at the Sackler Laboratory for Astrophysics in Leiden (Netherlands). Particularly, I will qualitatively and quantitatively discuss both the relative importance and the cumulative effect of atom-addition and VUV irradiation on the surface formation of complex species at 15 K [4, 5]. Results will be linked to current astronomical observations.

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Laboratory Simulation of Chemical Reactions on Pluto

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Stern et al. [1] used the Hubble Space Telescope with the Cosmic Origins Spectrograph (HST-COS) to record ultraviolet reflectance spectra of Pluto at two rotational phases. An absorption feature between 210 and 240 nm with an absorption maximum near 222 nm was found in the 95° longitude of Pluto. Because most nitriles and/or large hydrocarbons have UV absorptions in this spectral region, they suggested that complex molecules may exist on the surface of Pluto. In our previous works, we recorded the UV absorption spectrum of electron-bombarded CH₄ diluted in solid N₂ at 10 K [2]. The observed spectrum revealed a band within the 310–200 nm region, centered at 260 nm and with a shoulder near 220 nm. We further studied the UV spectra of electron-bombarded pure solid N₂ [3], C₂H₂ [4], and C₂H₄ [5] in solid N₂ at 10 K, but all the recorded spectra showed no significant features near 220 nm. The temperature on Pluto's surface ranges from 33 K to 55 K, which means that laboratory simulations of chemical reactions at 10 K might be improper. The current work presents a study of electron irradiated CH₄:N₂ ices during deposition at various temperatures. IR spectra show formation of N₃ and CH₃ radicals at low temperatures while only nitrile species were observed at higher deposition temperatures. This was attributed to radical recombination enabled by diffusion at the higher temperatures. UV absorption spectrum of electron irradiated samples at 44K, depicted in Fig. 1, shows a feature that compares well with the Pluto spectrum observed by Stern et al [1]. This along with the IR based identifications implies that nitriles exist on Pluto's surface [6].

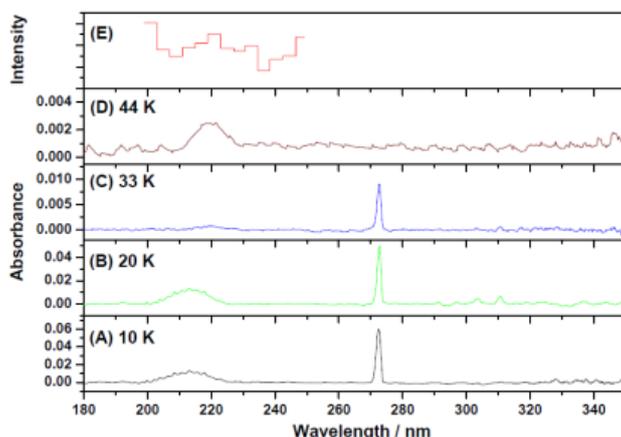


Figure 1: Ultraviolet (UV) absorption spectra of electron-bombarded CH₄/N₂ matrix samples during deposition at (A) 10 K, (B) 20 K, (C) 33 K, (D) 44 K. (E) The inverted HST-COS Pluto spectrum [1].

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Formation of Complex Organic Molecules on Interstellar Grain Surfaces. Insights from Periodic Quantum Chemical Simulations

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About 200 molecular species were detected in the ISM. Some of them are complex organic molecules (COMs), molecules with more than 6 atoms containing one or multiple C atoms. Some COMs can reach a certain degree of complexity and can have a prebiotic relevance. Knowing whether COMs contributed or not to the chemical evolution needed for the emergence of life is one of the open questions in the origin of life studies. Two classes of models are invoked to explain the interstellar synthesis of COMs. One advocates formation of COMs on the grain surfaces [1, 2], in which dissociation of frozen hydrogenated species gives radicals, which in turn recombine to form COMs. The other postulates that they form via gas-phase reactions [3, 4], in which the frozen hydrogenated species desorb into the gas phase and react with other gaseous species to form COMs through a series of gas-phase processes. The problem in knowing which of the two models is correct and in which conditions each model is applicable mostly comes from a dramatic lack of experimental and theoretical data of gas-phase and on-surface reactions. This communication focuses on the formation of several COMs by recombination of their precursor radicals (e.g., $\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_3\text{CHO}$; $\text{CH}_2\text{OH} + \text{HCO} \rightarrow \text{HOCH}_2\text{CHO}$, and others) on grain surfaces by means of quantum chemical simulations. Surfaces are based on a periodic approach of a slab model consisting of H_2O mixed with CO (Figure 1). Results indicate that, in addition to radical recombination, other processes are competitive reactive channels. The occurrence of these processes depends on several factors such as the nature of the radical recombination, the proximity of the reactants or the capability of the radicals to transfer their H atoms [5].

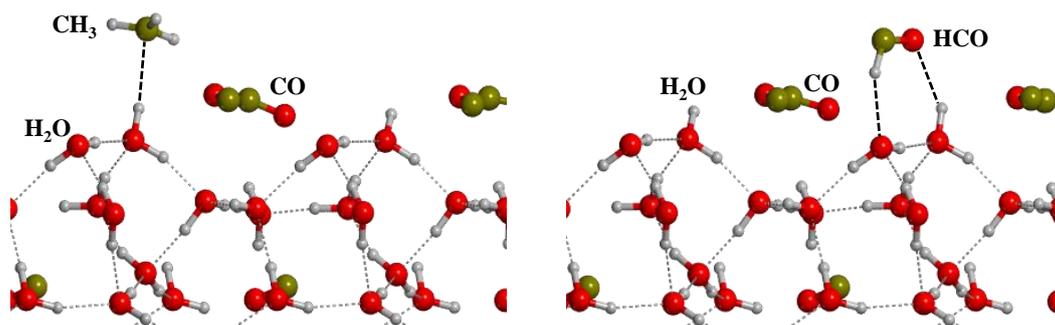


Figure 1: Surface slab model employed to simulate the recombination of radical species on surfaces. In this case the CH_3 and HCO radicals are adsorbed on the surface model.

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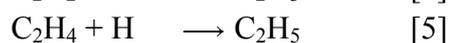
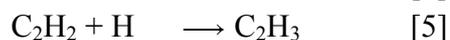
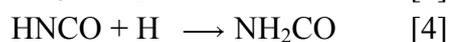
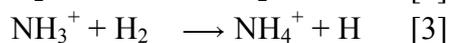
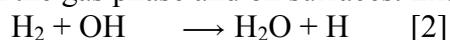
Instanton Theory: Prediction of Rate Constants for Astrochemical Reactions

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Simulations of reaction rates including quantum tunneling of atoms complement measurements and help to interpret data. An appropriate rate theory must be accurate enough to provide reliable predictions, but efficient enough to allow for computationally intensive electronic structure calculations at large enough structural models. Instanton theory, based on Feynman path integrals, matches these requirements [1]. It provides the dominant tunneling path at a given temperature or energy.

We have used it to calculate rate constants for a number of reactions of astrochemical interest both in the gas phase and on surfaces. Examples are:



Models of surface reactions need to include the interplay between reactions and diffusion.

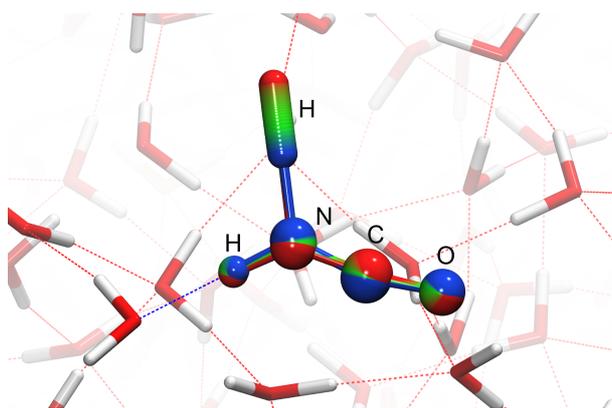


Figure 1: Tunneling path (instanton path) of the reaction $\text{HNCO} + \text{H} \longrightarrow \text{NH}_2\text{CO}$ on a surface of amorphous solid water [4]. The path is colored from the reactant side (red) to the product side (blue).

References

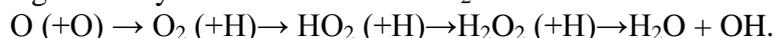
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Tunneling reaction rate constants on a surface: a case study of $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$

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In the dense and cold regions of the Interstellar Medium (ISM), water is known to be formed on the surface of dust grains via sequential hydrogenation of O, O₂, or O₃. The full water surface reaction network consists of ~ 15 reactions and depending on density, temperature and H, H₂, O abundance of the interstellar region, different reaction pathways towards the formation of water are important [1]. In the most dense regions, the absolute amount of oxygen becomes sufficiently high for the following reaction pathway to contribute significantly to the formation of H₂O and OH:



The final step in this reaction route has been reported to have a large activation barrier. It has been studied experimentally on the surface at low temperatures and a kinetic isotope effect was found [2]. This indicates the importance of tunneling yielding it efficient even at 15 K.

Furthermore, the detections and non-detections of H₂O₂ in a diverse sample of sources in different environments gave rise to the conclusion that the production of peroxide is very sensitive to temperature. The production of peroxide was taken into account by rescaling the reaction rate according to experimental data [3, 4]. Quantitatively rescaling rates is, however, not trivial for reactions that are deeply embedded in a reaction network.

Therefore, we present a theoretical study of the reaction $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$ within the framework of studying tunneled reactions on a surface. Calculations are performed using a DFT functional benchmarked to CCSD(T)-F12 single-point energies. Rate constants are calculated with instanton theory. We present activation barriers and rate constants for three different cases: the gas-phase reaction, the gas-phase reaction with several spectator H₂O molecules (small clusters) and we show how to extend these to studying the reaction on a crystalline water surface using a QM/MM method.

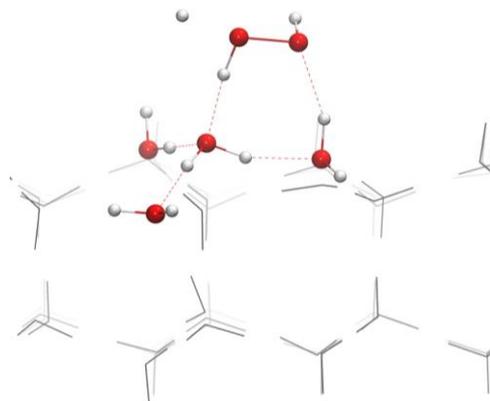


Figure 1: Example of a transition state structure on a water surface, the colored atoms are part of the QM region, whereas the grey lines represent water molecules described on an MM level.

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Investigations on IR spectra of astronomically important species using the *para*-hydrogen matrix-isolation technique

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Two types of methods using *para*-hydrogen (*p*-H₂) matrix isolation were employed to prepare species that might be important in astronomy. These species were characterized with infrared (IR) absorption.

(1) The bombardment of *p*-H₂ with electrons produces H₃⁺ and H via H₂ + e⁻ → H₂⁺ + 2e⁻ and H₂⁺ + H₂ → H₃⁺ + H reactions. Proton transfer from H₃⁺ to species of interest produces mainly protonated and mono-hydrogenated species trapped in a *p*-H₂ matrix. This method has been applied to produce protonated polycyclic aromatic hydrocarbons (designated H⁺PAH) and some small molecules. The protonated PAH are potential carriers of the unidentified infrared emission (UIR) bands in interstellar media. Our previous work on protonated pyrene and coronene [1–3] indicates that, as the size of aromatic ring increases, the spectral shifts of IR bands point the direction toward the positions of the UIR bands. When we extended the work to protonated ovalene (7-C₃₂H₁₅⁺), we found a close resemblance between the laboratory IR spectrum and the UIR emission bands, indicating that H⁺PAH can contribute to the UIR emission and protonated ovalene might be an important member of the interstellar PAH inventory [4]. The IR spectra of mono-hydrogenated ovalene 7-C₃₂H₁₅ were also identified for the first time.

(2) The N/O chemical network is important in understanding the formation mechanism of amino acids in dark interstellar clouds. We present the results of IR studies on the H + HONO reactions in solid *p*-H₂ at 3.3 K. Isolated HONO molecules were irradiated with light at 355 nm from a Nd:YAG laser. The photoproduct OH radicals react readily with nearby *p*-H₂ to produce H₂O and mobile H atoms. A few hours after irradiations, we observed absorption lines of products of hydrogenation of HONO: hydroxyl nitroxide HON(O)H, dihydroxyloamino radical HONOH, and dihydroxyl amine HONHOH. The spectral assignments were based on comparison with calculated vibrational wavenumbers and IR intensities, and were further confirmed with the observed isotopic ratios for D/H and N¹⁵/N¹⁴ species that were in agreements with predicted values. The formation mechanism including tunneling reactions of H + HONO and other secondary reactions will be discussed. The presented results show some new reaction paths which might lead to formation of prebiotic molecules in the dust grains in interstellar medium.

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High-resolution and high-accuracy infrared spectra of interstellar methylamine in the gas phase

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The study of the rotational and vibrational spectra of molecules in the interstellar medium is particularly useful to elucidate the physical conditions and chemical contents and evolutions of these interstellar gases. The spectroscopic study of methylamine (CH_3NH_2) in the laboratory has been directly led to the valuable application to the detection of CH_3NH_2 earlier in 1974 [1] and recently in 2011 [2] in the Universe. In fact, the spectra of CH_3NH_2 are rich and highly crowded due to the two coupled large-amplitude internal motions of torsion and inversion which can be caused in collisions with He and H_2 in a molecular cloud. Furthermore, the Universe has a very wide range of astrophysical sources, and the astrophysical observations now are increased in resolution and in sensitivity by ALMA (Atacama Large Millimeter Array), HIFI (Heterodyne Instrument for the Far Infrared), and FAST (Five-hundred-meter Aperture Spherical radio Telescope), which greatly need more and precisely expanded laboratory databases of CH_3NH_2 . However, since the first report about seventy years ago at low resolution of 1 cm^{-1} and an accuracy of about 0.1 cm^{-1} [3], the high-accuracy infrared spectra in the C–N vibrationally stretching band of CH_3NH_2 have just recently been studied by the technique of Lamb-dip saturated absorption spectrum by us for just a set of 43 saturation dips primarily in the C–N stretching *Q*-branch region in only two sub-states [4]. Currently, we have systematically expanded our sub-Doppler measurement to this band of gaseous CH_3NH_2 over a wider range of transitions in *P*-, *Q*-, and *R*-branch. More than 200 Lamb-dip signals in 27 sub-states have been observed individually at a spectral resolution of 0.4 MHz and the transition frequencies of them have been determined with an accuracy of ± 0.1 MHz. Our current experimental results constitute a high-accuracy spectral database in the important 9–11 micrometer region for various theoretical and experimental studies and applications to CH_3NH_2 for astrophysical and astrochemical communities.

Acknowledgements

We express our thanks to Prof. N. Ohashi for providing a list of calculated ground-state energies. This research was partially supported by the NSFC (Grants No. 11174186 and 91536105), the Tianshan Scholar Program and the JSPS BRIDGE Fellowship Program (BR161302). L.H.X and R.M.L acknowledge financial support from the NSERC.

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Recent Advances in Our Understanding of the Molecular Complexity in Astronomical Environments.

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Over the past several years, observations of a variety of astronomical environments has led to the detection and characterization of new molecular species as well as to a better understanding of the physical and chemical conditions of these regions. Molecular material is now found in a host of Galactic and extragalactic environments and has been used as tracers of a variety of conditions including but certainly not limited to, PDRs, XDRs, shocks, diffuse gas, dense gas, HMCs and UC HII regions. In the era of large single dish telescopes and broadband interferometric arrays, we are truly getting a chemical picture of the universe. This presentation will look at the recent advances our team has made in the detection of new astronomical molecules and how these new detections are driving better and more complex theories of large molecule formation in astronomical environments. Included in this presentation will be the first astronomical observation of a chiral molecule detected towards the high mass star forming region SgrB2N [1]. Figure 1 shows the detection of propylene oxide ($\text{CH}_3\text{CHCH}_2\text{O}$) (reproduced from [1])

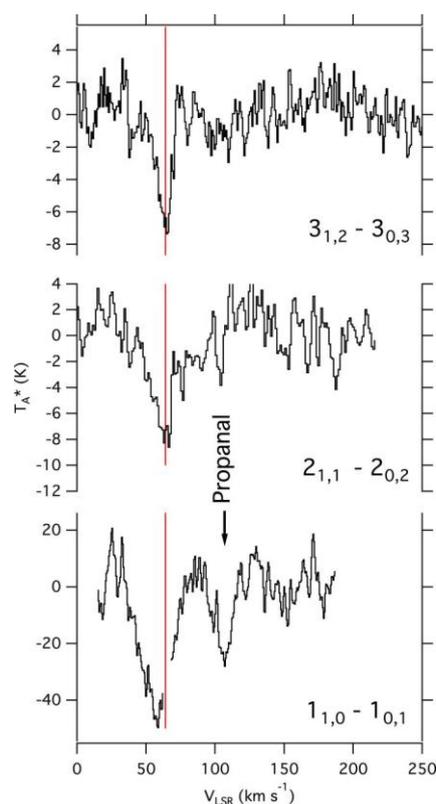


Figure. 1: Observations of the $1(1,0) - 1(0,1)$ (Parkes), $2(1,1) - 2(0,2)$ (GBT), and $3(1,2) - 3(0,3)$ (GBT) transitions of propylene oxide, in absorption, toward the Galactic center.

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Multi-scale polarization, chemistry and kinematics in the Pipe nebula

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Our team is involved in multi-wavelength observations of the Pipe nebula across several spatial scales and my goal is to present the most relevant results of this investigation. A recent comparison between *Planck* submm data and optical data has proven that polarization by emission and absorption are remarkably consistent [1]. Both techniques show an ordered magnetic field that may be the result of the interaction between two clouds [2, 3]. We are also investigating the ionization properties of the Pipe through observations of several species such as DCO+ and H¹³CO+. Preliminary results point to an unusually high ionization fraction and therefore a tighter coupling between matter and magnetic field.

I will also present results of a chemical survey that reveals a close correlation between deuteration in the cores and visual extinction [4]. One particular core, FeSt 1-457, shows chemical differentiation and polarization levels consistent with a starless core [5,6]. Finally, I will present ALMA observations toward B59, the only active core in the Pipe. Our data show impressive substructure in dust and molecular emission, suggesting that a centrifugal barrier may be the key mechanism regulating the kinematics of a young stellar object.

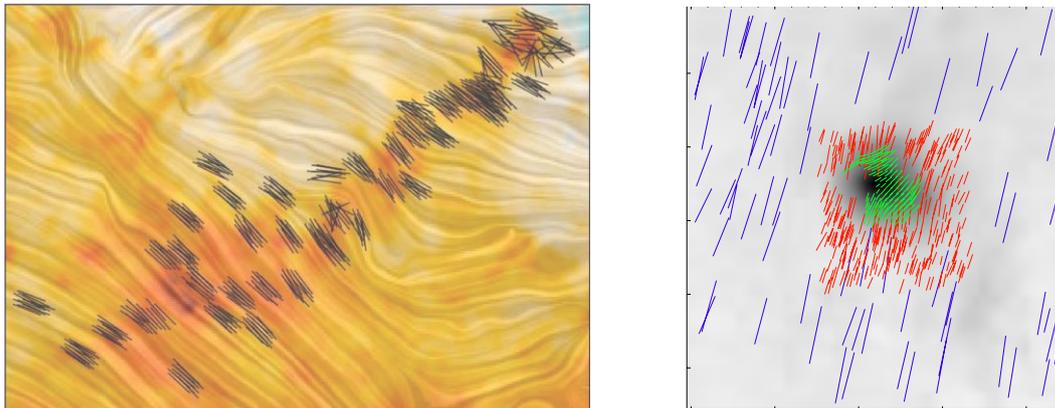


Figure 1: The left panel shows a comparison between the *Planck* polarization (drapery pattern) and optical polarization (black segments) in the Pipe nebula. The right panel shows optical (blue segments), near infrared (red segments) and submm polarization (green segments) in the prestellar core FeSt 1-457.

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HI-to-H2 Transitions in Galaxy Star-Forming Regions

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I will describe new analytic theory for the atomic to molecular (HI-to-H2) transitions, and the build-up of atomic-hydrogen (HI) gas columns in star-forming clouds, based on fundamental physics principles. I will discuss my general-purpose formula for the total HI columns produced by photodissociation in optically thick media, valid for beamed or isotropic radiation fields, the weak- to strong-field limits, gradual to sharp HI-to-H2 transitions, and for arbitrary metallicity. The analytic theory is validated with detailed numerical radiative transfer computations. The general theory may be broadly used for interpreting 21 cm studies of individual Galactic sources and global galaxy properties, and may also be incorporated into hydrodynamics simulations.

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The Detection and Synthesis of Large and Very Large Interstellar Molecules

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Interstellar molecules with six or more atoms are often referred to as “complex” organic molecules, or COMs, even though they are certainly not complex by the standards of organic chemistry [1]. Better adjectives to describe these molecules are “large” and “very large.” The large molecules are those with up to 13 atoms in size, whereas the “very large” molecules include PAH’s and, more specifically, fullerenes. The large organic molecules can be subdivided into unsaturated carbon chains and more terrestrial-like species similar to solvents in the terrestrial organic laboratory. Until recently, it was thought that the different classes of large molecules belonged to different sources based on the dominant mode of synthesis. New observations however have thrown this dichotomy into disarray, and new theoretical and laboratory results have shown that the synthesis of large and very large molecules can occur via a variety of methods under different conditions. These different mechanisms, including a variety of gas-phase and grain-surface reactions, will be discussed. The rebirth of neutral-neutral chemistry, outbursts, and grain bombardment by cosmic rays will be emphasized, as will possible syntheses of very large molecules [2,3].

How can we observe larger molecules than seen up to now? The relative merits of rotational, vibrational, and electronic spectroscopy will be discussed. One advantage of rotational spectroscopy is that the spectral frequencies are directly related to the geometry of the molecule. To detect molecules with significantly more than 13 atoms will probably require lower frequency observations that customary these days because of larger moments of inertia. Difficulties in observing molecules at lower frequencies require larger surface areas, such as will be available with the Square Kilometer Array (SKA) and the extended/refurbished Very Large Array (VLA). Infrared spectroscopy can also be of use despite atmospheric opacity. The new James Webb Space Telescope will be launched within a year, and allow infrared astronomers to search for less abundant molecules albeit with a not very high spectral resolution. The SOFIA aircraft has much higher spectral resolution, but may be limited to more abundant species. Finally, the use of visible and UV spectroscopy, which probe electronic transitions, is probably limited to diffuse clouds or borders of denser regions. In a sense, observations in the visible have already been undertaken and have given us the diffuse interstellar bands, which are still mainly unassigned.

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On the Chemistry of Hydrides of N Atoms and O⁺ Ions

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Previous work by various authors has suggested that the detection by Herschel/HIFI of nitrogen hydrides along the low-density lines of sight toward G10.6-0.4 (W31C) cannot be accounted for by gas-phase chemical models. In this paper we investigate the role of surface reactions on dust grains in diffuse regions, and we find that formation of the hydrides by surface reactions on dust grains with efficiency comparable to that for H₂ formation reconciles models with observations of nitrogen hydrides. However, similar surface reactions do not contribute significantly to the hydrides of O⁺ ions detected by Herschel/HIFI that are present along many sight lines in the Galaxy. The O⁺ hydrides can be accounted for by conventional gas-phase chemistry either in diffuse clouds of very low density with normal cosmic-ray fluxes or in somewhat denser diffuse clouds with high cosmic-ray fluxes. Hydride chemistry in dense dark clouds appears to be dominated by gas-phase ion–molecule reactions.

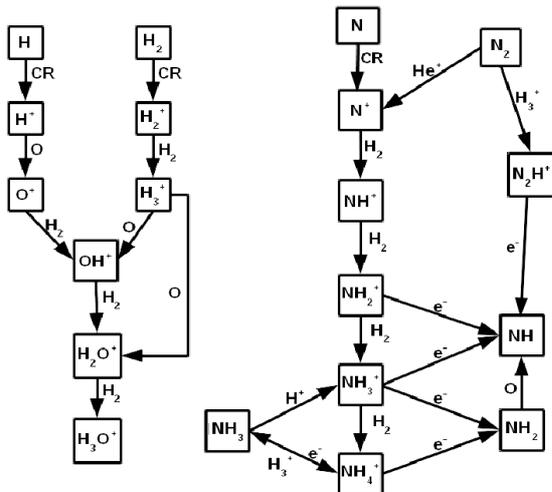


Figure 1: The main routes in the gas-phase chemistry forming hydrides of N and O⁺. Diagrams modified from [1] and [2].

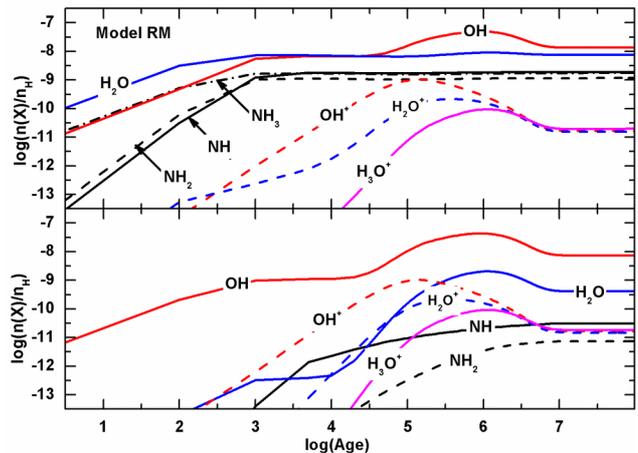


Figure 2: The time evolution of the fractional abundances of all the hydrides in the Reference Model (RM) with (top) and without (bottom) surface reactions.

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New Methods in Molecular Spectroscopy: Cologne Center for THz Spectroscopy

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The *Cologne Center for THz Spectroscopy* invites guests to use a wide variety of instruments to obtain spectra from the far-infrared to the mid-infrared region. Spectra of complex organic molecules (COMs) are recorded in several conventional absorption spectrometers in order to identify them in observations of the ALMA, Herschel and SOFIA telescopes. Driving questions in this area of research are, e.g., up to which molecular complexity do these species grow in the interstellar environment and how can they be formed under the prevailing low pressure and temperature conditions.

Apart from these traditional spectroscopy tools, new instruments are built in the Cologne laboratories to improve the sensitivity, frequency coverage and spectral resolution, in particular to allow the study of radicals and ions which shall be found in future observations. We present a 75-110 GHz emission spectrometer which is operated at room temperature. An immediate bandwidth of 2.5 GHz is recorded with this instrument at a noise temperature of only several hundred Kelvin. Apart from its high sensitivity new features will be discussed. A chirped pulse spectrometer has been constructed not only to record broad band spectra but in particular to determine rate coefficients for inelastic and reactive collisions.

The method of light induced reactions (LIR) has been developed over the last 20 years in our group in order to record spectra of mass selected, cold molecular ions which are stored in ion traps. Compared to traditional absorption spectroscopy in discharge cells the sensitivity of our devices is increased by many orders of magnitude. The spectral resolution is high enough to predict THz spectra at sub-MHz accuracy which is sufficient to identify those ions in astronomical observations [1]. Changing the population of the rotational states and interrogating them by LIR in double resonance experiments leads to predictions of THz transition frequencies at the 10^{-9} level [2], which challenge observations [3]. The ion trap instrument FELion allows to record spectra of cold ions over a range of 250 – 3200 cm^{-1} . This approach allows the identification of isomers and conformers of the molecular species selected by mass spectrometry. Moreover, identifying the vibrational bands of more complex molecular ions challenges quantum chemical predictions [4] and is used as a basis for high-resolution studies in order to find those molecules in space [5].

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A laboratory experiment of interstellar molecular reactions at RIKEN Cryogenic Electrostatic ring (RICE)

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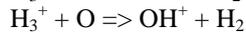
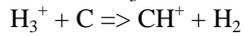
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A laboratory experiment of the interstellar molecular reactions is being developed at RIKEN cryogenic electrostatic ring (RICE). The RICE, shown in Figure 1, provides a novel opportunity to store atomic and molecular ion beams in a closed orbit under variable ambient temperatures (4-300 K). By injecting two different beams into the RICE at a low relative velocity to each other, the slow collision of interstellar molecules is reproduced in a cryogenic environment. The first cryogenic operation of the RICE was successfully performed in 2014 August, and a rotational laser spectroscopy of cold molecular ions is ongoing at 4 K.

Currently, an experimental setup for the neutral beam injection is under preparation. This aims to study the reaction of H_3^+ ions with C and O atoms, namely,



as the starting point of the C-H and O-H series molecular evolution in space. The rate and branching ratio for each reaction path will be investigated as a function of the collision energy and environment temperatures.

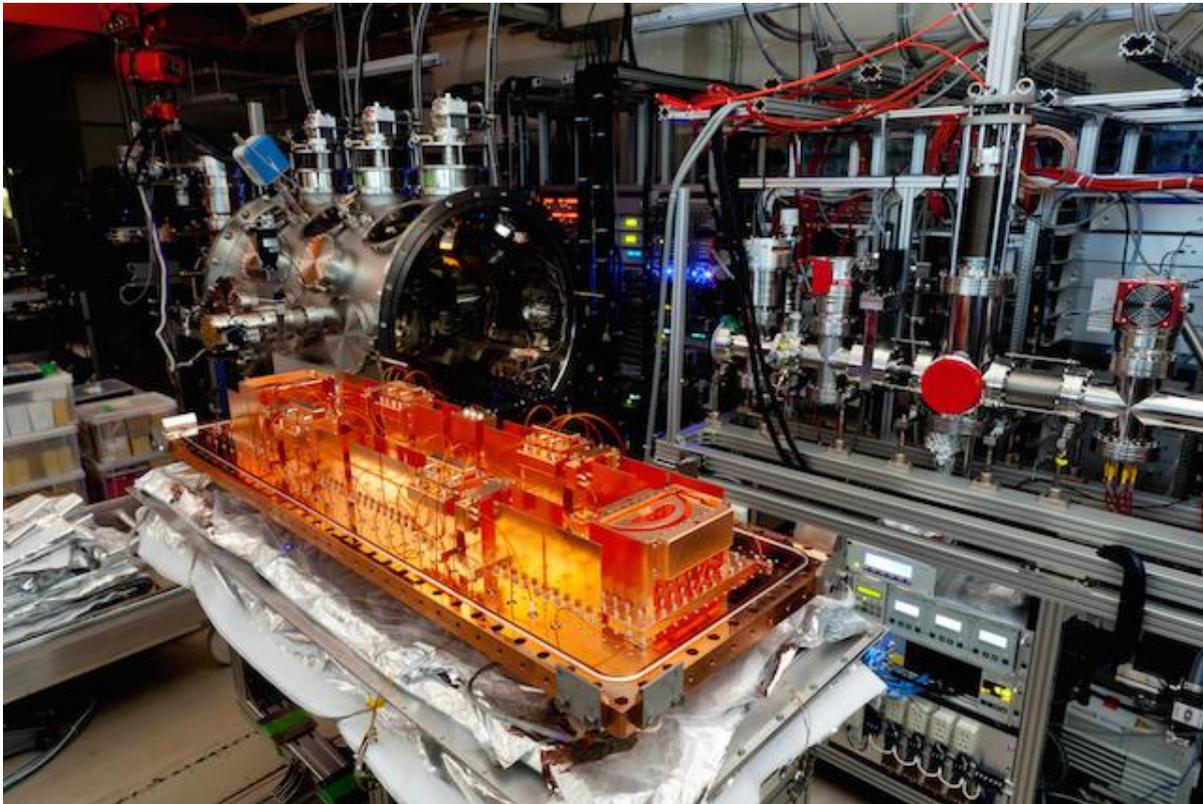


Figure 1: The photograph of the RIKEN Cryogenic Electrostatic ring (RICE); the copper-made electrostatic elements of the ring (center), the vacuum vessel with cryoheads (left), and the injection beamline (right).

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Unveiling subsurface hydrogen-bond structure of crystalline ice

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Determinations of structural reconstruction and molecular orientation at surfaces of ubiquitous water ice are challenging due to the inherent difficulty in probing surfaces of the fragile and insulating material through traditional experimental approaches. Because buried subsurface structures govern the physicochemical properties of topmost surfaces [1], unveiling the subsurface structures is of crucial importance for an ultimate understanding of various heterogeneous ice-surface processes vastly taking place on earth and in the universe. For the basal face of crystalline ice Ih, we have tackled this problem with a non-invasive surface-sensitive method of sum-frequency generation (SFG) vibrational spectroscopy with state-of-the-art phase detection [2] in combination with molecular dynamics simulations and *ab initio* quantum calculations [3].

Here we demonstrate that the SFG spectra of isotope-diluted crystalline ice Ih are highly sensitive to the symmetry breaking of inter-bilayer hydrogen bonds at subsurface. The observed $\text{Im}\chi^{(2)}$ spectrum for the hydrogen bonded OH-stretch vibration of HDO ice Ih(0001) at 120 K shows positive and negative peaks at lower and higher frequencies, respectively. As a H-bond that connects neighbouring molecules becomes stronger, the frequency of local OH-stretch vibration involved in the H-bond decreases [4]. Therefore, our result suggests that the OH oscillators pointing toward the bulk (negative peak) form weaker H-bond than those pointing toward the surface (positive peak). From the analysis of the observed spectra, we will discuss that, in contrast to the bulk, the strength of hydrogen bond strongly depends on the orientation of water molecules at subsurface due to asymmetric librational fluctuation and the cooperative nature of hydrogen bond.

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**Analog of interstellar carbonaceous dust:
processing by electron bombardment and theoretical modeling**

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Observational evidence, based on IR absorption spectra, indicates that interstellar (IS) carbonaceous dust in the diffuse interstellar medium is largely made of some sort of hydrogenated amorphous carbon (abbreviated HAC or a-C:H). Observations also show that the most prominent spectroscopic feature associated with the aliphatic component of IS carbonaceous dust (the 3.4 μm absorption band) disappears in dense molecular clouds, although the details of the destruction mechanism are not entirely clear. The effects of cosmic rays, which can reach the interior of dense clouds, on the carriers of this feature, have been investigated in this work by irradiating HAC samples with 5 keV electrons. High energetic electrons had proved previously [1] to have similar effects to MeV ion beams of different species tested in laboratory, which are usually accepted as good analogs of cosmic rays [2]. The HAC deposits were grown by plasma enhanced chemical vapor deposition (PECVD) in inductively coupled RF discharges of CH_4/He mixtures. The estimated effects are found to be small and are not enough to explain the disappearance of the 3.4 μm band in dense clouds.

On the other hand, two alternative models of the structure of the carbonaceous dust analogs can be found at present in the literature. One of them favors a solid made by small aromatic islands linked by aliphatic chains [3], whereas the other proposes large polyaromatic structures with small aliphatic substituents at the edges [4]. Theoretical models of amorphous HAC solids, based on the mentioned competing structures [3,4], have been constructed by our group using Density Functional Theory (DFT), and their calculated IR spectra have been compared to those of a-C:H samples generated by PECVD. The deposition conditions were selected to obtain a-C:H films with a variable proportion of aliphatic and aromatic structures. The results suggest that the estimation of the hydrogen contents and the aliphatic/aromatic ratios of a-C:H samples, using just literature IR band strengths advanced by some authors [5], is difficult and might be not reliable.

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Modification of the physico-chemical properties of interstellar organic analogues by UV-irradiation.

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In the interstellar medium (ISM), photochemical reactions in ice lead to the formation of relatively complex organic molecules [1]. These molecules are among the potential building blocks of our solar system and could be the precursors of a part of the organic matter found in comets and meteorites. However, it is not clear how the organic ice formed in the ISM may have evolved through temperature increase and irradiations by UV-photons and cosmic rays until their incorporation into the Solar System objects.

The experimental apparatus PICACHU developed at Hokkaido University was used to produce molecular cloud organic analogues and study their evolution through UV-irradiation. Typical ISM gases (H₂O, CH₃OH, NH₃, or CH₄,) are deposited onto the faces of a refrigerated substrate (~12 K) and simultaneously irradiated by UV under high vacuum. The organic residues that remain after the sublimation of volatiles are thus analogues of the organic matter formed in the dense and cold molecular clouds. In this study, we are characterizing these residues before and after UV photoprocessing at room temperature in order to simulate their alteration in diffuse clouds or protoplanetary disks, in which, the UV photon flux and temperature are higher than those in the dense molecular cloud [2].

By irradiating the residues with UV doses corresponding to short residence durations in diffuse cloud ($\leq 10^4$ yrs), significant changes occurred in the morphological and physical properties of the organic residues [3]. They became highly porous and more rigid, and contain amorphous nanoparticles similar to organic nanoglobules found in chondrites, IDPs and cometary samples. UV-photoprocessing of molecular cloud organics derived from D-rich ices seems thus to be a possible pathway to form D-rich amorphous nanoparticles.

According to the empirical formula of [4], the viscoelastic properties of the UV-irradiated organic residues would favor the merging of grains coated by organics after collision in protoplanetary disks. However, the organic coating might also reduce the growth efficiency of aggregates because the viscoelastic nature of organic coating could strengthen the grain-grain connections and make the dust aggregates brittle.

UV-irradiation in the diffuse clouds or in the outermost part of the protoplanetary disks thus has a strong influence on the evolution of the precursor organic compounds of protoplanetary disks.

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Infrared spectra of potential interstellar molecules: protonated PANH and OCS

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The infrared emission from many astronomical objects is dominated by the unidentified infrared (UIR) emission bands, which are characterized by main features at 3.3, 6.2, 7.7, 8.6, and 11.2 μm . Because these features are characteristic of the CH stretching, CC stretching, and CH bending modes of aromatic compounds, polycyclic aromatic hydrocarbons (PAHs) were proposed to be possible emitters. The nitrogen containing PAHs, known as polycyclic aromatic nitrogen heterocycles (PANHs), might be responsible for the 6.2- μm feature of UIR bands because the N atom induces a blue shift to the CC stretching modes of pure PAHs near 6.3 μm [1]. The existence of protonated PANHs is expected because of the large proton affinity at the nitrogen site of PANHs.

We have developed a new method to investigate the infrared spectra of protonated PAHs using electron bombardment during deposition of a PAH/*para*-H₂ mixture at 3.2 K [2]. The electron bombardment of *para*-H₂ produces H₃⁺, which subsequently react with PAH to form protonated PAH (H⁺PAH). We have applied this method to PAHs up to ovalene (C₃₂H₁₄) to obtain infrared spectra of protonated species with narrow lines and excellent signal-to-noise ratio [3]. In this work, we extended our investigation to quinoline and isoquinoline (C₉H₇N) as a first step toward the study of protonated PANHs. The IR spectra of protonated quinoline and isoquinoline (C₉H₇NH⁺) are characterized by features originating from NH stretching, CC stretching, and CH(NH) bending modes. Agreement between observed spectra of C₉H₇NH⁺ and the UIR emission spectrum is unsatisfactory, most probably because the size of molecule is too small; in the case of H⁺PAH, features close to the UIR bands were observed for only large H⁺PAH such as protonated ovalene (C₃₂H₁₅⁺). However, the blue shifts of the CC stretching bands of protonated quinoline and isoquinoline from the corresponding H⁺PAH, protonated naphthalene (C₁₀H₉⁺), are clearly observed. IR spectra of mono-hydrogenated quinoline and isoquinoline (C₉H₇NH[·]) radicals, with hydrogen atom attached on the N atom, were also identified for the first time.

We also applied this method to small molecules such as OCS, which has been postulated to exist in the ISM. The OCS molecule has two possible protonation sites, leading to isomers HOCS⁺ and HSCO⁺. Both HOCS⁺ and HSCO⁺ have been observed with microwave spectroscopy [5], but only the OH stretching mode of HOCS⁺ has been identified with gas-phase IR spectroscopy [6]. We identified three IR absorption lines of HOCS⁺ at 2945.9 (ν_1), 1875.3 (ν_2), and 1041.9 (ν_3) cm⁻¹ and two of HSCO⁺ at 2506.9 (ν_1) and 2074.2 (ν_2) cm⁻¹. Absorption lines of *t*-HOCS at 3563.4, 1394.8, and 1199.0 cm⁻¹ were also identified for the first time. Assignments were achieved according to expected chemistry, comparison between experimental spectra and theoretical predictions, and isotopic substitutions. The large red shift of the ν_1 of HOCS⁺ is attributed to partial proton sharing between OCS and H₂.

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Formation of high-density amorphous ice by matrix sublimation method

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Various methods for the preparation of amorphous ice have been developed to investigate the relationship between its structure and method of formation (Fig.1). However, unknown amorphous ice may still be discovered through new formation method.

A new method for the formation of amorphous ice has been developed. First, CO-rich ice mixture (CO:H₂O ice) was deposited at around 10 K. Then, ice mixture was warmed-up. After the sublimation of CO matrix at around 35 K, amorphous ice remained. We observed these process by ultra-high vacuum transmission electron microscope and Fourier transform infrared spectrometer. The amorphous ice formed shows highly porous texture, but it is high-density form similar to high-density amorphous ice formed under high pressure. The high-density amorphous ice is stable up to 140 K, where it transforms directly to ice Ic.

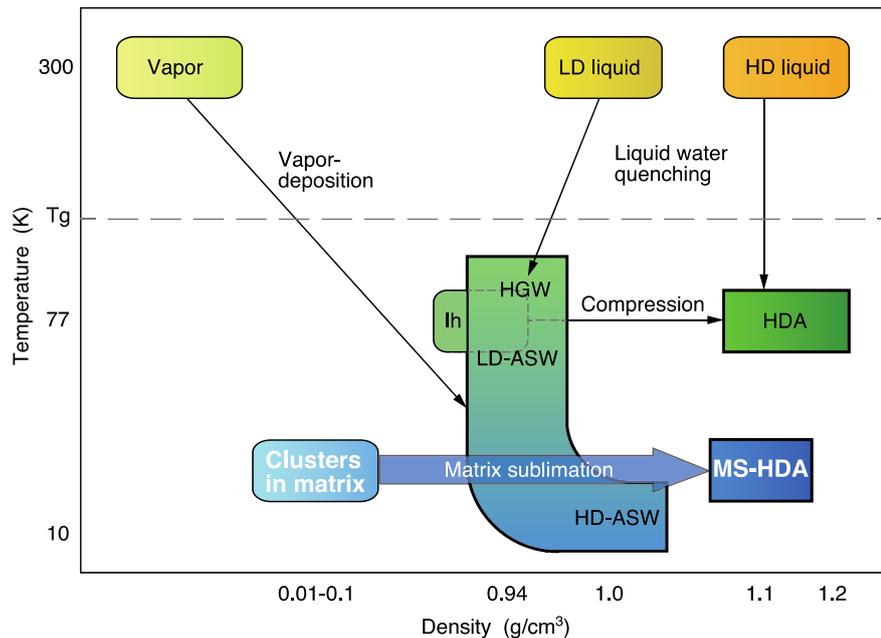


Figure 1: Schematic temperature-density diagram for the formation of amorphous ices. The starting materials are shown in rounded rectangles, formation routes as arrows with name of methods, and products in rectangles.

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Simulations of CH₄/H₂O ices as models for TNOs

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The arrival of the New Horizons mission to the limits of the solar system has provided new and exciting data on the distant objects found there. Among these data, infrared spectra on a range of locations of the surface of Pluto and Charon have shown the variety of composition of different spots. The spectra reveal the general abundance of CH₄ ice in Pluto, mixed with CO, N₂ and other hydrocarbons, and also the presence of H₂O at some specific points [1].

The observed spectra cover the near-infrared range, 1.1 to 2.5 μm. Our goal in this work is to make theoretical models for mixtures of ices with various compositions and predict their spectra, aiming to match the New Horizons observations. In a first stage, we are focused on mixtures of CH₄ and H₂O (see Figure). Previous experimental work of our group in this field consisted in the measurement of optical constants and band strengths of CH₄/C₂H₆ in the near- and mid-IR regions [2]. The methodology employed in this work consists in generating amorphous mixtures of the desired composition by means of a molecular dynamics and optimizing their structure searching for the minimum of their potential energy surface. This structure is taken to calculate the harmonic vibrational spectrum, and as a starting point for a molecular dynamics simulation, which will yield also the prediction of the near-IR spectrum. All calculations are carried out by means of Materials Studio software [3], using the Density Functional Theory method, with GGA-PBE functionals and Grimme D2 dispersion correction.

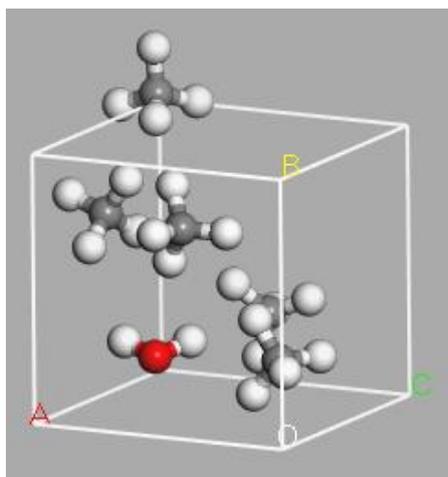


Figure : Relaxed amorphous structure for a 5:1 CH₄/H₂O mixture.

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Infrared spectra of ice mixtures: Methane/Ethylene

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Ethylene, a product of energetic processing of methane ices [1] is known to be an astromolecule present in our solar system [2]. In addition, methane is thought to be the most abundant of hydrocarbons among those present in the surface of transneptunian objects (TNOs) [3]. Recently, the New Horizons mission has provided abundant data of Pluto's surface, and assignment of several spectroscopic features associated with planetary ices is required.

In the present work, the second of a series dedicated to astrophysical relevant mixtures[4], a full set of spectroscopic data from 6000 cm^{-1} ($1.6\mu\text{m}$) to 800 cm^{-1} ($12.5\mu\text{m}$) has been obtained of ice mixtures at 30K of $\text{CH}_4/\text{C}_2\text{H}_4$ in several proportions, namely 100/0, 75/25, 50/50, 25/75 and 0/100. Band displacements, band strengths and imaginary and real components of the complex refractive index have been determined for these materials in the spectral window under consideration. Along with the spectroscopic features, density and visible refractive index of these ices have also been measured.

For the study of the subtle spectroscopic effects arising from the mixtures with respect to the pure species, we have built several theoretical models at the DFT level using the CASTEP code [5]. Simulation cells are randomly built using Montecarlo simulations and then, molecules in the cell are relaxed until a minimum in the potential energy surface of the system is reached. Infrared spectra are computed at this minimum.

From our experiments we observe a deviation in several factors such as band positions and band strengths with respect to the pure species, as expected from previous works [6]. Band displacements follow the trend expected for methane, in which a dilution in a non polar environment displaces the methane vibrations to lower wavenumbers with an increase in the wavenumbers of the second molecule. An abrupt decrease of the density of ethylene in comparison with previous diffractometric measurements has also been observed [7]. Band strengths for methane also behave as in our previous work, leading to decays in the total band strength with the dilution. However, for ethylene, strengthening and weakening have been observed for different bands, leading to a complex interpretation in which atomistic calculations play an important role.

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The OC-HOCO Complex: Identification and Implications for ISM Chemistry

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Abstract

Water (H₂O) and carbon monoxide (CO) are two of the most abundant molecular constituents of ices that accrete onto dust grains in the interstellar medium (ISM) [1]. Irradiation of such ices increases the chemical complexity of the ISM through generation of molecules such as carbon dioxide (CO₂), formaldehyde (H₂CO), and methanol (CH₃OH) [2]. While the study of such ices in the laboratory can easily identify end products, reaction mechanisms are often much harder to determine experimentally in ices. The reactions of reactive intermediates can, however, be investigated by using a combination of matrix-isolation spectroscopy and theoretical chemistry.

In the present work, we identified the formation of an OC-HOCO complex in argon matrices using infrared spectroscopy. The complex is formed in the matrix after deposition of a discharged dilute mixture of H₂O and CO in argon at 6 K.

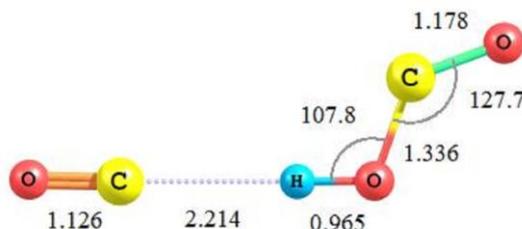


Figure 1: The structure of the OC-HOCO complex as was determined at the CCSD/cc-pVTZ theory level. Bond lengths and bond angles are given in Å and degrees, respectively.

The proposed mechanism of formation involves the reaction between a hydroxyl (OH) radical and CO, and so should also occur in the irradiated CO/H₂O ices. This reactive intermediate is likely a key participant in the formation of CO₂ in CO-rich ices through a proton-transfer reaction resulting in HCO and CO₂ production.



The OH/2CO potential energy surface has been investigated theoretically and shows that the exothermic decomposition of the OC-HOCO to CO₂ is likely. This previously unrecognized complex could be an important intermediate in the formation of CO₂ in CO-rich ices.

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Structural transitions of amorphous ice during heating

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In molecular clouds, elements such as hydrogen, oxygen, carbon, and nitrogen deposit on dust grains, and are transformed into amorphous H₂O ice and other various molecules. Because the molecules undergo chemical evolutions through various processes on amorphous ice, the amorphous ice has an important role for the chemical evolutions in the universe. Vapor deposition method is often used for formation of amorphous ice, because deposition process is similar to the situation of amorphous ice formation in the universe. When water vapor is deposited at a low temperature, high density amorphous ice (HDA) ice is formed [1]. HDA ice is transformed into low density amorphous (LDA) ice with warming. However, the phase transition dynamics is less conclusive because the structure of deposited amorphous ice depends on various factors; deposited temperature, growth velocity, impurities, thermal history after deposition, and so on. To investigate the effects of deposition temperature on phase transition dynamics, we analyzed sublimation and structural changes of water with heating process using mass spectrometry and infra-red (IR) spectroscopy.

Amorphous ice was prepared with vapor deposition of distilled and degassed water on a substrate of oxygen-free copper at 42–100 K. The total pressure in the vacuum chamber was about 2.0×10^{-4} Pa during the deposition. After deposition of amorphous ice, the substrate was warmed to 180 K at a rate of 2 K/min. The IR spectra were measured using Shimadzu IRPrestage-21 at 2 K intervals during warming. The mass spectra were measured by Pfeiffer QME220.

From the analyses of mass spectra, the four steps of gas desorption was observed in the temperature range of 42–140 K. For the sample from deposition at 42 K, for instance, the observed gas-desorption temperatures are 70, 100, 110 and 126 K. The desorption temperature decreases as the deposition temperature increases. From the temperature dependence of wave number of O–H stretching modes in IR spectra, the crystallization point to cubic ice (Ic) and transition point from Ic to hexagonal ice (Ih) are confirmed to be around 145 and 175 K, respectively. Thus, the present result suggests that the five types of amorphous phases exist in the temperature range of 42–140 K. The first phase at $< \sim 70$ K and the second phase at $\sim 70 < T < \sim 100$ K are assigned to HDA and LDA ice, respectively [1]. The fifth phase at > 126 K is probably attributed to a precursor of ice Ic due to glass transition of water [2]. The precursor exists because the crystallization to ice Ic is inhibited. For the third and fourth phases observed at $\sim 100 < T < \sim 126$ K, the assignments are less conclusive. However, the gas desorption observed in this temperature range may be due to a collapse of pore structures, because wave number of the O–H stretching mode in IR spectra increases with warming. This indicates the strength of hydrogen bonds increases as the temperature rise.

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Measurements of surface profile of amorphous solid water by a non-contact atomic force microscope

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Amorphous solid water (ASW) is abundant material of interstellar ice and is mainly present so as to cover the interstellar dust grains which are mineral particles with sub-micron size. The physical and chemical phenomena occurring on ASW surface are affected by the surface profile, because the adsorption, the desorption and the diffusion processes of atoms and molecules depend on the that profile. Therefore, the surface profile of ASW is one of the important information for understanding of the surface reactions on icy dust grains. However, the profile of ASW in nano-scale range depending on the growth conditions is still unknown.

Recently, we performed the real-space observations of surface profile of ASW formed by a vapor deposition method by using non-contact atomic force microscope (NC-AFM) at 45 and 103 K. The low-temperature ultrahigh-vacuum NC-AFM which was built by incorporating a self-designed cooling system into JSPM-4500A (JEOL) was used in this study. Measured ASW films were prepared on a cold Si(111)7×7 surface by a oblique deposition using a effusive H₂O beam collimated by a micro capillary plate. An injection angle of H₂O beam to the substrate was selected to be 60°.

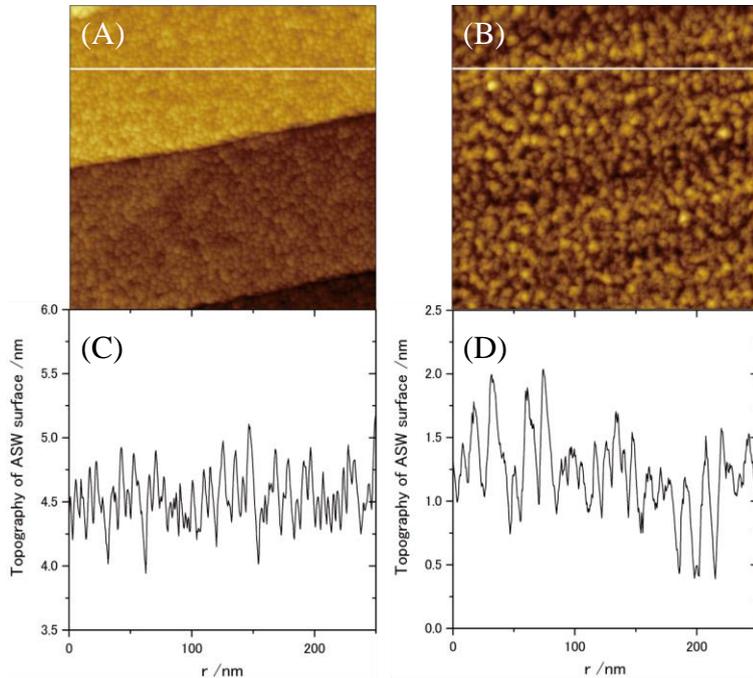


Figure 1: Comparison of surface profile of ASW formed by the oblique deposition method at (A) 45 and (B) 103K. The image size is $250 \times 250 \text{ nm}^2$. Thickness and deposition rates of both samples are 2 nm and 1 pm/s, respectively. (C) and (D) Height profiles at solid lines in Fig.1 (A) and 1(B), respectively.

Figure 1(A) and 1(B) show surface profiles of ASW formed at 45 and 103K, respectively. The ice thickness and growth rate of those samples are about 2 nm (54 BL) and 1 pm/s, respectively. The surface structure at 45K shows the relatively flat and uniform size structure than that at 103K. From the height profiles of Fig. 1(C) and 1(D) on the lines of Fig. 1(A) and 1(B), respectively, it is found that the surface roughness at 103K sometimes exceeds 1 nm within the ice thickness of 2 nm, whereas the roughness almost falls within $\pm 0.5 \text{ nm}$ at 45K.

In this presentation, the formation mechanisms of observed surface profiles depending on growth temperatures will be discussed.

Effects of ion adsorption on surface structure of amorphous ice

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In interstellar molecular clouds, various molecules (for instance, H₂O, NH₃, CO, CO₂, and so on) are formed from elements such as H, C, O, and N [1]. Most of H₂O exists as a thin shell of amorphous ice around dust grain. The molecules undergo chemical evolutions to organic molecules through various processes on the surface of amorphous ice [2]. Thus, the surface structure of amorphous ice is an important factor to understand the molecular evolution of organic molecules in molecular clouds. To investigate the effects of adsorption of ion on the surface structure of amorphous ice, the molecular dynamics (MD) calculations of amorphous ice with NO₃⁻ and NH₄⁺ were performed.

The MD calculations were performed using an atom-atom potential model, KAWAMURA potential model [3]. The amorphous ice was prepared by quenching of a liquid phase consisting of 2760 water molecules from 280 to 235 K with 2.5 K/fs in cooling rate. After annealing at 235 K, the system was cooled to 10 K. The density of amorphous ice at 10 K was controlled with the time period of the annealing at 235 K. To equilibrate the fundamental cell, the MD code was run for 40 ps at 10 K. Then, an ion (NO₃⁻ or NH₄⁺) was put in a position, such the center of nitrogen in ion was at a distance of 0.5 nm from the outermost hydrogen atom in surface. An infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The pressure was kept at 0.1 MPa. The layer with 0.5 nm in thickness from the outmost atom was analyzed as the surface layer.

The result shows that the atomic displacement parameters (ADP) of oxygen and hydrogen of water molecules in surface layer increase during the adsorption of NO₃⁻ and NH₄⁺. The maximum value of ADP for surface with NH₄⁺ is larger than that with NO₃⁻. The values are diminished with formation of hydrogen bonds with surrounding water molecules, and gradually approach the values of pure amorphous ice without ions. For surface with NO₃⁻, three oxygen atoms of NO₃⁻ form hydrogen bonds with hydrogen atoms in dangling bonds of water on the surface layer. In the case of surface with NH₄⁺, hydrogen atoms form hydrogen bonds with oxygen atoms of water molecule in the surface layer. When an ion is adsorbed, surrounding water molecules rotate to form hydrogen bonds with the ion. Thus, the rearrangement of water molecules occur even at low temperature. The result indicates that the thermal vibrations of water molecules are enhanced with adsorption and diffusion of ions on the surface, and the effects depend on ion species. The effects of ion adsorption might have important implications for surface reaction in interstellar molecular clouds.

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Experiments on hydrogenation and deuteration of C₂H₂ and C₂H₄ on low temperature surfaces : formation mechanism of C₂H₆ with astronomical interest

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Simple hydrocarbons, acetylene (C₂H₂), ethylene (C₂H₄) and ethane (C₂H₆) widely exist in various circumstances in space. Although the gas phase C₂H₂ and C₂H₄ are detected in limited objects of interstellar medium (ISM, e.g., [1,2]), C₂H₆ was not detected in the ISM yet. Observational bias might be a reason for this difference because the bands of these species in infrared region are greatly affected by severe telluric absorptions. Alternatively the observational results may reflect the result of chemical evolution in ISM. Thus we performed quantitative experiments providing a precious clue for understanding the evolution of these hydrocarbons. As previously proposed, one of most important processes to form C₂H₆ is hydrogenation of C₂H₂ on low temperature surface (C₂H₂ → C₂H₃ → C₂H₄ → C₂H₅ → C₂H₆) [3, 4]. We conducted hydrogenation experiments of pure C₂H₂ and C₂H₄ solids (to compare our results with the previous studies [3, 4]) and those on amorphous solid water (ASW, to reproduce the ISM condition) at 10K and 20K, respectively. Deuteration experiments of C₂H₂ and C₂H₄ on ASW were also performed. All experiments were conducted by using laboratory setup for surface reaction in interstellar environment (LASSIE) at Institute of Low Temperature Science, Hokkaido University [5].

Obtained effective reaction rate constants, which are defined by a reaction rate constant times a number density of atomic hydrogen/deuterium adsorbed on the surface, are shown in Figure 1 with a result of CO hydrogenation on ASW reported by Hidaka et al. [6]. At 10K, the difference in the effective hydrogenation reaction rate constants between C₂H₂ and C₂H₄ was found to be a factor of ~3 on both pure solids and ASW samples, whereas previous experimental studies [3, 4] reported that the hydrogenation rate of C₂H₄ is larger than that of C₂H₂ by orders of magnitude. The kinetic isotope effects of hydrogenation/deuteration are found to be very small in both C₂H₂ and C₂H₄ reactions at 10 K. This significantly small kinetic isotope effect for tunneling reactions can be explained as “diffusive reaction” where the reaction process is dominated by diffusion of H and D atoms on the surface. At 20 K, the effective rate constants of deuteration became larger than those of the hydrogenation. This unusual behavior would be attributable to the difference of the number densities of H and D atoms on the surface.

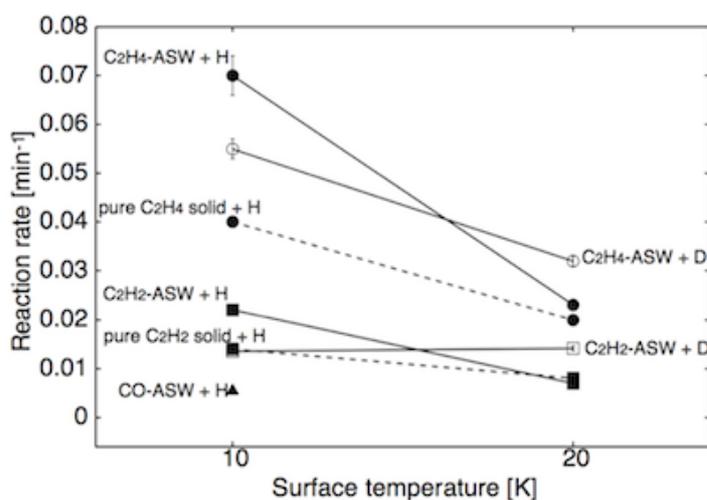


Figure 1: Temperature dependences of the effective reaction rate constants for the H and D atom exposure for each sample (filled square with solid line; C₂H₂-ASW + H, filled square with dashed line; pure-C₂H₂ solid + H, filled circle with solid line; C₂H₄-ASW + H, filled circle with dashed line; pure C₂H₄ solid + H, open square with solid line; C₂H₂-ASW + D, open circle with solid line; C₂H₄-ASW + H, triangle; CO-ASW + H).

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Negative catalytic effect of amorphous solid water on the hydrogen abstraction from dimethyl ether with deuterium atoms at low temperatures

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Amorphous solid water (ASW) plays crucial roles in interstellar chemistry as a cold catalytic surface for various chemical and physical processes. Previous studies reported that the surface of ASW lowers an activation barrier of some reactions such as tunneling hydrogen addition to formaldehyde [1]. In addition, some reactions of H and D atoms with molecules such as CO were found to be enhanced on ASW at higher temperatures due to the longer residence time of the atoms on ASW [2]. So, does ASW always act as a “positive” catalyst for chemical reactions on interstellar grains? In the present poster, we will show experimental results on the “negative” catalytic effect of ASW on the quantum-tunneling hydrogen abstraction from dimethyl ether (DME: CH₃OCH₃) by deuterium (D) atoms at low temperatures. By forming a complex with water via a hydrogen bond, the C-H stretching band of DME shows a blue-shift as a result of the C-H bond contraction [3], which may suppress the reaction compared to that of pure solid DME with D atoms.

The experiments were performed in an apparatus named ASURA, which is mainly composed of an ultra-high vacuum chamber, an atomic source, and a FTIR. The base pressure of the reaction chamber is about 10⁻⁸ Pa. DME-H₂O complex with the thickness of ~25 monolayers (1 monolayer = 10¹⁵ molecules cm⁻²) was produced by the vapor-deposition of the mixed gas (DME:H₂O = 1:4) onto an Al substrate at 15 K. D atoms were produced by the dissociation of D₂ molecules in microwave-induced plasma and cooled to 100 K. The sample solid was exposed to D atoms for up to 240 min at 15 K. Progress in reaction was monitored in-situ by the FTIR. The reaction of pure solid DME (~10 monolayers) with D atoms was also investigated under the same experimental conditions for comparison.

When pure solid DME was exposed to D atoms at 15 K, the formation of deuterated DME was observed on the FTIR spectrum of the reaction product, which indicates the occurrence of hydrogen (H)-D substitution of DME. We propose the successive H-abstraction and D-addition occurred as follows: (1) CH₃OCH₃ + D → CH₂OCH₃ + HD, (2) CH₂OCH₃ + D → CH₂DOCH₃. Since reaction (1) has a large activation barrier of ~3600 K in the gas phase [4], quantum-tunneling is required for the reaction to occur at 15 K.

When solid DME in the complex reacted with D atoms, the H-D substitution reactions also occurred under the same experimental conditions. However, the reaction was more than 20 times slower than pure solid DME + D. This would be due to the strengthening of the C-H bond, which is attributable to the formation of a complex with H₂O via hydrogen bond.

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Photodesorption and CO₂ formation induced by 157 nm irradiation to CO on water ice

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Photodesorption of CO is suggested as a possible process which maintains a measurable amount of gaseous CO in cold interstellar clouds, where thermal desorption is negligible. Observations have indicated that the water-rich ice layer forms first on the grain and that most CO ice is present on top of the water ice [1]. Previous study indicates that there are two types of CO adsorption sites, free hydroxyl groups and oxygen atoms of surface coordinately unsaturated water molecules [2]. UV-induced CO₂ formation using CO/H₂O binary ice was reported [3]. However, the effect of adsorption states of CO on CO₂ formation has not been studied. In this study, we have investigated 157 nm photodesorption of CO on water ice at 8 K by measuring the time-of-flight (TOF) spectra of CO ($v=0$) detected by (2+1) resonance enhanced multiphoton ionization technique. Using the reflection absorption infrared (RAIR) spectroscopy, adsorption sites of CO on water ice and photoproducts was measured.

Figure 1 shows typical TOF spectrum of CO from 0.15 ML CO on water ice at 8 K. Measured spectrum could be characterized by a combination of three different Maxwell-Boltzmann distributions. It was described by a fast component (A) with $T_{\text{trans}} = 1700 \pm 300$ K, a middle component (B) with $T_{\text{trans}} = 450 \pm 100$ K and a slow component (C) with $T_{\text{trans}} = 100 \pm 30$ K. The result indicates that there are three possible processes for photodesorption. Figure 2 shows RAIR spectra after 2, 6, 10 $\times 10^4$ shots of 157 nm irradiation to 0.4 ML CO on water ice at 8 K. The peak is attributed to CO₂. CO₂ was produced via the reaction of CO with OH radical which was generated by photodissociation of water ice. In this presentation, we evaluate the possible link between adsorption sites of CO and CO₂ formation induced by 157 nm irradiation.

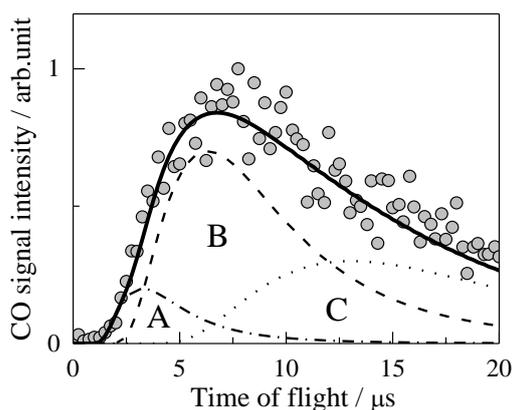


Figure 1: TOF spectrum of photodesorbed CO ($v=0$) from 0.15 ML CO on water ice.

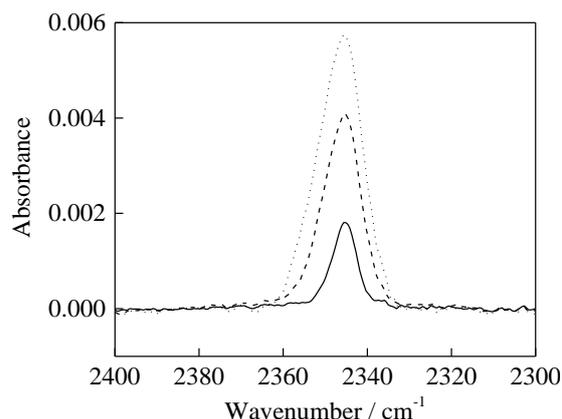


Figure 2: RAIR spectra measured after 2 (solid), 6 (dashed), 10 (dotted) $\times 10^4$ shots of 157 nm irradiation to 0.4 ML CO on water ice.

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Nuclear spin isomers of photodesorbed water from ice at 10 K

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Recent astronomical observations have observed H₂O in space. The ubiquity of H₂O makes it essential to clarify the chemistry of interstellar H₂O to further our understanding of the formation of stars and planetary systems, including our solar system. [1]

A key observable related to interstellar water chemistry is the abundance ratio of nuclear spin isomers (the ortho-to-para ratio, OPR), because it is a valuable tracer of the physical and chemical history of H₂O. Cometary comae, and star- and planet-forming regions have of OPRs for gaseous H₂O (0.1–2.4), which are anomalously lower than the statistical value of 3. The OPR of H₂O in a comet has been considered a indicator that gives the past formation temperature (30 K) of the ice nucleus in the solar nebula. The low OPR of interstellar H₂O has also been used to determine the formation temperature (<50 K) of water ice on cold interstellar dust. However, the use of the OPR as a temperature probe requires the assumption that the OPR of H₂O desorbed from ice is related to the ice temperature. However, the OPR of H₂O desorbed from ice remains poorly understood, especially at low temperatures, and the above assumption has not been validated. Therefore, the significance of the OPR of water is unknown and remains one of the most problematic issues in astronomy and planetary science. [2]

The present study performed direct measurements of the OPR of water photodesorbed from water ice at 10 K. The photodesorbed water showed the statistical high-temperature OPR of 3, even when the ice is produced in situ by hydrogenation of O₂, a known formation process of interstellar water. Our results indicate that the OPR did not reflect the formation temperature of the ice (10 K, OPR = 0.3). Reinterpretation of previous observations is necessary and will improve our understanding of interstellar chemistry, and the formation of the solar system and comets. [3]

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Temperature dependence of ortho-to-para conversion of H₂ on amorphous solid water at around 10 K

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The ortho-to-para abundance ratio (OPR) of H₂ is crucial for chemical evolution and deuterium fractionation of molecules in molecular clouds, because H₂ in the ortho-ground state (J=1) is more energetic (and thus reactive) than that in the para-ground state (J=0) by approximately 14.6 meV corresponding to 170 K, which is significantly higher than typical temperatures of molecular clouds. Since the radiative transformation of molecular nuclear spins is forbidden in the gas phase, the OPRs of hydrogen molecule (H₂) observed toward various astronomical objects have been often considered as tracers of chemical history of the molecule.

In the gas phase, spin-exchange reaction with either ionic or neutral hydrogens can alter the OPR of H₂. In contrast, little is known about how the nuclear spins behave on cosmic ice dust. It was often assumed without the experimental evidences that the OPR of H₂ formed on the cosmic dust surface is statistical value of 3. Recently, our group has tackled this issue experimentally and found that the OPR of nascent H₂ is 3 at the formation by H-H recombination on cosmic ice dust [1]. In the present study, using experimental techniques of molecular beam, photostimulated-desorption, and resonance-enhanced multiphoton ionization, we measured the OPRs of H₂ photodesorbed from amorphous solid water (ASW) at temperatures around 10 K, which is an ice dust analogue. We demonstrated that the OPR of H₂ easily varies on ASW and that the rate of spin conversion from ortho to para steeply increases from 2.4×10^{-4} to 1.6×10^{-3} s⁻¹ within the very narrow temperature window of 9.5 to 12 K and reach a plateau at temperatures above 12 K [2]. This temperature dependence cannot be explained solely by state-mixing models ever proposed [3]. The temperature dependence of the conversion rate was very well represented by the power law of T⁷ where T is the surface temperature. This indicates that the conversion rate at lower temperatures is dominated by the two-phonon energy dissipation process (Raman process) for the excess energy (~14.6 meV) arising from the conversion, and at higher temperatures the rate may be limited by a spin-flip transition rate.

From the present and our previous results, astrochemical history of interstellar H₂-OPR is depicted as follows. When H₂ molecule is produced by H-H recombination on cosmic ice dust, the OPR of nascent H₂ is 3 [1]. If the H₂ is immediately desorbed at the formation, the OPR of H₂ released should be near 3. However, if H₂ is trapped even for a short period on the ice dust surface before desorption, the OPR at desorption strongly depends on the surface temperature and duration of trapped.

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Sublimation dynamics and isotope fractionation of crystalline- and amorphous-ice thin films

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Ice sublimation is one of the most fundamental processes associated with growth of ice particles and snow on earth and in the universe [1, 2]. In spite of the fundamental importance of molecular level understanding of the sublimation process, little is known about mechanistic details including isotope effects. It was recently reported that not only the translational degree of freedom but also the rotational degree of freedom play key roles in the desorption process of water molecules, based on the comparison of sublimation rates of pure H₂O, D₂O and H₂¹⁸O ice [3]. However, the effects of neighboring water molecules on desorption process have not been investigated, although water molecules at ice surfaces are strongly interacted each other through hydrogen bonds.

Here, using temperature-programmed desorption (TPD) under ultra-high vacuum condition, we have investigated the sublimation dynamics of H₂O, HDO, and D₂O from isotope mixed crystalline-ice (CI) and amorphous-ice (AI) thin films, whose D to H ratio x_D was systematically controlled. For both CI and AI, desorption rate of each isotope becomes smaller as the x_D become increased (Fig. 1). This result indicates that desorption of water molecules from ice surface is not a unimolecular process; neighboring water molecules indeed affect the desorption rate. Based on the Arrhenius plots, we found that many-body cooperative isotope effects appear at larger x_D , especially in the pre-exponential factor of the desorption rate rather than the activation energy of desorption. Additionally, we found the extraordinary isotope fractionation of AI under and after the crystallization process at ~155 K. We will discuss these results in details.

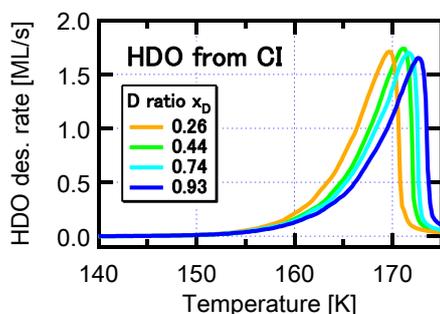


Figure 1: D to H ratio dependence of the desorption rate of HDO molecules from isotope mixed CI.

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A theoretical study on physisorption states of non-metal adatom on graphene

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Because of the low density of gases in cosmic space, molecular formation reaction can not release the heats of exothermal chemical reactions. On the other hand, if the chemical reaction occurs on dust grain surfaces, heat of formation can be dissipated to substrates. Therefore, dust grains are considered as one of the most important stages for various molecular formation reaction.[1] Dust grains are generally in low temperature condition. For instance, the temperature of dense clouds is about 10 K. In these low temperature conditions, adsorbates cannot thermally diffuse because of its strong chemical bonding to substrates, which indicates that the physisorbed adsorbates play an important role of chemical reaction on dust grain. Therefore, in this study, we investigated the physisorption properties of non-metal atoms on carbon materials.

In this study, we performed the first principles calculations based on density functional theory, which is implemented in the plane-wave and projector-augmented wave method code, the Vienna Ab-initio Simulation Package (VASP 5.3.3).[2-7] We applied a 550 eV cutoff to limit the plane-wave basis set without compromising computational accuracy. A $5 \times 5 \times 1$ Monkhorst–Pack special k-point grid [8] for the first Brillouin zone sampling and a Gaussian smearing model of $\sigma=0.05$ eV was used. Moreover, we took the van der Waals interaction into consideration with the non-local correlation functional rev-vdW-DF2 [9,10] to treat physisorption states on graphene accurately. We focused on the H, N, and P adsorption on 4×4 graphene. The supercell was constructed with a 20 Å vacuum separation between slabs to reduce the interaction between slabs.

At first, we studied the dependence of H adsorption energy on the H coverage. We considered the H coverage of 0.02 to 1 ML. We found that the interaction between H atoms on graphene is smaller than 1 meV with H-H distance of 10 Å. Therefore, in this study, we adopted 4×4 graphene as substrates. The adsorption energies of H, N, P atoms on graphene correspond to 80, 120, 130 meV, respectively. In the workshop, we will also report the diffusion properties of adsorbates on graphene.

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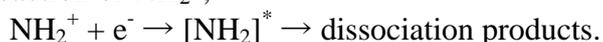
Theoretical study on dissociative recombination reaction of NH_2^+

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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 process or the indirect process. In the direct process, the molecule system makes transitions directly from the electronic ground state of cation to the dissociative excited state of neutral molecule after capturing an electron. In the indirect process, this transition proceeds via Rydberg states. In the interstellar space, temperature and pressure is so low that the DR reaction which proceeds with electrostatic attraction is very important.

We have studied the DR reactions of HCNH^+ [1], H_3O^+ [2], and HD_2O^+ [3], using *ab initio* molecular dynamics (AIMD) simulation with a surface hopping scheme, and discussed non-adiabatic dynamics and the branching mechanism. In the present study we investigate the mechanism of the DR reaction of NH_2^+ ,



While in the previous studies initial condition of AIMD simulation was determined by conservation of energy before and after the collision, in this study we aim to take electron dynamics into account for the initial condition. The electron dynamics can be described by real-time propagation of time-dependent density functional theory (RT-TDDFT).

For preparation of electron dynamics, geometry of positive molecular ion NH_2^+ was optimized first by the B3LYP/cc-pVTZ method. Then, excited states of NH_2 which are produced after the collision were calculated by CASPT2 and TDDFT(B3LYP) with the cc-pVTZ basis-set. The TDDFT result was very close to the highly accurate CASPT2 result, and so we decided to adopt TDDFT in the following. Because the indirect process needs the Rydberg states, TDDFT calculation including Rydberg basis-set was also carried out. The result of this calculation shows that Rydberg state lies at low level, indicating that this reaction may proceed via the indirect process. Next, we will perform electron dynamics to determine the initial distribution of electronic states just after the collision, and execute AIMD simulation.

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Electron dynamics described by real-time time-dependent Hartree-Fock and/or time-dependent density functional theory (RT-TDHF/TDDFT) calculation

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Electron dynamics, which is an ultrafast phenomenon occurring in attoseconds or femtoseconds, was recently observed by experiments and has attracted much attention. Electron dynamics is caused by change of external field of the intriguing system, such as light or collision of molecules and electrons. Therefore, electron dynamics should play an important role in reaction of interstellar matters which is sometimes concerned with electronically excited states. To elucidate mechanism of electron dynamics, theoretical calculation would be a powerful tool. Real-time propagation (RT) of time-dependent theories, such as time-dependent Hartree-Fock (TDHF) method and time-dependent density functional theory (TDDFT), have been applied to describing electron dynamics,.

In previous studies, electron dynamics described by RT-TDHF/TDDFT calculations was analyzed by the Fourier transform technique to obtain frequency-domain properties and directly through time evolution of molecular properties. In this study, we proposed short-time Fourier transform (STFT) analysis for electron dynamics [1]. STFT is a time-frequency analysis technique to provide time evolution of spectrum, which is called spectrogram. Figure 1 shows absorption spectrograms obtained by STFT analysis of RT-TDHF calculation of formaldehyde dimer as a model system. The STFT analysis of RT-TDHF calculation enables us to directly observe the electron dynamics associated with the excited states.

Furthermore, the RT-TDHF/TDDFT approaches have limited applications because evaluation of the time evolution operator is computationally demanding. In this study, we developed an efficient time evolution method based on three-term recurrence relation (3TRR) [2]. 3TRR is derived by introducing transformation of the operator in time-dependent equation, such as Hamiltonian. The 3TRR method achieved efficiency that is about four times faster than conventional fourth-order Runge-Kutta method.

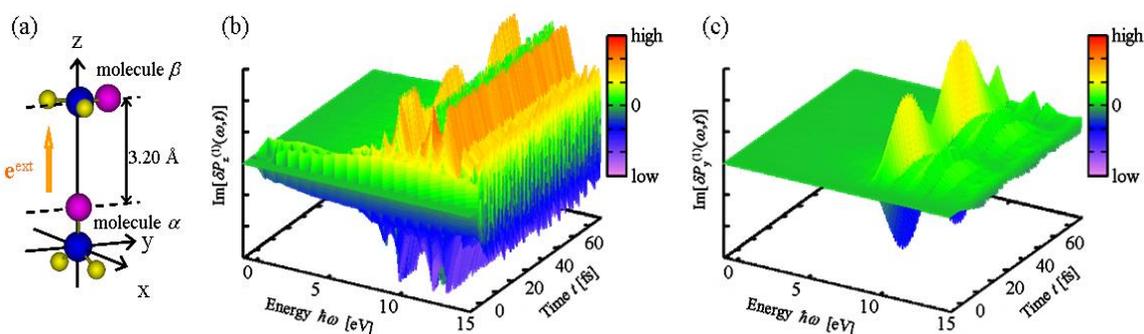


Figure 1: (a) Formaldehyde dimer model, in which two molecules are vertically arranged; (b) Absorption spectrogram for z direction; (c) Absorption spectrogram for y direction.

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Laser Spectroscopic Study of CaH B/B'(v=10, 11) -X bands

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Fusakazu Matsushima¹, Yoshiki Moriwaki¹ and Stephen C. Ross²

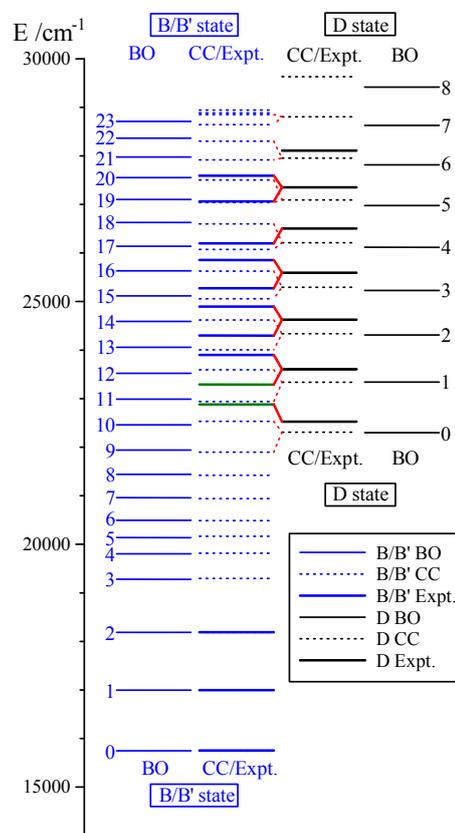
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Electric transitions of Calcium monohydride (CaH) have been found in sunspots and M dwarf stars [1], and have been used to investigate them. Despite the long history of study of this molecule the first two excited $^2\Sigma^+$ states, B/B' and $D^2\Sigma^+$, have continued to pose challenges for experiment and theory. The B/B' state is formed by the avoided crossing between two diabatic states and a non-bonding diabatic state, resulting in a double minimum potential energy function. Martin calculated energy levels in Born-Oppenheimer approximation [2]. He was able to perform a least-squares fitting to the available rovibronic data. The result was a set of empirically generated, but physically-constrained, potential energy curves for the X, B/B', D states. Carlsund-Levin et al. used updated versions of Martin's potential but also accounted for Martin's R-dependent interaction term in a coupled-channel (CC) calculation of the rovibronic energies [3]. In a bid to resolve discrepancies in vibronic assignments of these states we observed the rotational-resolved fluorescence spectrum of CaH.

In previous work, we observed four vibronic levels and attributed them to B/B' (v=12, 13, 14 and 16) lying above the double-minimum potential energy barrier, and five levels previously assigned to the D state [4], to the B/B' state. In addition to this, we recently observed the B/B' (v=10, 11) levels. Fig 1 shows the vibrational levels of D and B/B'. The levels' properties alternate strongly with vibrational excitation and the new assignment brings the experimental vibronic structure into remarkably good agreement with the CC calculation values of Carlsund-Levin.

Figure 1: Vibronic energy levels of the B/B' $^2\Sigma^+$ and $D^2\Sigma^+$ states of CaH. Outer lines show values calculated in the Born-Oppenheimer approximation [2]. Dotted lines in the center show the couple-channel (CC) calculated values [3]. Thick solid lines in the center show experimental values [4-7]. B/B' (v=10, 11) are shown by the green lines. Close lying levels are connected (in the center) to highlight interactions between the B/B' $^2\Sigma^+$ and $D^2\Sigma^+$ states.



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A New Terahertz Emission Spectrometer at RIKEN

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In radioastronomy, rotational emission lines of molecules are extensively observed to investigate physical and chemical structures of target sources. For secure identification of molecules and accurate analyses of Doppler shifts caused by overall/internal motions of the target sources, accurate rest frequencies of molecular transitions are indispensable. Rest frequencies of various molecules have been measured by spectroscopic studies in the laboratory, and are tabulated in the spectral line catalogs with the aid of extrapolation based on spectroscopic data analyses. However, their accuracies are sometimes insufficient for identification of molecules and detailed discussions of the velocity structure of the sources, which causes serious limitation and uncertainty in astrophysical and astrochemical interpretations. Hence, it is important to measure rest frequencies of the transitions used for astronomical observations directly by the laboratory spectroscopy. Such an effort is more and more important in the ALMA era, because even faint rotational spectral lines of various isotopic species as well as those in vibrationally excited states, which have not been well studied in the laboratory, are readily observed, thanks to high sensitivity of ALMA.

With this in mind, we are constructing a new laboratory THz emission spectrometer at RIKEN. A block diagram of the spectrometer is shown in Figure 1. We measure the emission of rotational transitions of molecules in the 2 m long glass cell by using the superconducting hot electron bolometer (HEB) mixer receiver, which has been developed for the THz astronomical observations [1]. The HEB mixer is mounted on the ALMA-type cartridge receiver system. The THz emission from the molecule is down-converted to the 1.0-1.6 GHz range, and is frequency-analyzed by the XFFTS spectrometer with the spectral resolution of 0.8 MHz. We are now assembling the components toward test measurements. At this moment, the frequency coverage is limited to 0.8 THz-0.9 THz and 1.3-1.5 THz. We are planning to extend it to the lower frequencies by employing the SIS mixer receivers.

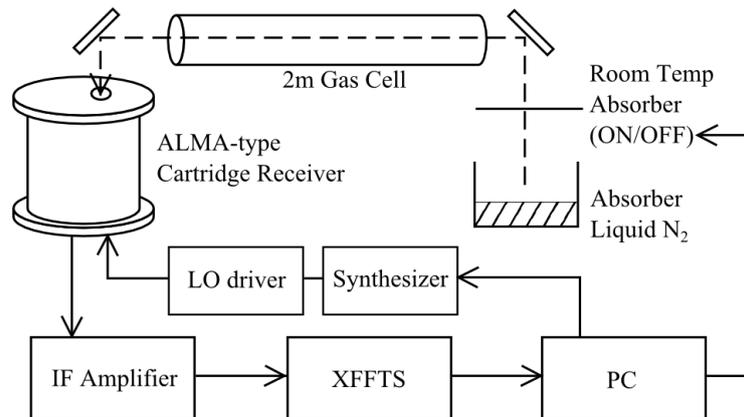


Figure 1: The block diagram of the spectrometer at RIKEN

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Detections of long carbon chains CH₃CCCCH, C₆H, *linear*-C₆H₂ and C₇H in the low-mass star forming region L1527

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Long carbon chains CH₃CCCCH, C₆H, *l*-C₆H₂, and C₇H were detected in the low-mass star forming region L1527, showing a warm carbon chain chemistry (WCCC), by using Green Bank 100 m telescope. The $K = 0, 1,$ and 2 lines of the $J = 11-10$ transition of CH₃CCCCH were detected, and the column density and the gas kinetic temperature were determined to be $5.6 \times 10^{12} \text{ cm}^{-2}$ and 20 K, respectively. The ${}^2\Pi_{1/2}$ state of C₆H, locating 15.04 cm^{-1} higher than the ${}^2\Pi_{3/2}$ state, was detected for the first time except for the circumstellar envelope IRC+10216. The column densities of the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ states of C₆H in L1527 were derived to be 1.6×10^{11} and $1.1 \times 10^{12} \text{ cm}^{-2}$, respectively, leading the temperature of 11 K between the two states. In the present observations, the $K_a = 0$ line of para species of *l*-C₆H₂ was detected, although the detection was limited for the $K_a = 1$ line of ortho species so far except for IRC+10216. The column densities of the ortho and para species of *l*-C₆H₂ were independently obtained to be 1.3×10^{11} and $0.6 \times 10^{11} \text{ cm}^{-2}$, respectively. C₇H was detected for the first time except for IRC+10216. The column density of C₇H was estimated to be $6.2 \times 10^{10} \text{ cm}^{-2}$ from the $J = 24.5-23.5$ and $25.5-24.5$ lines. These results of detections would suggest that C₇H and C₆H₂ are remarkably abundant species in L1527 although they are long carbon chains. These species can be good probes of chemical composition for heavy molecules in WCCC regions.

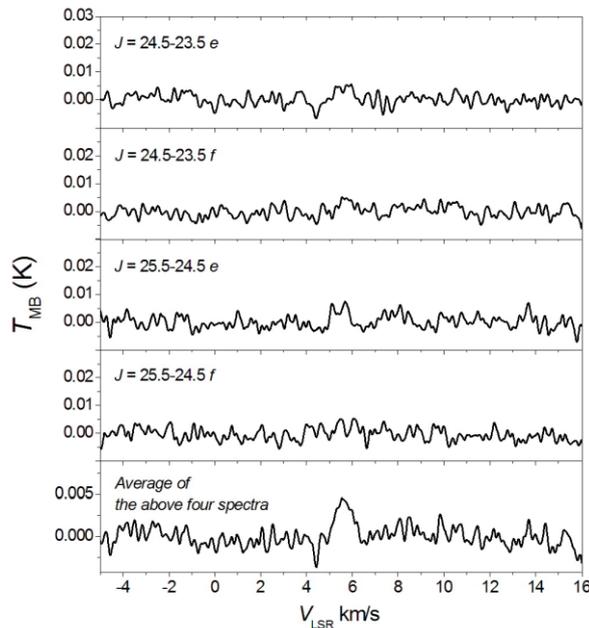


Figure 1: The $J = 24.5-23.5$ and $25.5-24.5$ rotational transitions of C₇H (${}^2\Pi_{1/2}$) observed by the Green Bank 100 m telescope .

Study of CH₃CN in Diffuse Clouds by “Hot Axis Effect”

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The diffuse interstellar bands (DIBs) are optical absorption lines by molecules in diffuse clouds. Initially observed more than 100 years ago, they still remain the longest standing unsolved problem in spectroscopy and astrochemistry, although five DIBs have recently been identified as due to fullerene ion C₆₀⁺ [1]. Identifications of DIBs are important because they can give us information on chemical composition in diffuse clouds. To further identify carrier molecules of DIBs we have measured DIB candidate molecules produced in the laboratory to compare their absorption spectra with astronomically observed DIB spectra. In this work, we first present our latest results on the search for the thiophenoxy radical C₆H₅S, benzene derivative, by using our cavity ringdown spectrometer [2]. We then present a new insight into diffuse clouds. Molecules in diffuse clouds are collisionally heated and radiatively cooled. In diffuse clouds the latter is dominant. Due to the spectroscopic selection rules, acetonitrile CH₃CN is cooled well for the end-over-end rotation but is not cooled for rotation around its molecular axis, as shown in Figure 1. We made a model of this non-thermal rotation as “Hot Axis Effect.” Based on this model, we estimated a rotational absorption spectrum of CH₃CN in the radio frequency region. By using Nobeyama 45 m radio telescope, the absorption lines were searched in the diffuse clouds in front of the Orion IRC2 region and the radio continuum source B0212+735 quasar. The upper limits of column densities of CH₃CN toward Orion IRC2 and B0212+735 were determined to be 2×10¹² and 2×10¹³ cm⁻², respectively. On the other hand, a possible absorption feature, as a disturbed feature around the K = 3, 2, 1, and 0 lines, by Hot-axis effect for CH₃CN was found in the spectrum toward Sgr B2 in the reported line survey data [3], as shown in Figure 2.

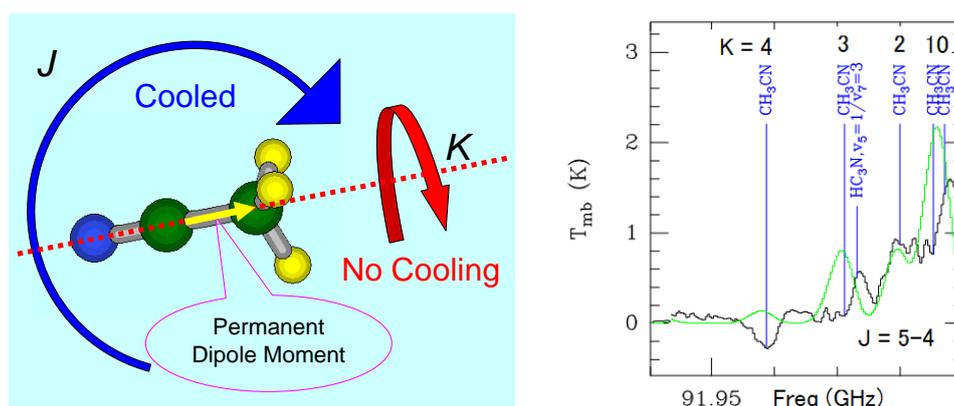


Figure 1 (Left): Hot-axis effect for a symmetric-top molecule. The red dotted line is the hot-axis.

Figure 2 (Right): Absorption feature of K = 4 and a disturbed feature around the K = 3, 2, 1, and 0 lines by Hot-axis effect for CH₃CN in the spectrum of Ref. [3]. The black line is an observed profile, and green a mode one.

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Computational Molecular Spectroscopy: Fe-containing Molecules of Astrochemical Interest

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The aim of Astrochemistry is to elucidate how molecules have evolved in space, *i.e.*, to determine which molecules are there and which reactions have formed them. More than 180 molecules have been detected already. Although Fe is known to have a large cosmic abundance comparable to those of Mg and Si, the only iron-containing molecules detected in the cosmic environment so far are FeH in sunspots [1], FeO toward Sgr B2 [2,3], and FeCN toward IRC +10216 [4]. In 1994, we made a preliminary *ab initio* calculation for FeCO as a candidate for observation in interstellar space, but attempts to detect it in space failed [5,6]. Then we started *ab initio* calculations on several Fe-containing molecules of astrochemical interest, including FeC [7], FeN [8], FeS, FeNC [9], FeCN [10], FeOH [11,12], and FeCO [13 (electronic properties)]. We will report here recent progress of computational molecular spectroscopy on Fe-containing molecules.

For FeCO, we have published a very accurate 3D potential energy surface [14], and reported many ro-vibrational properties. The calculated rotational constant B_0 deviates by only 0.03% from experimental value. For FeCN, observed by the Ziurys group toward IRC +10216 [4], the electronic ground state was erroneously claimed to be $^4\Delta_i$ [4] simply because rotational spectrum for the other electronic states was not observed in their laboratory. Our MR-SDCI+Q calculations show that the $^4\Delta_i$ state is higher in energy than the $^6\Delta_i$ state by *ca.* 4000 cm^{-1} .

FeOH is another possible interstellar molecule candidate, but neither laboratory experiments nor space observations have been reported. Stimulated by IR cold-chemistry experiments on FeO^+ reactions by the Dieter Gerlich group [15], we have calculated the equilibrium structures and energy levels of FeO, FeO^+ , and FeOH^+ . Presently, 3D PES calculations for FeOH^+ are in progress.

We hope these studies will be helpful for identification of more Fe-containing molecules in space.

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A search for the HOCO radical in the massive star-forming region Sgr B2(M)

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Despite importance of the origin of life, long lasting challenges to detect the simplest amino acid glycine ($\text{H}_2\text{NCH}_2\text{COOH}$) in interstellar medium has not been successful. As a preliminary step toward search for glycine, the detection of its precursor has received attention. It is considered that glycine is produced by a reaction of the HOCO radical and the aminomethyl radical (CH_2NH_2) on interstellar grain surface [1]:



HOCO is produced by the reaction of $\text{OH} + \text{CO} \rightarrow \text{HOCO}$, and or $\text{HCOOH} \rightarrow \text{HOCO} + \text{H}$. However, HOCO and CH_2NH_2 have not been investigated in interstellar medium. Recently, we determined the accurate molecular constants of HOCO [2]. Thus, accurate rest frequencies were derived from the constants. In the present study, we carried out the observations of HOCO in Sgr B2(M) with Nobeyama 45 m radio telescope, where Sgr B2(M) is a massive star-forming region and almost all reported interstellar molecules are observed in this region. Although HOCO could not be detected in Sgr B2(M) (Fig. 1), the upper limit of the column density was derived to be $9.0 \times 10^{12} \text{ cm}^{-2}$ via the spectrum in the 88 GHz region by the rotational diagram method [3]. If the reaction (1) is main process of the glycine production in this region, the column density of glycine can be assumed to be comparable to that of HOCO [1]. This assumption allows us to derive the upper limit of column density of glycine which is one or two order smaller than the reported ones [4-8].

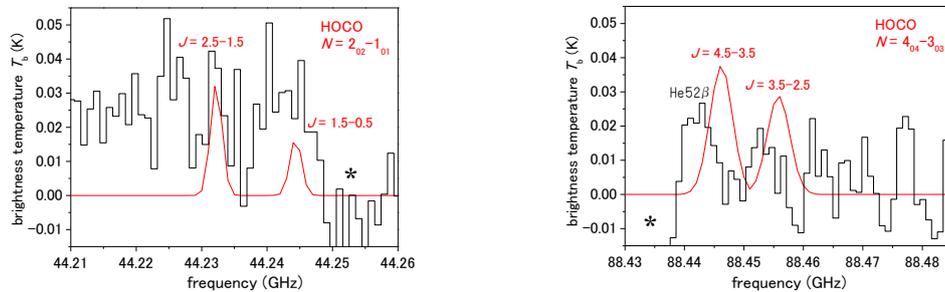


Fig. 1. The estimated lines of the $J = 2.5-1.5$, $1.5-0.5$, $4.5-3.5$ and $3.5-2.5$ transitions (red), and the observational results (black). The dips labeled by asterisks are absorption feature. Total ON times are 1.0 and 4.0 hours in the 44 and 88 GHz regions, respectively.

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Molecular-Cloud-Scale Chemical Composition: Mapping Spectral Line Survey toward W3(OH)

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In order to study a molecular-cloud-scale chemical composition, we have conducted a mapping spectral line survey toward the Galactic molecular cloud W3(OH) with the NRO 45 m telescope. W3(OH) is one of the most active star forming regions in our Galaxy, lying on the Perseus arm. We have observed the area of $16' \times 16'$, which corresponds to $9.0 \text{ pc} \times 9.0 \text{ pc}$. The observed frequency ranges are 87 – 91, 96 – 103, and 108 – 112 GHz. As a result, 8 molecular species CCH, HCN, HCO⁺, HNC, CS, SO, C¹⁸O, and ¹³CO are identified in the spectrum averaged over all the observed area. The spectral pattern is found to be different from that of the hot core observed at a 0.17 pc resolution. We find the following characteristics in the specially averaged spectrum: (1) Emission of the species concentrated just around the star-forming core, such as CH₃OH, HC₃N, and CH₃CCH, is fainter than the hot core spectrum and (2) whereas emission of the species widely extended over the cloud, such as CCH, is relatively stronger. The averaged spectrum is rather similar to the spectra observed in external galaxies such as M51 [1] and the Large Magellanic Cloud [2]. We have divided the observed area into 5 sub-regions according to the integrated intensity of ¹³CO, and have evaluated the contribution to the averaged spectrum from each sub-region. The sub-region with the ¹³CO integrated intensity from 10 K km s⁻¹ to 30 K km s⁻¹, which does not involve the hot core, shows the most similar characteristics to the averaged spectrum. Hence, the molecular-cloud-scale averaged spectrum seems to represent the gas extended around the star-forming core, rather than the core itself.

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A line survey of the massive star-forming region Sgr B2(M) in the 3 and 7 mm regions

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Line survey is an intensive investigation of chemical composition of a molecular cloud. The galactic center region is still primitive for detail chemical composition. In the present study, we carried out line survey of the massive star-forming region Sgr B2(M) in the 3 and 7 mm regions with Nobeyama 45 m radio telescope. Especially the 7 mm region was firstly surveyed in this cloud. Fig. 1 shows the observed peaks in the 3 and 7 mm regions. The $J = 7_{16}-6_{15}$ and $7_{25}-6_{24}$ transitions of HCOOCH_3 were observed for the first time in Sgr B2(M). The column density was determined to be $9.3 \times 10^{13} \text{ cm}^{-2}$, where the rotational temperature was fixed at 23 K reported by Cummins *et al* [1]. The lines of the $J = 6-5$ transition for CH_3CCH were also observed. The column density and the rotational temperature were determined to be $1.1 \times 10^{16} \text{ cm}^{-2}$ and 38 K, respectively. In addition, the lines of $\text{CH}_3^{13}\text{CCH}$ were observed for the first time as an interstellar molecule. In the 7 mm region, the absorption lines of the $J = 1-0$ transition were observed for ^{28}SiO and ^{29}SiO . Although both the components of the envelop of Sgr B2(M) and the clouds in front of it were found for ^{28}SiO , the former was only detected for ^{29}SiO . This difference is thought to be due to a higher $^{29}\text{Si}/^{28}\text{Si}$ ratio in Sgr B2(M).

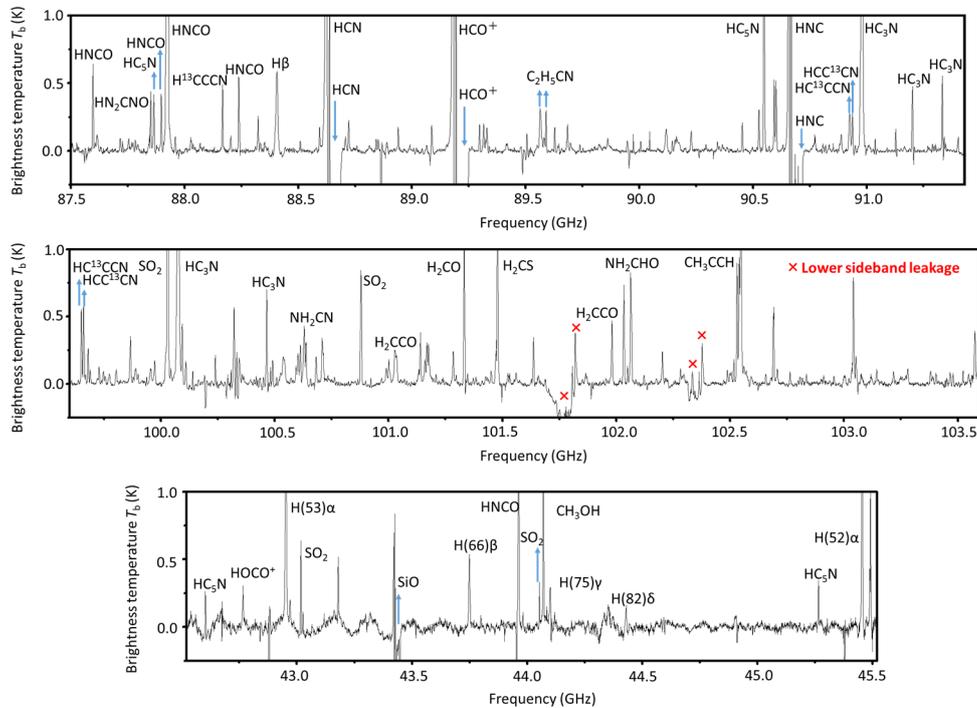


Fig. 1: The observed peaks in the 3 mm and 7 mm regions with Nobeyama radio telescope. Upper panel: 87.5~91.5 GHz. Middle panel: 99.6~103.6 GHz. Lower panel: 42.5~45.5 GHz.

Reference: [1] S. E. Cummins *et al.*, *ApJS*, **60**, 819 (1986).

Line Survey of Large Organic Molecules toward Orion IRC2 in the 73-89 GHz region

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Orion cloud located distance at 440 pc (1400 ly) is the nearest massive star-forming region. IRC2, which is an infrared star, is located at the center of this cloud and the region toward this star has been investigated so far. In this survey, we observed between 73 and 89 GHz by using 45m telescope of the Nobeyama Radio Observatory (NRO), which has a narrow beam size of $\sim 20''$. As major examples, the 17 lines of methyl formate HCOOCH_3 , the 20 lines of dimethyl ether CH_3OCH_3 , and the 4 lines of the ^{13}C isotopic species of acetonitrile $\text{CH}_3^{13}\text{CN}$ were detected in this cloud.

Large saturated organic molecules, such as methyl formate, are often found in cores of massive star-forming regions. Methyl formate is one of the molecules responsible for many rotational transitions in such regions. Thus, detection of the vibrational excited states of methyl formate can give us information of physical condition of molecules. The rotational lines of the vibrational excited states for methyl formate have been reported for $\nu_t = 1$ and 2 by Kobayashi *et al.* [1] and Takano *et al.* [2], respectively. However, the number of the lines on the vibrational excited states is still limited. In this survey, the 12 lines in the $\nu_t = 1$ state were newly detected.

The present observations show that the center of this cloud has a higher vibrational temperature than outside, because the narrow beam size of this telescope gives new lines of the vibrational excited state.

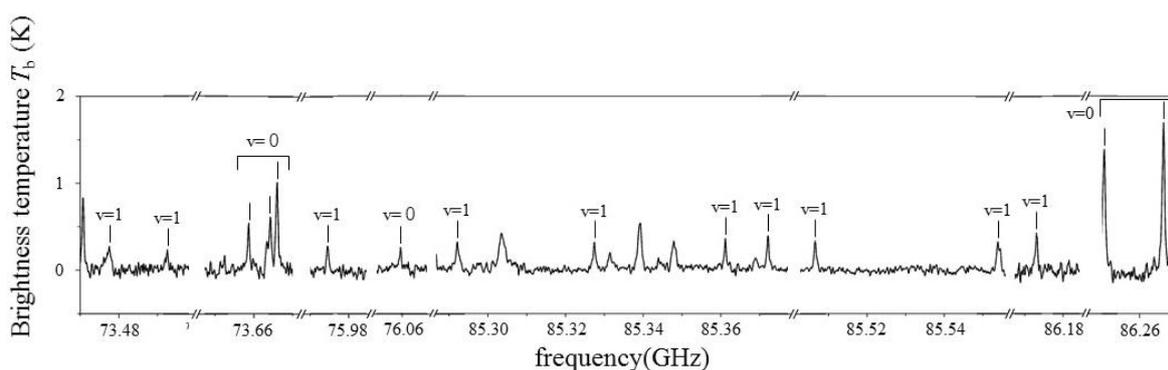


Figure 1 : Observed spectra of methyl formate toward Orion IRC2

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Spectral Line Survey Observations toward the Low-mass Star-forming Region L1527 with the Nobeyama 45-m Telescope

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We have carried out spectral line survey observations toward the low-mass star-forming region L1527 with the Nobeyama 45 m telescope in the 3 mm region. L1527 is a prototypical Warm Carbon-Chain Chemistry (WCCC) source, which harbors various carbon-chain molecules and their isomers in a dense and warm region (~ 1000 au) around the protostar [1]. In this spectral survey covering 80 GHz to 116 GHz, we have detected about 300 spectral lines and have identified more than 60 molecules including minor isotopic species. In this paper, we summarize the result of the line survey.

We have detected many carbon-chain molecules and their isomers. In particular, cyclic-C₃H and cyclic-C₃H₂ are found to be abundant in comparison with the other sources, resulting in the first detection of c-C₃D and c-¹³CCCH₂ in cold clouds [2]. We have also detected the lines of cyclopropanone (c-C₃H₂O) and propynal (HCCCHO). We compare the chemical composition of L1527 with those of the well-known hot corino source IRAS16293-2422 and the starless core TMC-1. The chemical compositions of L1527 and IRAS16293-2422 are exclusive to each other: the line survey observations toward IRAS16293-2422 shows rich spectral lines of complex organic molecules and deficient carbon-chain molecules, while the L1527 survey shows an opposite trend [3]. On the other hand, column densities of carbon-chain molecules in L1527 are found to be well correlated with those in TMC-1. When compared with TMC-1, longer carbon-chain molecules and N-bearing carbon-chain molecules tend to be less abundant in L1527. This would be due to the difference in the dynamical time scale of the molecular cloud cores.

NRO3mm_.eps -

Figure 1: Spectral line survey toward L1527.

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Spectral Line Survey toward NGC 2264 CMM3 with ALMA

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NGC2264 CMM3 is a massive protostellar core associated with a very young outflow (Saruwatari et al. 2011). According to the theoretical prediction (Maury et al. 2009), a protostar in this source will evolve into a main-sequence star with 8 Msun. In order to explore the chemical composition of this high-mass protostellar candidate in the earliest evolutionary phase, we conducted a spectral line survey with the Nobeyama 45 m telescope and the ASTE 10 m telescope in the 4, 3, and 0.8 mm bands (Watanabe et al. 2015). Carbon-chain molecules are found to be abundant in this source, whereas saturated complex organic molecules and S-bearing molecules are deficient. This result confirms chemical youth of the source.

Recently, we conducted a spectral line survey in the 0.8 mm band toward NGC2264 CMM3 with ALMA at an angular resolution of 0.3''-0.9''. As the result, this source is found to be a binary (A and B) separated by 660 au (Figure 1 Left). Furthermore, the binary is surrounded by 4 isolated continuum peaks, which are likely low-mass young stellar objects. CMM3A is very rich in molecular lines, as shown in Figure 1 Right), and possesses a hot core. On the other hand, CMM3B is rather deficient in molecular lines. This distinct chemical differentiation would originate from the different ages and/or the different temperatures of these two sources. This result will give us an important constraint on the mechanism of cluster/binary formation in this region.

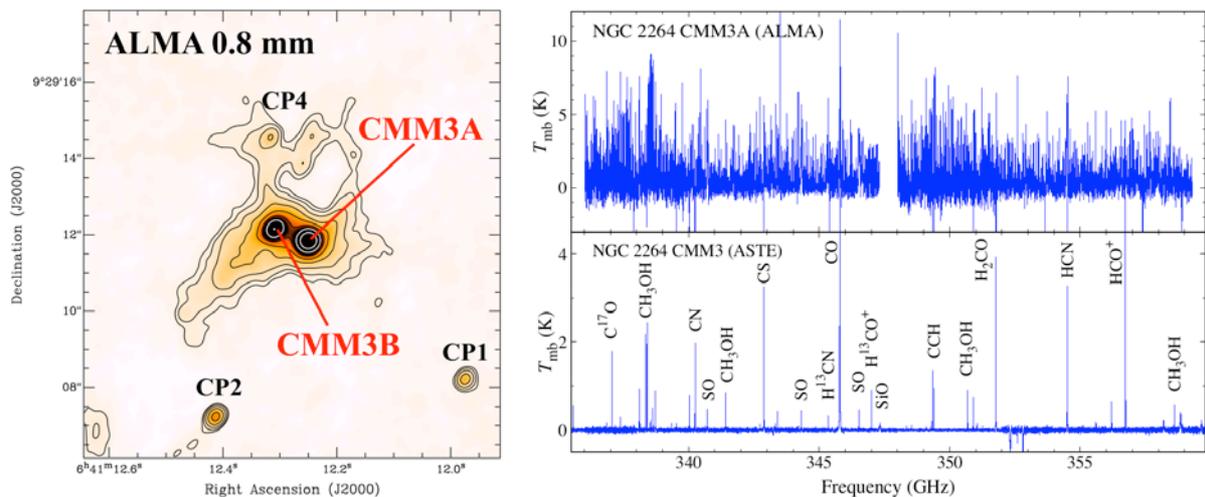


Figure 1: (Left) Continuum map observed with ALMA in the 0.8 mm band around CMM3. (Right) Spectra in the CMM3A observed the ALMA (Top) and that observed with the ASTE 10 m telescope (Bottom).

References

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Methanol maser survey observation with the Nobeyama 45 m telescope

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Circular polarization from methanol masers are observed in star-forming regions at several frequencies (6.7 GHz etc.) [1, 2]. If this circular polarization is caused by the Zeeman effect, it is possible to get information on magnetic field strength. It has been proposed that magnetic field is related to star formation closely and it will be a clue to understanding star formation by obtaining information on magnetic field in star-forming regions. For this purpose, it is essential to know laboratory data of the Zeeman effect of methanol (or, g-factor) so that the magnetic field can be deduced from the splitting of the observed methanol masers. There is a preliminary study on the Zeeman effect of methanol. A series of transitions in the 25 GHz range were observed [3] and the results were applied to the different transitions. This is not appropriate treatment and we have started laboratory measurements of methanol transitions to determine gfactor to obtain Zeeman effect on any transitions.[4]

It is generally expected that the splittings of methanol transitions are larger for low J , K transitions. From this point of view, the 108 GHz transition, $J, K = (0, 0)-(1, -1)$ (E sublevel) is one of the most promising transitions. However, the observations of this transition were limited and hence, we carried out a survey of 108 GHz methanol masers along with other transitions at 95, 96, and 107 GHz by using Nobeyama 45 m telescope in April 2016. We observed in total 36 high-mass star-forming regions associated with 6.7 GHz methanol masers. We will discuss the comparison between the sources and the relative intensities of the 4 transitions above.

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Analysis of Ice Absorption Features toward YSOs Candidates Using AKARI

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We present a study of near- to mid-infrared spectra (2.5–12 μ m) of two galactic YSO candidates, which have been discovered in serendipitous spectroscopy in the Galactic plane using the slit-less mode of the InfraRed Camera (IRC) on board AKARI. These sources do not belong to any known star-forming region. Absorption bands of molecular species, including solid phase H₂O, CO₂, CO, and possibly gas phase CO, are seen in the spectra towards both sources. Absorption bands of XCN, organics and silicates are also seen towards one of the sources.

We found that the column densities of the above detected species are large column densities of them, especially for XCN. These results suggest that the objects are highly embedded class I protostars or class II YSOs with an edge-on ($i \sim 70^\circ$) disk [1]. However, their SEDs are peculiar as class I or II YSOs since their peaks are located at around 4 μ m, while usual YSOs show a peak at a much longer wavelength (Figure 1) [2,3]. Their spectral energy distributions (SED) are quite blue as YSOs and no FIR emission has been detected. They are similar to that of class III YSOs, which do not show deep absorption bands of molecular species. Any existing SED models of YSOs cannot well account for the entire infrared SEDs.

On the other hand, the presence of the XCN and organics and CO gas features and no apparent associated nebulosity in the regions suggest that they are not likely background stars.

In this presentation, we will discuss the properties of these objects and their physical implications.

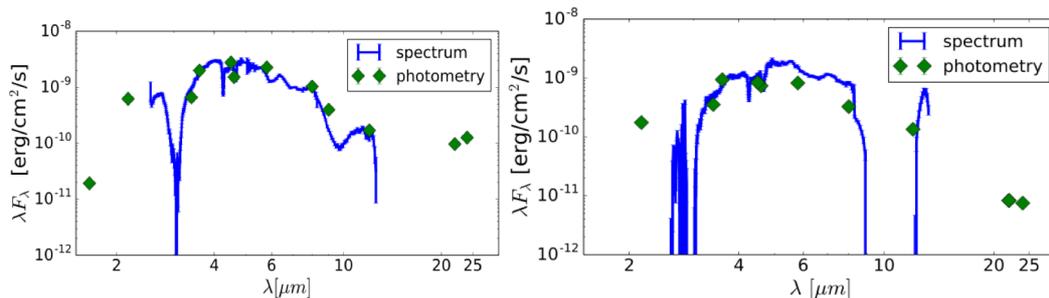


Figure 1: IRC spectra (blue) and photometry (green) of Object 1 (left) and Object 2 (right). The spectrum of Object 2 is reliable only at 3 - 5.5 μ m because of overlaps by neighboring sources.

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The Effects of the Star-forming Environments on the Thermal and Chemical Evolution of Protostellar Cores

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Stars form from clouds with wide ranges of surface densities. In the core accretion theory, such initial and environmental conditions may affect the evolution of the protostars and their cores, which further affects the chemical conditions of these cores. We explore such possibility by constructing evolution models of stars forming from cores embedded in different star formation environments. Each evolutionary track is built from three initial conditions: environmental surface density (which sets the pressure on the core), initial core mass, and its initial rotation. The model self-consistently calculates the collapse of the envelopes, growth of the accretion disks, gradually opening of the outflow cavities, and evolution of the protostars. We use continuum radiation transfer simulation to predict the dust temperature profile inside the core and its time evolution. By coupling such a physical model with chemical simulations, we are able to further predict the distribution of the molecules inside the protostellar core at a given evolutionary stage. The model shows that the star-forming environment strongly affects the thermal and chemical conditions of the cores which can be tested by observations. We present the preliminary results of our ALMA observation of 8 massive cores/regions. While the focus of this project is on the (sub-)structures of the cores and filaments, it also reveals rich information on the chemical conditions of these cores which are in different environments and evolutionary stages.

References

Shock heating of dusts and icy planetesimals due to bow shocks in protoplanetary disks

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In protoplanetary disks, planetesimals grow to planets through mutual collisions and accretions. The gravitational interactions among planetesimals increase the eccentricities of their orbits. Especially, large planetesimals have high eccentric orbits and supersonic velocities relative to the nebular gas. Small silicate particles in the nebular gas are heated and could be melted by passages through the bow shocks of such planetesimals [1-3]. It is proposed that the planetesimals perturbed by Jovian mean-motion resonances are the promising source of shock waves that form chondrules in chondritic meteorites because the shocks give short-time-scale heating of dust grains appropriate for the formation of chondrules [1]. In the previous studies on the planetesimal excitation, however, the velocities obtained were at most 8 km s⁻¹ in the asteroid belt, which is insufficient to account for the ubiquitous existence of chondrules. Recently Nagasawa et al. [4] reexamined the effect of Jovian resonances, taking into account the secular resonance in the asteroid belt caused by the gravity of the gas disk. They found that the velocities of planetesimals relative to the gas disk exceed 12 km s⁻¹ and the heating region is restricted to a relatively narrowband (1.5-3.5 au). These results suggest that chondrules were produced effectively in the asteroid region.

The planetesimal bow shocks also lead to heating of the planetesimal itself. Tanaka et al. [5] presented that icy planetesimals with radii larger than 100 km suffer from significant evaporation even outside the snow line. In [5], we focused on the oligarchic growth stage of protoplanets, in which planetesimals have velocities of 1-5 km s⁻¹ relative to the gas due to stirring by protoplanets. In this study, we investigate the evaporation of planetesimal in the stage of the formation of gas giant planets. In such a stage, the evaporation of planetesimal proceeds much more effectively because of the stronger shocks and the evaporation time is much shorter than the disk lifetime of 10⁶ yr. The evaporated H₂O vapor from the planetesimal surface recondenses as it cools and form a large amount of icy fine grains. During the evaporation of icy planetesimals, the silicate dust is also expected to be released from the planetesimal surface by the strong flow of the disk gas. This process provides a large amount of chondrule precursors. Our results may also relate to the origin of crystalline silicate observed in various comets and protoplanetary disks. The planetesimal bow shocks also lead to chemical reactions among various evaporated molecules. We propose a possibility that we can diagnose the shock heating and evaporation of icy planetesimals, using observations of lines of the molecules in the protoplanetary disks.

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Interstellar Dust Properties Revealed by Diffuse Galactic Light Measurements

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In this presentation, we constrain interstellar dust properties by observing diffuse Galactic light (DGL). The DGL consists of scattered light and thermal emission from interstellar dust grains illuminated by the interstellar radiation field. Therefore, the DGL measurement is useful in constraining some properties of interstellar dust, such as size distribution, albedo, and scattering asymmetry of dust grains.

In the diffuse interstellar medium, the DGL observation has been limited due to its faintness, particularly in the near-infrared wavelengths. We thus reanalyze all-sky maps obtained from Diffuse Infrared Background Experiment (DIRBE) onboard the Cosmic Background Explorer (COBE) satellite in the four near-infrared bands (1.25, 2.2, 3.5, and 4.9 micron). As a result, we succeed in detecting the near-infrared DGL as a component that linearly correlates with interstellar 100 micron emission.

At 1.25 and 2.2 micron, our results are marginally consistent with the expected spectrum of scattered light assuming a recent interstellar dust model. At 3.5 and 4.9 micron, thermal emission from stochastic heating of very small grains and fluorescence of polycyclic aromatic hydrocarbon (PAH) dominate the DGL. Compared with a recent thermal emission model in the diffuse interstellar medium, we constrain the mass fraction of very small grains and PAH to the total dust to be more than 2%.

We also find that the intensity ratios of DGL to 100 micron emission are higher toward low Galactic latitudes at 1.25 and 2.2 micron. Since this trend is expected from forward scattering characteristic of dust grains, we compare the obtained latitude dependence with the scattered light model that takes into account the scattering asymmetry. The derived forward scattering characteristic is stronger than that expected from the recent dust model. This may indicate that size or shape of the interstellar dust grain is different from the model prediction.

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Infalling-Rotating Motion and Associated Chemical Change in the Envelope of IRAS 16293-2422 Source A Studied with ALMA

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We have analyzed rotational spectral line emission of OCS, CH₃OH, HCOOCH₃, and H₂CS observed toward the low-mass Class 0 protostellar source IRAS 16293-2422 Source A at a sub-arcsecond resolution ($\sim 0''.6 \times 0''.5$) with ALMA [1]. Significant chemical differentiation is found at a 50 au scale. The OCS line is found to well trace the infalling-rotating envelope in this source. On the other hand, the CH₃OH and HCOOCH₃ distributions are found to be concentrated around the inner part of the infalling-rotating envelope. The kinematic structure of the infalling-rotating envelope is well explained with a simple ballistic model, as in the case of L1527 [2,3]. With this model, the radius of the centrifugal barrier (a half of the centrifugal radius) and the protostellar mass are evaluated from the OCS data to be from 40 to 60 au and from 0.5 to 1.0 M_{\odot} , respectively, assuming the inclination angle of the envelope/disk structure to be 60° (90° for the edge-on configuration). Although the protostellar mass is correlated with the inclination angle, the radius of the centrifugal barrier is not. This is the first indication of the centrifugal barrier of the infalling-rotating envelope in a hot corino source. CH₃OH and HCOOCH₃ may be liberated from ice mantles due to weak accretion shocks around the centrifugal barrier, and/or due to protostellar heating. H₂CS emission seems to come from the disk component inside the centrifugal barrier in addition to the envelope component. This study has further revealed that the centrifugal barrier plays a central role not only in the formation of a rotationally-supported disk but also in the chemical evolution from the envelope to the protoplanetary disk.

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CO gas depletion and formation of organic molecules in protoplanetary disks

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Protoplanetary disks are the natal place of planets and ALMA observations are now revealing the physical and chemical structure of planet forming regions in the disks. Understanding chemical components of gas, dust and ice in the disks is essential to investigate the origins of materials in the plants. In the talk, I shall report our recent ALMA Band 7 observations of CO isotopologue lines from the protoplanetary disk around TW Hya. The result shows a significant decrement in CO gas throughout the disk even inside the CO snowline, indicating freeze-out of gas-phase CO onto grain surfaces and possible subsequent surface reactions to form larger molecules. Complex organic molecules could be efficiently produced in the observed CO gas depleted regions. Actually, methanol has been detected towards the TW Hya, whose abundance relative to water is consistent with that of comets in our Solar system.

In addition, we performed model calculations of formation of complex organic molecules in protoplanetary disks, taking into account of thermal reactions including acid-based reactions in ice based on laboratory experiments. The result suggests relatively effective formation of some nitrogen-bearing species, such as CH₃NH₂, NH₂CHO, CH₃NHCOOH, NH₂COOH.

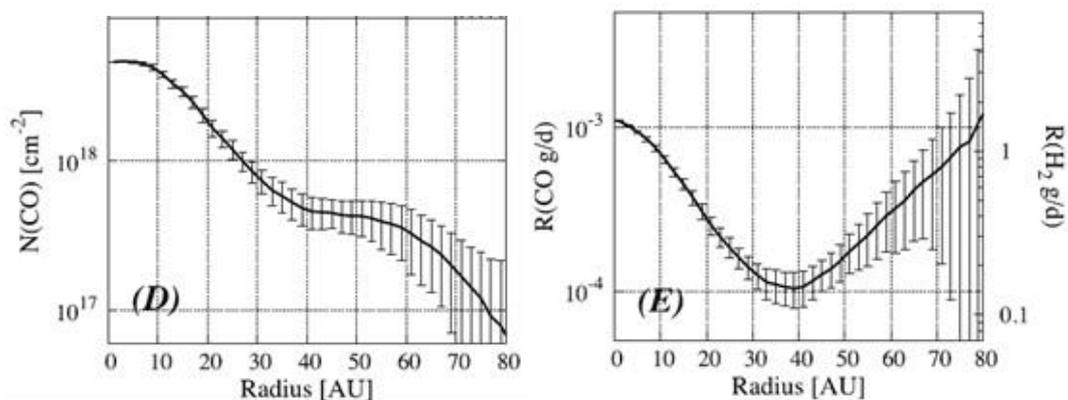


Figure 1: The CO gas column density profile (*left*) and the CO gas-to-dust ratio profile (*right*) in the protoplanetary disk around TW Hya, derived from our ALMA observations..

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Spatial variations of PAH properties in M17 revealed by Spitzer/IRS spectral mapping

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PAH (polycyclic aromatic hydrocarbon) emission features in mid-infrared spectra (e.g., 6.2, 7.7, 8.6, 11.3, 12.7 μm) are characteristic of PDRs (photo-dissociation regions). Past studies have shown that the PAH interband ratios are useful probes of the PAH properties (e.g., degree of ionization, size, and edge structure). The PAH properties have been discussed based on pencil-beam observations for many objects. In order to examine the effects of the surrounding interstellar environment on the PAH properties in detail, however, spatially-resolved observations are essential.

We analyzed Spitzer/IRS mid-infrared (5.5-14.5 μm) spectral mapping data of the Galactic star-forming region M17 as well as the IRSF Bry and Nobeyama 45-m ^{13}CO (J=1-0) maps. We decomposed the mid-infrared spectra using PAHFIT[1], and obtained spectral maps of the PAH features. As a result, we find that the PAH emission features are bright in the region between the HII region traced by Bry and the molecular cloud traced by ^{13}CO , supporting that the PAH features originate from PDRs. We also find that the PAH7.7/PAH11.3 ratios are independent to the distance from the M17 center (Fig.1), suggesting that the degree of PAH ionization is mainly controlled by the local interstellar environment. Based on these results, we examine the effects of the intense star-forming activity on the PAH properties in detail.

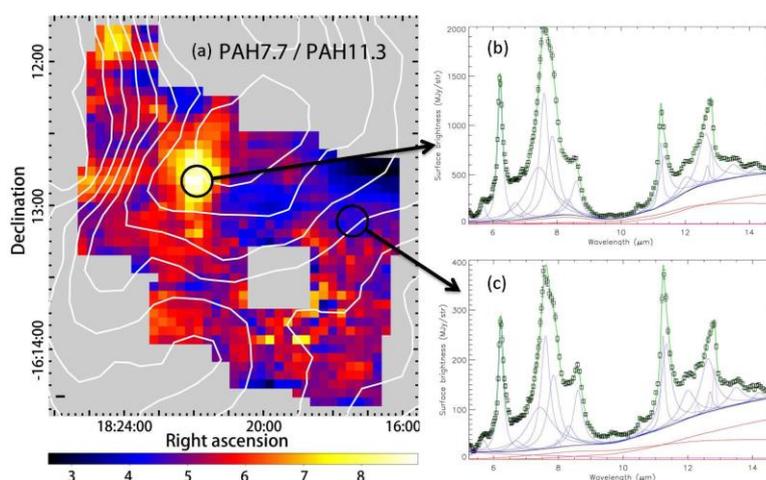


Figure 1: (a) PAH7.7/PAH11.3 interband ratio map. Contours are the ^{13}CO integrated intensity. (b,c) Examples of the mid-infrared spectra. The green, blue, and red curves indicate the best-fit models using PAHFIT.

References

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Chemistry in a forming protoplanetary disk: main accretion phase

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Protostellar cores harbor rich chemistry: i.e. complex organic molecules (COMs) and carbon chains. At the core center, a protostar and disk system are formed. Thus various molecules currently observed in protostellar cores will eventually be incorporated into disk. The main accretion phase, in which a protostar accretes most of its mass from the envelope via circumstellar disk, could also be an important transition phase for chemistry: from interstellar matter to disk material. Due to the high mass accretion rate, the forming disk could be much warmer than the Class II disk, and thus could enhance chemical reactions.

In this presentation, we report our numerical calculation of the molecular evolution[1] in a radiation-hydrodynamics model of star-forming core[2]. The model evolves from a cold (~ 10 K) prestellar core to the main accretion phase in $\sim 10^5$ yr, which corresponds to Class 0 objects. A rotationally-supported gravitationally unstable disk is formed around the protostar. We extract the temporal variation of physical parameters of 10^3 SPH particles which end up in the disk, and perform post-processing calculations of the gas-grain chemistry adopting a three-phase model. Inside the disk, SPH particles migrate both inward and outward. Since a significant fraction of volatiles such as CO can be trapped in the water-dominant ice in the three-phase model, ice mantle composition depends not only on the current position in the disk but also on whether the dust grain has ever migrated inside the water snow line. Stable molecules such as H₂O, CH₄, NH₃ and CH₃OH are abundantly formed in the molecular cloud before the onset of collapse and simply sublimated as the fluid parcels migrate inside the water snow line. On the other hand, various molecules such as carbon chains and complex organic molecules (COMs) are formed in the disk. COMs abundances sensitively depend on the efficiency of photodissociation and diffusion of photofragments in bulk ice mantle. As for S-bearing species, H₂S is abundant in the collapse phase. In the warm regions in the disk, H₂S is sublimated to be destroyed, while SO, H₂CS, OCS and SO₂ become abundant.

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Discovery of a Hot Corino in the Bok Globule B335

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We report the first evidence of a hot corino in a Bok globule. This is based on the ALMA observations in the 1.2 mm band toward the low-mass Class 0 protostar IRAS 19347+0727 in B335. Saturated complex organic molecules (COMs), CH₃CHO, HCOOCH₃, and NH₂CHO, are detected in a compact region within a few 10 au around the protostar. Additionally, CH₃OCH₃, C₂H₅OH, C₂H₅CN, and CH₃COCH₃ are tentatively detected. Carbon-chain related molecules, CCH and c-C₃H₂, are also found in this source, whose distributions are extended over a few 100 au scale. On the other hand, sulfur-bearing molecules CS, SO, and SO₂, have both compact and extended components. Fractional abundances of the COMs relative to H₂ are found to be comparable to those in known hot-corino sources. Though the COMs lines are as broad as 5-8 km/s, they do not show obvious rotation motion in the present observation. Thus, the COMs mainly exist in an infalling gas to the protostar, or in a rotating disk (ring) much smaller than the synthesized beam (0''58 x 0''52).

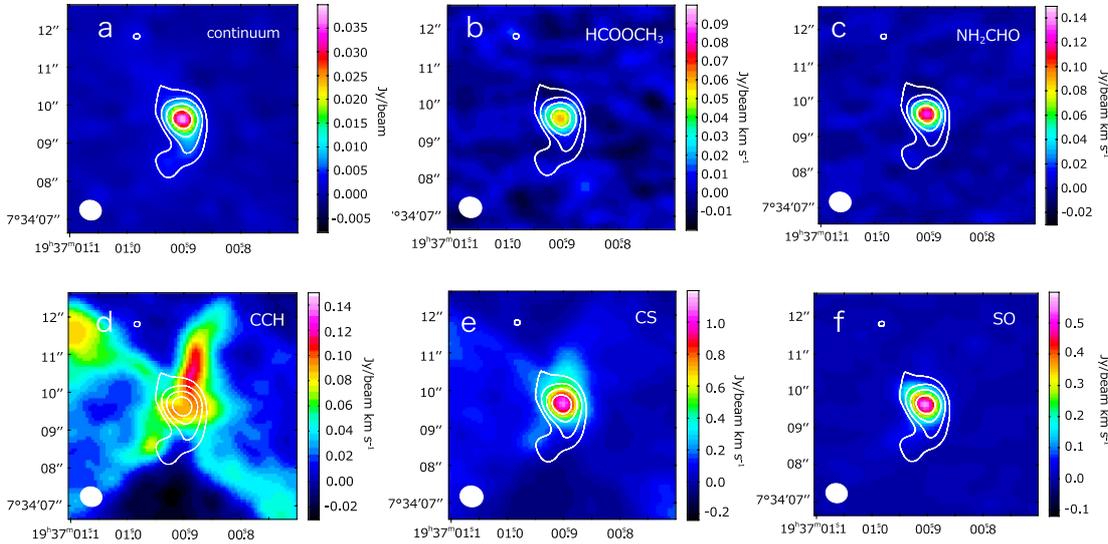


Figure 1: The continuum map and the moment 0 maps of HCOOCH₃, NH₂CHO, (CH₃)₂CO, CCH, CS, and SO. The contours represent the continuum flux of 10, 20, 40, 80 sigma levels. Compared with the synthesized beam shown in the bottom left in each figure, distribution of COMs are not resolved.

Hot water molecule around Orion Source I

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We report ALMA observations of submillimeter H₂O lines at bands 6, 7, 8 and 9 toward a massive protostar candidate Source I in the Orion KL region. We detect in total seven H₂O lines including vibrationally ground and excited ($v_2=1$) transitions at the highest upper state energy of ~ 3500 K. Their maps show compact structures associated with a close vicinity to Source I (< 200 au). The 321 GHz ($10_{2,9}-9_{3,6}$) and 658 GHz ($v_2=1$, $1_{1,0}-1_{0,1}$) lines show elongated structure along the northeast-southwest bipolar outflow[1,2]. On the other hand, higher excitation transitions such as 336 GHz ($v_2=1$, $5_{2,3}-6_{1,6}$) and 232 GHz ($v_2=1$, $5_{5,0}-6_{4,3}$) lines show more compact structures[1], as shown in Figure 1.

All the H₂O line maps show velocity gradients perpendicular to the bipolar outflow indicating rotation motions about the outflow axis. We interpret that the 321 GHz and 658 GHz lines trace the base of the bipolar outflow similar to the vibrationally excited SiO masers[3]. According to their brightness, the 321 GHz and 658 GHz lines are thought to be maser emissions. In contrast, some of the other H₂O lines could be explained via thermal excitation emitted from a midplane of the edge-on hot (~ 3000 K) molecular gas disk rotating around Source I. Based on the spectral profiles and intensity maps of the detected lines, we will discuss physical and dynamical properties of the hot molecular gas disk around Source I.

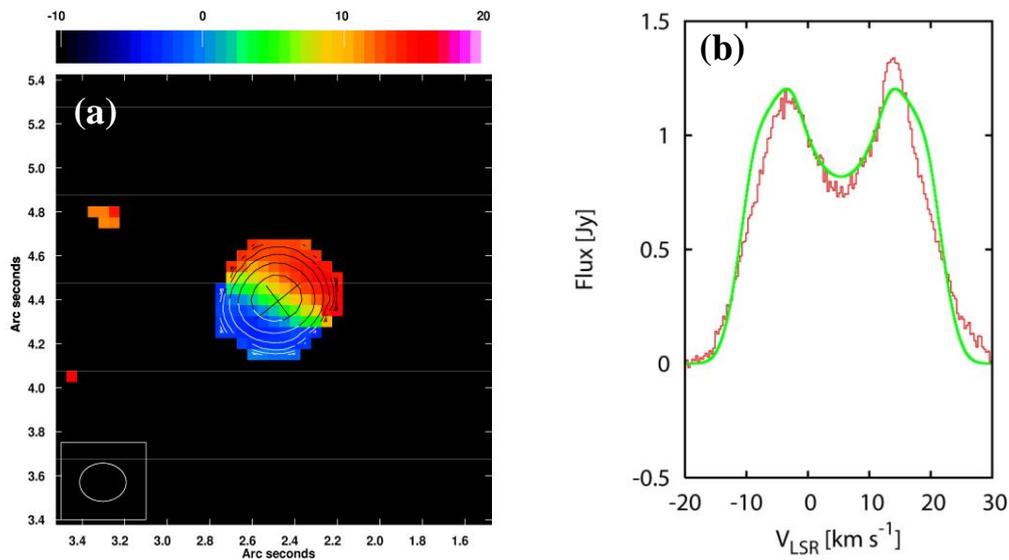


Figure 1: (a) Moment 0 (contour, integrated intensity) and 1 (color scale, peak velocity) maps of the 232 GHz H₂O line. A cross indicates the position of Source I determined from the continuum emission peak. (b) Observed (red) and model (green) spectra of the 232 GHz H₂O line.

References

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Chemistry of Cyanopolyynes in Hot Core Regions

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Cyanopolyynes (HC_{2n+1}N ; $n=1-5$) are one of the representative series of carbon-chain molecules. Carbon-chain molecules are good indicators of starless and star-forming cores; carbon-chain molecules are abundant in young starless cores and decrease as progress of the star formation processes^[1]. However, two low-mass star forming cores where various carbon-chain molecules are abundant were discovered, and these regions were named Warm Carbon Chain Chemistry (WCCC) sources^[2].

On the other hand, there are few studies about carbon-chain molecules in high-mass star forming regions, and our understanding is poor. We then carried out observations toward hot cores with the Nobeyama 45-m radio telescope, the Green Bank 100-m telescope, and the Very Large Array (VLA) in order to study chemical mechanisms of carbon-chain molecules in hot core regions.

We derived ^{13}C isotopic fractionation of HC_3N toward G28.28-0.36 by observations of the three ^{13}C isotopologues with the Nobeyama 45-m telescope. The abundance ratios are found to be $1.0(\pm 0.2):1.00:1.47(\pm 0.17)$ for $[\text{H}^{13}\text{CCCN}] : [\text{HC}^{13}\text{CCN}] : [\text{HCC}^{13}\text{CN}]$. The observational results imply that the neutral-neutral reaction between C_2H_2 and CN overwhelms other formation pathways, which is consistent with the chemical model calculation^[3].

We also detected HC_7N toward 2 hot cores, G28.28-0.36 and G12.89+0.49, with the Green Bank 100-m telescope at the time of writing the abstract (Figure 1). Our high-spatial-resolution maps with the VLA toward G28.28-0.36 show that the spatial distributions of cyanopolyynes (HC_3N , HC_5N , and HC_7N) are similar to that of CH_3CN , which is a hot core tracer. Based on these observational results, we consider that there is a possibility that cyanopolyynes can be efficiently formed in hot core regions.

References

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- [2] N. Sakai & S. Yamamoto, 2013, Chem. Rev., 113(12), 8981
- [3] J. F. Chapman et al., 2009, MNRAS, 394, 221

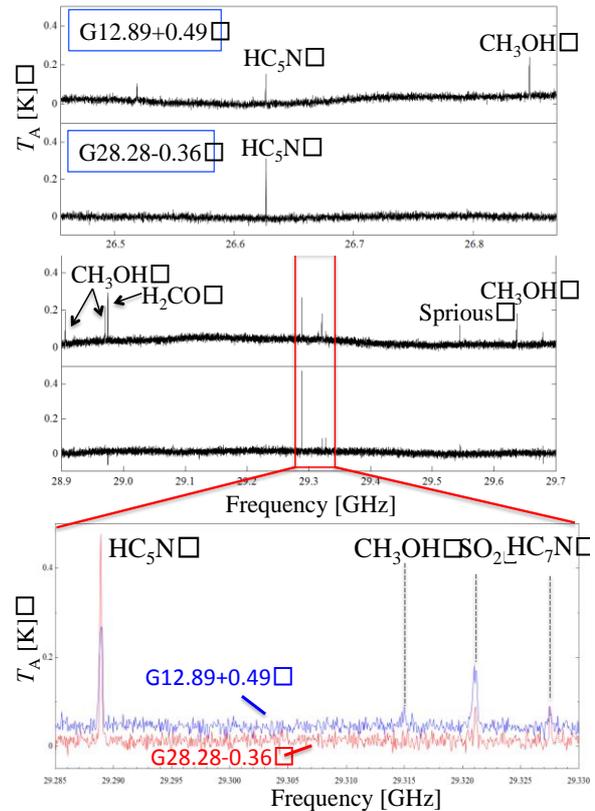


Figure 1. The spectra in two hot cores obtained with the Green Bank 100-m telescope.