Quest for the Compositional identification and Chemical evolutional understanding of the interstellar carbonaceous dust based on the experiment using JEM/ExHAM on the ISS

I. Sakon,[1] T. Onaka,[1] Y. Kimura,[2] S. Kimura,[3] M. Nakamura,[4] A. Ichimura,[5] and S. Wada[3]

[1]*Department of Astronomy, Graduate School of Science, University of Tokyo, Japan*

[2]*Institute of Low Temperature Science, Hokkaido University, Japan*

[3]*Coordinated Center for UEC Research Facilities, The University of Electro-Communication, Japan*

[4]*Collage of Science and Technology, Nihon University, Japan*

[5]*Institute of Space and Astronautical Science, JAXA, Japan*

The primordial form of cosmic solid is produced as a result of the dust/molecular nucleation in the stellar gas wind ejected from the evolved stars and is denatured in the circumstellar environment to become the member of the interstellar dust. However, the true compositional identification of cosmic carbonaceous dust grains has not been made successfully and, as a consequence, the evolutionary processes of interstellar dust in galaxies are not fully understood. Laboratory approaches have played an important role in providing observational astronomers accurate knowledge to derive the compositional, chemical, and physical properties of interstellar dust from the observed infrared spectrum of various astrophysical sources. In many cases, however, the dust particles that we treat in the laboratory are not always identical to the actual interstellar dust and, therefore, the attempts to identify the physical/chemical processes that associate the laboratory-synthesized dust with the actual interstellar dust are highly in demand.

We have proposed an experimental investigation program using JEM/ExHAM on the International Space Station (ISS) aiming to obtain accurate knowledge on the compositional, chemical and physical properties of interstellar dust. In this program, several laboratory-synthesized carbonaceous compounds including quenched carbonaceous composites (QCCs; Sakata et al. 1983) and nitrogen-bearing hydrocarbons, which are the valid candidates of primordial carbonaceous dust condensed in the AGB stellar ejecta, are planned to be brought and exposed to the cosmic environment at ISS orbit for ~1 year by means of JEM/ExHAM. The primary goal of this project is to identify the true carriers of the unidentified infrared (UIR) bands (e.g., Gillett et al. 1973) and those of the 2175Å interstellar extinction bump (Stecher 1965). In this presentation, we introduce the current status of our exposure experiment program titled "Quest for the Compositional identification and Chemical evolutional understanding of the Interstellar Carbonaceous Dust based on the experiment using JEM/ExHAM on the ISS".

References

[1]   A. Sakata et al. 1983, Nature, 301, 493
[2]   F.C.Gillett, W.J.Forrest, and K.M.Merrill 1973, The Astrophysical Journal, 183, 87-93
[3]   T. P. Stecher, 1965, The Astrophysical Journal, 142, 1683

Chemical Evolution of N-bearing Organic Molecules Leading to Glycine

M. Ohishi[1,4], T. Hirota,[2,4] M. Saito[3,4], T. Suzuki[4,1], and N. Kaifu[1]

[1]Astronomy Data Center, NAOJ, Japan,
[2]Mizusawa VLBI Observatory, NAOJ, Japan
[3]Nobeyama Radio Observatory, NAOJ, Japan
[4]Graduate University for Advanced Studies, Japan

It is widely accepted that prebiotic chemical evolution from small to large and complex molecules would have resulted in the Origin of Life. On the other hand there are two conflicting views where inorganic formation of complex organic molecules (hereafter COMs) occurred in the early Earth, on the Earth or out of the Earth. Ehrenfreund et al.[1] indicated that exogenous delivery of COMs by comets and/or asteroids to the early Earth could be larger than their terrestrial formation by three orders of magnitude. If amino acids are formed in interstellar clouds, significant amount of them may be delivered to planets. Detection of amino acids would accelerate the discussion concerning the universality of "life".

So far, many trials to detect the simplest amino acid, glycine (NH_2CH_2COOH), were made towards Sgr B2 and other high-mass forming regions, but none of them were successful. One idea to overcome this situation would be to search for precursors to glycine. Although the chemical evolution of interstellar N-bearing COMs is poorly known, methylamine (CH_3NH_2) is proposed as one precursor to glycine. CH_3NH_2 can be formed from abundant species, CH_4 and NH_3, on icy dust surface. Further methyleneimine (CH_2NH) would be related to CH_3NH_2 [2][3]. Another possible route to form CH_3NH_2 is hydrogenation to HCN on dust surface [4][5]: HCN $\rightarrow CH_2NH \rightarrow CH_3NH_2$. Figure 1 shows a possible formation route to glycine, which is based on the laboratory studies mentioned above.
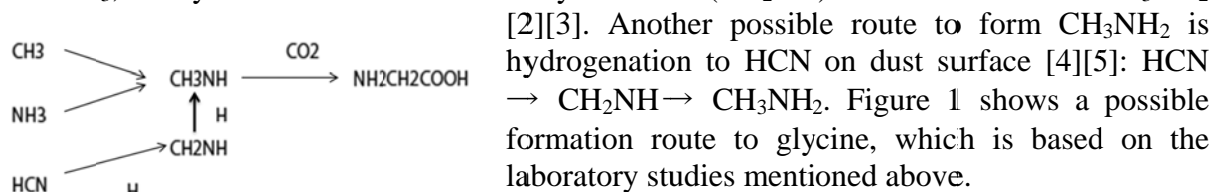

Fig.1   A Possible Formation Route to Glycine

In the past CH_2NH was reported only in Sgr B2, W51, Orion KL, and G34.3+0.15 [2]. In April 2013, we extended this survey by using the Nobeyama 45 m radio telescope towards CH_3OH-rich sources. We succeeded to detect four new CH_2NH sources. The derived fractional abundances of CH_2NH relative to H_2 are as high as 6×10^{-8}, implying that CH_2NH may exist widely in the ISM [6].

If this is the case, further hydrogenation would efficiently produce CH_3NH_2. Based on this idea we conducted a survey of CH_3NH_2 towards CH_2NH-rich sources in the spring of 2014, and succeeded to detect CH_3NH_2 towards two sources. The estimated fractional abundance of CH_3NH_2 to H_2 was $\sim 10^{-8}$, about 10 times higher than the value reported towards SgrB2(N) [7].

Since it is well known that CO_2 exists in most of molecular clouds, CH_3NH_2 could be a direct precursor candidate to glycine – the simplest amino acid— , CH_3NH_2-rich sources would turn into promising glycine targets by ALMA. Such studies would also accelerate discussion regarding the exogenous delivery of prebiotic species to planets and connection between the Universe and life.

References:
[1]   Ehrenfreund et al. Rep. Prog. Phys., 65, 1427, 2002
[2]   Holtom et al., ApJ, 626, 940, 2005
[3]   Kim & Kaiser et al. ApJ, 729:68, 2011
[4]   Dickens et al., ApJ, 479, 307, 1997
[5]   Theule et al., 2011, A& A, 534, A64
[6]   Suzuki et al., 2014, this workshop
[7]   Halfen et al., ApJ, 767, id.66

Chemical / Physical Properties of CH₂NH Sources

T. Suzuki,[1] T. M. Ohishi[1] ,Hirota,[2] and Saito Masao[3]

[1]*Astronomy Data Center, NAOJ, Japan*
[2]*Mizusawa VLBI Observatory, NAOJ, Japan*
[3]*Nobeyama Radio Observatory, NAOJ, Japan*

Despite its importance for the Origin of Life, long lasting challenges to detect interstellar simplest amino acid, glycine (NH_2CH_2COOH) were not successful. Since precursor-rich sources would be potential glycine-rich sources, understanding the chemistry of its precursors will lead a breakthrough of future glycine surveys with ALMA. For the formation mechanism, laboratory experiments demonstrated that dust surface reactions could form glycine. This process start with the hydrogenation (H added) to HCN : HCN → CH_2NH (Methylenimine)→ CH_3NH_2 (Methylamine) (Theule et al. (2011)), similar to well known formation process of CH_3OH: CO→H_2CO→CH_3OH. After that, reaction of CH_3NH_2 with CO_2 will form glycine (Kim & Kaiser (2011)). However, precursors of glycine, CH_2NH and CH_3NH_2, were also not well investigated in the actual interstellar medium.

Since 2013 April, we have conducted survey observations of CH_2NH using NRO 45m telescope towards 11 high-mass and three low-mass star-forming regions. As a result, CH_2NH was detected in eight sources, including four new ones. Among them, G10.47+0.03 and G31.41+0.3 showed especially high CH_2NH abundance.

The chemical properties of CH_2NH sources give us clues to reveal the CH_2NH chemistry. The positive correlations between "CH_2NH vs CH_3OH" and "CH_2NH vs $HC^{15}N$" would suggest that hydrogenation to HCN is plausible way to form CH_2NH in the actual interstellar medium. Further, other complex N-bearing species, like C_2H_5CN and C_2H_3CN also tend to be higher in CH_2NH-rich sources, while non N-bearing species does not show this trend   (figure 1). Such chemical properties might be linked to the evolutional phase and/or initial condition of star formation. In this work shop, we will show our results and would like to discuss the connection between physical and chemical properties of CH_2NH-rich sources.
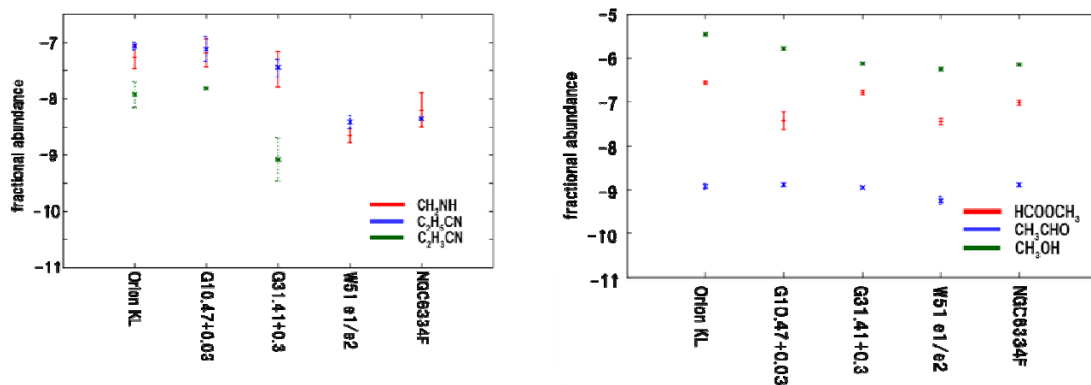

Figure 1: Comparison of fractional abundances among complex organic species

References

[1] Kim & Kaiser. ApJ, 729:68
[2] Theule et al., 2011, A& A, 534, A64

Chemical Evolution of Star-Forming Cores toward Protostellar/planetary Disks

N. Sakai,[1] & S. Yamamoto[1]

[1]*Department of Physics, The University of Tokyo, Japan*

In the last decade, it is clearly demonstrated that low-mass protostellar cores harbor various complex organic molecules (COMs) in the vicinity of the protostar. This result attracted much attention of astronomers and planetary scientists in relation to the origin of pre-solar organic materials found in meteorites and comets. In the course of these studies, significant chemical diversity was recognized among the observed sources. Now, we know at least two distinct families in chemical compositions; one is a hot corino characterized by abundant saturated COMs such as $HCOOCH_3$, $(CH_3)_2O$, and C_2H_5CN [e.g. 1], whereas the other is a warm-carbon-chain-chemistry (WCCC) source characterized by abundant unsaturated COMs such as carbon-chain molecules and their related molecules [e.g. 2]. The chemical diversity would originate from the different duration time of the starless core phase, although a larger, statistically significant, sample is needed to confirm this prediction. On the other hand, the most interesting issue to be studied is how the chemical diversity in the Class 0 stage is brought into the later stages toward protoplanetary disks. Fortunately, such a study is now feasible with high-sensitivity and high-angular-resolution capabilities of ALMA. In this talk, I will present recent chemical studies on disk formation done by ALMA [e.g. 3-5].

References

[1]   S. Cazaux, A. G. G. M. Tielens, C. Ceccarelli, A. Castets, V. Wakelam, E. Caux, B. Parise, & D. Teyssier, 2003, ApJ, 593, L51.

[2]   N. Sakai & S. Yamamoto, 2013, Chem. Rev. 113, 8981.

[3]   N. Sakai et al. 2014, Nature, 507, 78.

[4]   N. Sakai et al. 2014, ApJ, 791, L38.

[5]   Y. Oya et al. 2014, ApJ, 795, in press.

The origin of complex organic molecules in prestellar cores.

C. Vastel,[1] B.Lefloch,[2] and C. Ceccarelli[2,3]

[1]*Université de Toulouse, UPS-OMP, IRAP, Toulouse, France*
[2]*Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France*

Complex organic molecules (COMs) have been detected in a variety of environments, including cold prestellar cores. Given the low temperature of these objects, these last detections challenge existing models. We report here new observations towards the prestellar core L1544, based on an unbiased spectral survey of the 3mm band at the IRAM-30m telescope, as part of the Large Program ASAI. The observations allow us to provide the full census of the oxygen bearing COMs in this source and to derive their abundance. The non-LTE analysis of the methanol lines shows that they are likely emitted at the border of the core, in the same region layer where H_2O was detected by the *Herschel* space mission

We discuss the origin of this emission and propose that a non-thermal desorption mechanism is also responsible for the observed emission of methanol and COMs. We find that the desorbed oxygen and a tiny amount of desorbed methanol and ethane are enough to reproduce the abundances of COMs measured in L1544.

These new findings open the possibility that COMs in prestellar cores originate in a similar outer layer rather than in the dense inner cores, as previously assumed, and that their formation is driven by the non-thermally desorbed species.

Formamide (NH$_2$CHO) in star-forming regions: A crucial precursor of prebiotic material

A. López-Sepulcre,[1,2,3] E. Mendoza[4], B. Lefloch,[2,3] C. Ceccarelli[2,3], R. Bachiller[5], and the ASAI team

[1]*Dep. Physics, University of Tokyo, Japan*
[2]*Université Grenoble Alpes, IPAG, France*
[3]*CNRS, IPAG, France*
[4]*Observatório do Valongo, Universidade Federal Rio de Janeiro, Brasil*
[5IGN,] *Observatorio Astronómico Nacional, Spain*

Understanding the origin of life on Earth represents one of the hot topics in modern science. One of the big questions is whether the original mechanism that led from simple molecules to life was connected to metabolism or to genetics, both intimately linked in living beings. Formamide (NH$_2$CHO) contains the four most important elements for biological systems, and it has recently been proposed as a prebiotic precursor of both metabolic and genetic material, suggesting a common chemical origin for the two mechanisms [1].

Even though formamide was first detected in molecular clouds in 1971 [2], dedicated studies have started only very recently, as its potential as a key prebiotic molecule has become more evident. These studies report the presence of formamide in massive hot molecular cores [3,4], one low-mass protostar [5], and the comet Hale-Bopp [6]. In the past months, the IRAM Large Program ASAI, dedicated to astrochemical studies of star-forming regions, has revealed new discoveries of NH$_2$CHO [7], including its detection, for the first time, in outflow shock spots [8]. The presence of formamide in such a variety of star-forming environments, as well as on a Solar System comet, suggests that it could have been exogenously delivered onto a young Earth in the past.

In this contribution, we will present our new ASAI results on formamide, and compare them to previous studies, to try to understand its formation mechanisms in the interstellar medium. We will discuss the different chemical pathways that have been proposed, which include gas-phase as well as gas-grain reactions, and we will explain why we favor the latter. Lastly, we will emphasize the importance of joining efforts with experts on both theoretical and experimental chemistry in order to make progress.
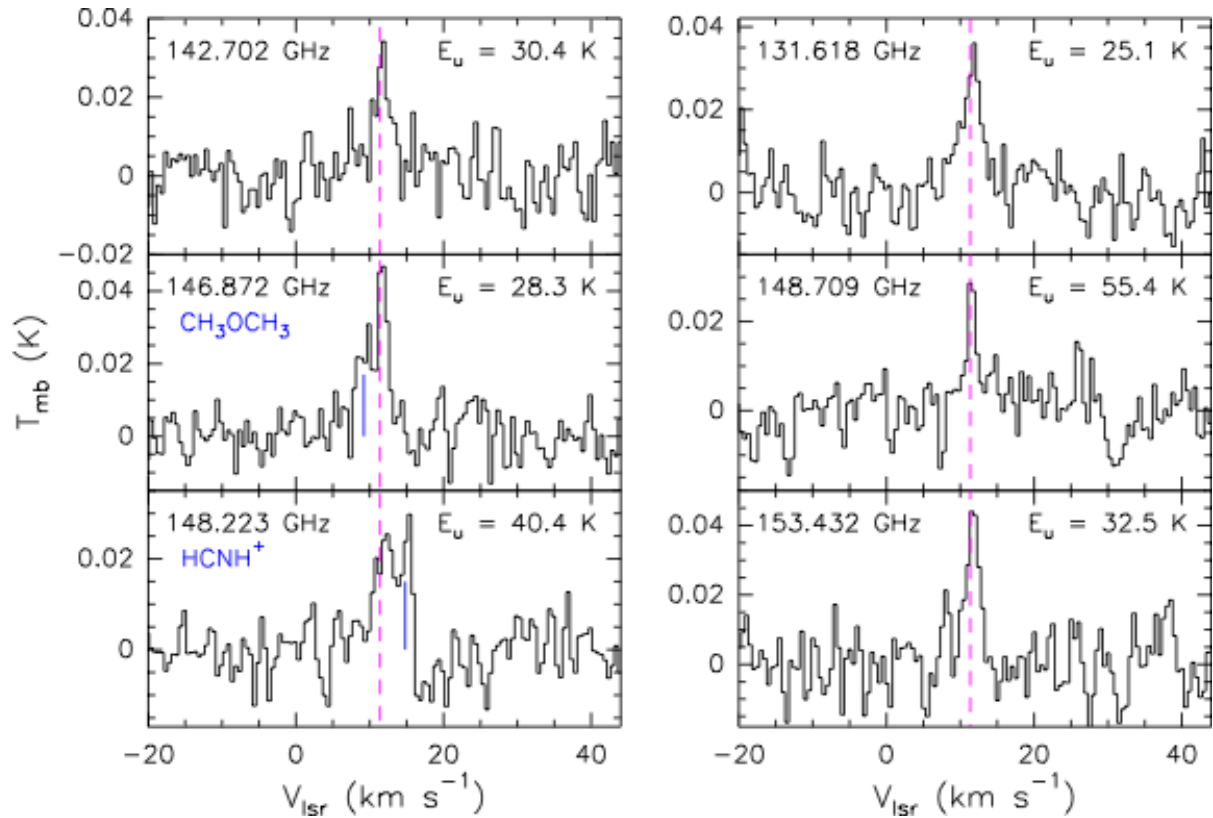
Figure 1: Some of the NH$_2$CHO lines detected in the intermediate-mass star-forming region OMC-2 FIR 4.

References

[1]   Saladino, R., Botta, G., Pino, S., Costanzo, G., Di Mauro, E. 2012, CSRv, 41, 5526.
[2]   Rubin, R. H., Swenson, G. W., Jr., Benson, R. C., Tigelaar, H. L., Flygare, W. H. 1971, ApJ, 169, 39.
[3]   Adande, G.R., Woolf, N.J., G., Ziurys, L.M. 2011, Astrobiology, 13, 439.
[4]   Bisschop, S. E., Jørgensen, J. K., van Dishoeck, E. F., de Wachter, E. B. M. 2007, A&A, 465, 913.
[5]   Kahane, C., Ceccarelli, C., Faure, A., Caux, E. 2013, ApJ, 763, L38.
[6]   Bockelée-Morvan, D., Lis, D. C., Wink, J. E. et al. 2000, A&A, 53, 1101.
[7]   López-Sepulcre, A., Mendoza, E., Lefloch, B. et al. (in prep.).
[8]   Mendoza, E., Lefloch, B., López-Sepulcre, A. et al. 2014, MNRAS (in press).

Volatiles in protoplanetary disks - setting the stage for planetary atmospheres

K. M. Pontoppidan,[1] A. Banzatti,[1] and S. Blevins[1]

[1]*Space Telescope Science Institute, Baltimore, MD 21218, USA*

Volatile molecules are the main condensible carriers of the elements essential for life; carbon, hydrogen and nitrogen. Their chemical evolution during star and planet formation determines the compositions of planets, including those destined to orbit in a habitable zone. The composition of our own solar system has been mapped in great detail, and we are now beginning to obtain direct measurements of the compositions of exoplanetary systems [1].

Since planetary compositions are ultimately driven by chemical and dynamical processes in the protoplanetary and debris disk phases, we aim to understand the early evolution of volatiles in protoplanetary disks. However, the path from the interstellar medium to planets is one fraught with complexity and twists, making it very difficult to derive purely theoretical predictions for chemistry. Direct observations of bulk molecular abundances are therefore critical for answering the question of how chemically common the Earth is among exoplanets [2,3].

In the past few years, great observational strides have been made, in particular in measuring the molecular composition in protoplanetary disks across the planet-forming regions from 1 to 10s of AU. I will review our current understanding of volatiles in protoplanetary disks and present recent observational work that demonstrates strong chemical evolution between the interstellar medium and planet-forming material [4], and I will discuss why this is important for our understanding of exoplanet composition and habitability.

References

[1]   Madhusudhan 2012, 758, 36
[2]   Oberg et al. 2011, ApJ, 743, 16
[3]   Pontoppidan et al. 2014, Protostars & Planets VI, in press
[4]   Pontoppidan and Blevins 2014, Faraday Discussions 168, 49

The N_2H^+ ring in Protoplanetary Disks

Yuri Aikawa,[1] Kenji Furuya,[2] Hideko Nomura[3] and Chunhua Qi[4]

[1]*Department of Earth and Planetary Sciences, Kobe University, Japan*
[2]*Leiden Observatory, Netherland (JSPS Fellow)*
[3] *Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan*
[4]*Center for Astrophysics, USA*

We investigate the chemistry of ion molecules in protoplanetary disks, motivated by the detection of N_2H^+ ring around TW Hya[1]. While the observed ring coincides with the CO snow line, it is not apparent why N_2H^+ is abundant outside the CO snow line, because the sublimation temperature of N_2, the mother molecule of N_2H^+, is similar to that of CO. We reproduced a ring of N_2H^+ in a disk model with mm grains, but not in a model with ISM dust. In the former, the ring is formed by a combination of the CO sink and photo-reactions, which prevent the N_2 sink. We also derived analytical formulas of molecular ion abundances as functions of density, ionization rate and abundances of major neutral molecules. The formulas are useful in constraining the ionization rate and also abundances of major molecules, such as CO and N_2, from the observations. Using the analytical formulas, we show that without the CO sink effect, N_2H^+ ring is reproduced only if the sublimation temperature of N_2 is lower than that of CO. We also found that in the model without the sink effect, N_2H^+ exists mostly in the disk midplane, while in the model with CO sink, N_2H^+ is abundant in the layer relocated from the midplane. In the former case, the N_2H^+ abundance would depend also on whether cosmic-ray can reach the disk midplane[2].

References
[1]   Qi, C, Oberg, K. I., Wilner, D. J., D'Alessio, P., Bergin, E.A., Andrews, S. M., Blake, G. A., Hogerheijde, M. R., van Dishoeck, E. F. 2013, Science, 341, 6146
[2]   Aikawa, Y. et al. in prep

In-situ observation of ices by ultrahigh vacuum transmission electron microscope and atomic force microscope

A. Kouchi,[1] H. Hidaka,[1] Y. Kimura,[1] T. Hama,[1] and N. Watanabe[1]

[1]*Institute of Low Temperature Science/Hokkaido University, Japan*

The importance of H_2O ice, both amorphous and crystalline phases, at low temperatures has been widely realized not only for the formation and evolution of ices but also for substrates of surface reactions. A vapor-deposited amorphous H_2O ice (amorphous solid water, ASW) have been studied extensively as an analogue of amorphous ices in molecular clouds. ASWs deposited at around 10 K and deposited or annealed at temperatures higher than 70 K are acknowledged to be high-density and low-density forms, respectively, from electron diffraction patterns [1]. However, much more problems remain to be solved. Meanwhile, ASW deposited at around 10 K is considered to very porous from the measurements of surface area and bulk density, and ASW deposited or annealed at temperatures higher than 70 K has been assumed to be compact (not porous). Although the importance of surface structure of ASW has been implicitly realized, there has been no direct observation of surface structure. In the studies of surface reactions, ASW is treated as "black box" at present. It is therefore highly desirable to investigate the structure and surface structure of ASW by direct methods.

We have developed an ultrahigh vacuum (UHV) transmission electron microscope (TEM) and an atomic force microscope (AFM) for *in-situ* observation of ASWs and ice crystals. In the workshop, we will present preliminary results on the following topics: 1) Surface structure of ASW, and 2) Novel method for the formation of high-density amorphous ice.

Figure 1: UHV-TEM (left) and UHV-AFM (right).

References

[1]   P. Jenniskens & D. F. Blake, 1996, Science 265, 753.

Oxygen chemistry on dust grains

G. Vidali,[1] J.He[1,2]

[1]*Physics Department, Syracuse University, USA*
[2]*Current address: Chemistry Department, University of Hawai'i at Manoa, USA*

Oxygen, the third most abundant element in space, intervenes in the formation of many molecular species, some of which are important in the generation of molecules relevant to the emergence of life. The realization that many gas-phase processes are insufficient to justify the abundance of some of these molecules has led to laboratory studies of the formation of molecules, such as H_2O, CO_2, and others) on the surface of dust grain analogs in simulated ISM conditions[1,2].

As these surface processes rely on the residence time and diffusion of reactants, we devised a combination of experiments and theoretical simulations to obtain desorption energy and energy barriers for diffusion of oxygen atoms and of important oxygen-containing molecules[3].
Here we present the results of recent experiments and simulations of the interaction of oxygen with surfaces of amorphous silicates and amorphous water ice[4]. We also report on the formation of water on warm grains[5], i.e., grains that are present at the edge of molecular clouds or of photodissociation regions, and on the formation of precursors of biogenic molecules[6].
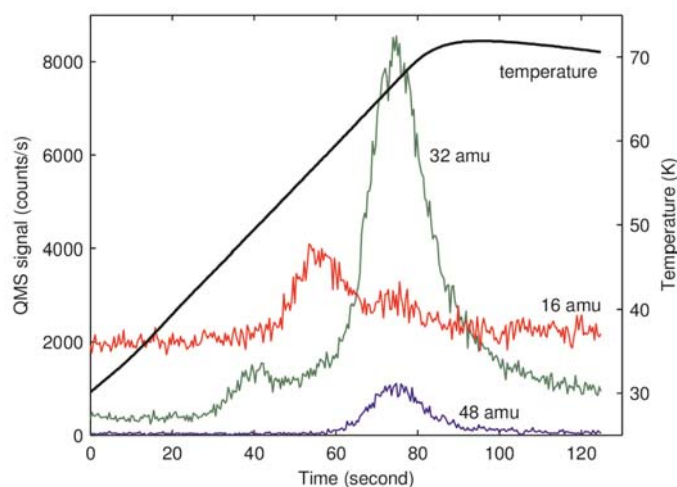

Figure 1: TPD traces of mass 16, 32, and 48 amu after depositing 8 minute O/O_2 at 48 K on porous amorphous water ice. The heating ramp is 10 K/minute. From Ref. 4.

References
[1]   G.Vidali, 2013, J. Low Temp. Phys., 170, 1.
[2]   T. Hama & N.Watanabe, 2013, Chem. Rev. 113, 8783.
[3]   J.He & G.Vidali:, 2014, Faraday Discuss. 168, 5.
[4]   J.He, J.Shi, T.Hopkins, G.Vidali & M.Kaufman, 2014, in preparation.
[5]   J.He & G.Vidali, 2014, Astrophys.J., 788, 50.
[6]   J.He, G.Vidali, J.L.Lemaire, & R.Garrod, 2014, Astrophys. J., submitted.

Photodesorption of CO ice induced by a non-monochromatic light source

Yu-Jung Chen,[1,2] Ko-Ju Chuang,[1] Guillermo M. Muñoz Caro,[3] Michel Nuevo,[4,5]
Ching-Chi Chu,[1] Tai-Sone Yih,[1] Wing H. Ip,[6] and C.-Y. Robert Wu[2]

[1] Department of Physics, National Central University, Taiwan
[2] Space Sciences Center and Department of Physics and Astronomy, University of Southern California, USA
[3] Centro de Astrobiología, INTA-CSIC, Spain
[4] NASA Ames Research Center, USA
[5] BAER Institute, USA
[6] Graduate Institute of Astronomy, National Central University, Taiwan

The microwave-discharge hydrogen-flow lamp (MDHL) provides hydrogen Lyman α (H Ly-α, 121.6 nm) and H_2 molecular emission in the 110–180 nm range. We show that the spectral characteristics of the VUV light emitted in this range, in particular the relative proportion of Lyman α to molecular emission bands, strongly depend on the pressure of H_2 inside the lamp, the lamp geometry (F type vs. T type), the gas used (pure H_2 vs. H_2 seeded in He), and the optical property of the window used (MgF_2 vs. CaF_2). These different experimental configurations of the MDHL are then used to study the VUV irradiation of CO ice at 14 K.

Experimental results show that the processes induced by photons in CO ice from a broad energy range are different and more complex than the sum of individual processes induced by monochromatic sources scanning the same energy range, due to the existence of multi-state electronic transitions and discrepancy of absorption cross-section between parent molecules and products in Ly-α and H_2 molecular emission ranges.
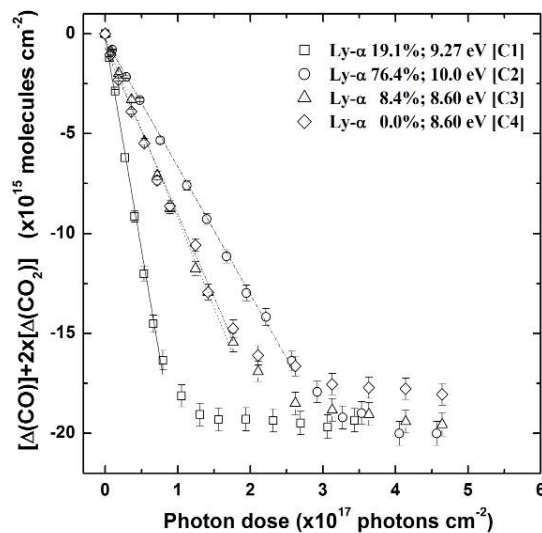
Figure 1: Photodesorbed column density of CO ice irradiated by the MDHL in several operating conditions as a function of the photon dose, derived after taking the column densities of photodepletion CO and photoproduced CO_2 into account.

References

[1] Muñoz Caro, G. M., Jiménez-Escobar, A., Martin-Gago, J. A., et al. 2010, A&A, 522, A108
[2] Chen, Y.-J., Chuang, K.-J., Muñoz Caro, G. M., et al. 2014, ApJ, 781, 15

Probing the Formation of Biorelvant Molecules in Kuiper Belts by Tunable Vacuum Ultraviolet Photoionization Mass Spectrometry (PI-TOF-MS)

R.I Kaiser & B.M. Jones

Department of Chemistry & W.M. Keck Research Laboratory in Astrochemistry
University of Hawaii at Manoa, Honolulu, HI 96822, USA

During the last decade, Kuiper Belt Objects (KBOs) emerged in their role as a repository of primitive planetary material on Earth and are dubbed 'primordial fossils' helping to understand the origin and astrobiological evolution of the Solar System. Using a novel surface scattering machine[1], we simulate the interaction of ionizing radiation with KBO analog ices and apply these findings to elucidate the formation of key classes of biorelevant molecules[2-3] (amino acids, dipeptides, sugars, fatty acids, RNA nitrogen-bases). First, we mimic the space environment under clean, contamination-free conditions at ultra-high vacuum (10^{-11} torr). Second, this setup allows a simulation of the interaction of ionizing radiation with surfaces systematically over a wide range of KBO relevant chemical and physical parameters in the same machine: i) the chemical composition of the ices [methane (CH_4), water (H_2O), nitrogen (N_2), carbon monoxide (CO), methanol (CH_3OH)], ii) ice temperatures 30-50 K, and iii) ionizing radiation in the form of 1 keV protons and 10.2 eV photons (Lyman α) simulating the most significant component of Solar Wind ions and photons interacting with KBO surfaces. Third, we interface four complementary detection schemes to a single machine to probe individual biorelevant molecules on line and in situ. This enables us to identify key functional groups in the ices via infrared (IR), Raman (Ra), and ultraviolet-visual (UV-VIS) spectroscopy. Individual molecules subliming into the gas phase upon warm-up of the samples can be identified via fragment-free reflectron time-of-flight mass spectrometry (ReTOF) coupled with vacuum ultraviolet (VUV) soft photoionization (ReTOF-PI). This technique has the unique power to identify the molecules based on a cross correlation of their mass-to-charge ratios, their ionization energies (IE), and photoionization efficiency curves (PIE) ultimately unraveling an inventory of individual biorelevant molecules formed upon interaction of ionizing radiation and KBO analog ices and also their interstellar precursors.

(1)   Jones, B. M.; Kaiser, R. I., Application of Reflectron Time-of-Flight Mass Spectroscopy in the Analysis of Astrophysically Relevant Ices Exposed to Ionization Radiation: Methane (CH_4) and D4-Methane (CD_4) as a Case Study. *The Journal of Physical Chemistry Letters* **2013**, *4* (11), 1965-1971.

(2)   Kaiser, R. I.; Maity, S.; Jones, B. M., Infrared and reflectron time-of-flight mass spectroscopic analysis of methane (CH_4)-carbon monoxide (CO) ices exposed to ionization radiation - toward the formation of carbonyl-bearing molecules in extraterrestrial ices. *Physical Chemistry Chemical Physics* **2014**, *16* (8), 3399-3424.

(3)   Maity, S.; Kaiser, R. I.; Jones, B. M., Infrared and Reflectron Time-of-Flight Mass Spectroscopic Study on the Synthesis of Glycolaldehyde in Methanol (CH_3OH) and Methanol-Carbon Monoxide (CH_3OH-CO) Ices Exposed to Ionization Radiation. *Faraday Discuss.* **2014**, *168* (1), 485-516.

Astrochemistry in ion traps: from cold hydrogen to hot carbon

Dieter Gerlich

Department of Physics, Technische Universität Chemnitz, Germany

Astrochemistry deals with the formation and destruction of matter in very different environments including the early universe, cold dense interstellar clouds, hot circumstellar regions, or planetary atmospheres. In this contribution I summarize our recent experimental activities in this field using radio frequency (rf) traps for confining ions and nanoparticles. Two electrode arrangements are shown in Figure 1. The cryogenic 22-pole is meanwhile a very common ion trap used for reaction dynamics and spectroscopy (see [1] and references therein), while the split ring electrode trap (SRET) has been developed for high temperature applications [2]. With closed cycle refrigerators, wall temperatures of 2.6 K have been achieved [3] while heating an C_{60}^+ ensemble with a CW CO_2 laser has resulted in temperatures above 2000 K [2].
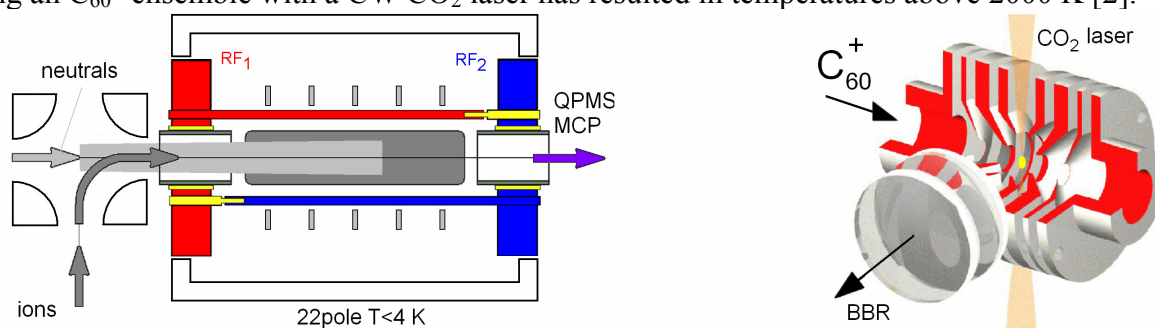

Figure 1: Left: 22pole ion trap for studying the interaction between cold stored ions and a beam of neutrals. Right: Special quadrupole trap for monitoring hot particles via their black body radiation (BBR).

Many gas phase processes involving ions have been studied in rf traps, including bi- and termolecular reactions, radiative association, clustering, isomerization, and isotope fractionation. In this talk, I will mention a few examples: (i) Associative detachment in $H^- + H$ collisions measured in the temperature range between 10 and 135 K. (ii) So far unexplained is the experimental result that $CH^+(v{=}0,J)$ does not react with H atoms for $J = 0$ at low temperatures, although the reaction is exothermic. (iii) In contrast to simple expectations, radiative association of H^+ colliding with $H_2(J)$ is a factor of 2 slower for $J = 0$ than for $J = 1$. (iv) For reactions of $N^+(^3P_{ja})$ with $H_2(J)$, first state specific rate coefficients $k(J, j_a)$ have been derived [1].

There are many innovative activities based on the combination of lasers and ion traps [4]. A powerful new instrument used a cryogenic wire quadrupole and tunable IR lasers [3]. Very versatile is the new spectroscopy method called Laser Induced Inhibition of Complex Growth (LIICG) which has been developed in Basel [5] for studying candidates for the diffuse interstellar bands (e.g. C_{60}^+). This method has been applied first to N_2^+ ions and extended in Köln to CH_5^+ and H_3^+. As an example for measuring the stability of objects in a high temperature stationary state, the decay rates of a cloud of C_{60}^+ ions also will be mentioned [2].

References
[1]   I. Zymak, M. Hejduk, D. Mulin, R. Plašil, J. Glosík, D. Gerlich, 2013, Ap.J. **768,** 86.
[2]   D. Gerlich, S. Decker, 2014, Appl. Phys. B, **114,** 257.
[3]   J. Jašík, J. Žabka, J. Roithová, and D. Gerlich, 2013, Int. J. Mass Spectrom. **354-355,** 204.
[4]   For more information and references see https://www.tu-chemnitz.de/physik/ION
[5]   S. Chakrabarty, M.Holz, E.K. Campbell, A. Banerjee, D. Gerlich, and J. Maier, 2013, JPC Lett **4,** 4051.

Formation of hydrated-alumina clusters
toward elucidation of chemical processes on mineral surfaces

M. Arakawa, K. Kohara, and A. Terasaki

Department of Chemistry, Kyushu University, Japan

Small particles consisting of ice, minerals, and organic molecules exist in the early stage of planetary formation. It is a prevalent hypothesis that, in protoplanetary nebulae, organic molecules are formed through catalytic reactions on mineral particles. To investigate essential reaction steps of the organic-molecule formation, size-selected clusters of mineral composition can be used as models for chemistry on mineral surfaces. As a first step, we investigated generation of mineral-composition clusters by focusing on compounds of aluminum, whose elemental abundance is relatively high in the earth and in space.

Aluminum is known as a reactive metal as we can imagine from the fact that it is readily oxidized by O_2 and/or H_2O in the air to form a passive surface. We have reported that aluminum-cluster cations, Al_N^+, react with a H_2O molecule to form Al_NO^+, which implies H_2 generation [1]. In the present study, we investigated reaction of Al_N^+ with a mixture of O_2 and H_2O gases to observe formation of clusters with composition of aluminum minerals abundant naturally.

In the experiment, Al_N^+ ($N = 1$–14) were generated by a magnetron-sputter cluster-ion source. They were mass-selected and guided into a reaction cell filled with a buffer He gas containing H_2O and O_2. The ions produced by the reaction of Al_N^+ with H_2O and O_2 were identified by a quadrupole mass analyzer.

Reaction products with a mass of 157 and 175 amu were observed for all the sizes except $N = 1$. Since only Al^+ was found to be inert, we speculated that these products originate from Al_2^+, which is produced by dissociation of Al_N^+ ($N \geq 3$). By controlling the partial pressures of O_2 and H_2O, reaction intermediates such as Al_2O^+, $Al_2O_3^+$, $Al_2O_4H_3^+$, and $Al_2O_5H_5^+$ were observed, and the prominent products were assigned to be $Al_2O_6H_7^+$ and $Al_2O_7H_9^+$ for 157 and 175 amu, respectively. The chemical composition of these products, $Al_2O_3(H_2O)_nH^+$, is similar to that of hydrated alumina such as boehmite, diaspore, and gibbsite except for the excess proton. To obtain structural information of these products, we performed collision-induced dissociation experiment of $Al_2O_6H_7^+$ (157 amu) with an Ar gas, where products of 139 and 121 amu were observed. The prominent product of 157 amu was thus identified as $Al_2O_4H_3(H_2O)_2^+$ with two H_2O molecules remaining intact.

We further investigated formation processes of these protonated hydrated-alumina clusters by observing the reaction steps to model reactions of aluminum in natural environments; each reaction intermediate was generated in the cluster source, and reaction with either H_2O or O_2 was examined in a step-by-step manner. It was found that reaction of aluminum with O_2 and H_2O to form alumina, Al_2O_3, at initial steps is followed by successive hydroxylation and hydration reactions.

References

[1]   M. Arakawa, K. Kohara, and A. Terasaki, 2013, Eur. Phys. J. D 67, 80.

H_2F^+ : Herschel observation and laboratory chemical reaction study

K. Kawaguchi,

Department of Chemistry, Okayama University, Okayama, Japan

In 2013, the pure rotational lines $J_{KaKc} = 2_{12} - 1_{01}$ and $1_{10} - 1_{01}$ of H_2F^+ were searched toward W31C, NGC 6334I, GC IRS21, 2Mass J1747 with the Heterodyne Instrument for the Far-Infrared (HIFI) on board the Herschel Space Observatory [1]. The transition frequencies have been measured in laboratory [2,3]. The proton affinity of HF is smaller than that of CO or N_2, so H_2F^+ is expected to be produced in diffuse cloud by proton transfer from H_3^+ to HF. In the two sources W31C and NGC 6334I, HF and H_2Cl^+ have been detected, and other two sources are known to have abundant H_3^+. By data analysis, the abundance of H_2F^+ is found to be less than 1/57 of H_2Cl^+ for NGC 6334I. Since the cosmic abundance of fluorine is one-half of that of chlorine, the small abundance of H_2F^+ may be explained by difference in production and/or destruction mechanism of both ions.

In laboratory, we investigated time-variation of the absorption intensities of H_2F^+ and H_2Cl^+ vibration-rotation lines in the 3 μm region to determine ion-electron recombination reaction rate constants, which have important roles for ion abundances in low density interstellar clouds. We used an optical parametric oscillator (OPO) laser with high resolution for absorption measurements. We employed pulsed discharge and measured time profiles of the absorption lines of H_2F^+ at $\nu = 3251.99$ cm^{-1} (v$_3$ = 1-0, $J_{KaKc} = 3_{13} \leftarrow 4_{14}$), and H_2Cl^+ at $\nu = 2691.24$ cm^{-1} (v$_3$ = 1-0, $J_{KaKc} = 6_{06} \leftarrow 5_{05}$). Figure 1 shows an example of observed time profiles.

Initially, assuming the same densities of electron and positive ion, we attempted $1/N$(density) plot in the secondary reaction scheme, but it was not possible to fit well. On the other hand, the decay was explained well by an exponential function, so we assumed the decay by the pseudo-first-order reaction between ion and electron. We used the Langmuir probe method for determination of electron density and derive the recombination rate constants, as follows, $k_e(H_2F^+) = 3.8\ (1.6) \times 10^{-8}$ cm^{3}s^{-1}, and $k_e(H_2Cl^+) = 2.4(1.0) \times 10^{-8}$ cm^{3}s^{-1}. We did not find major difference between the H_2Cl^+ and H_2F^+ ions for recombination rates. Small abundance of H_2F^+ compared with H_2Cl^+ in interstellar space is thought to be due to the difference in the formation reaction.

In diffuse clouds, the presence of HCl$^+$ is important for production of H_2Cl^+, where the ion has been detected by Herschel. The ion can produce H_2Cl^+ by a reaction with H_2. On the other hand, HF is not ionized in interstellar radiation field. F$^+$ reaction with H_2 produces HF$^+$ [4], but F$^+$ is not abundant in diffuse clouds.
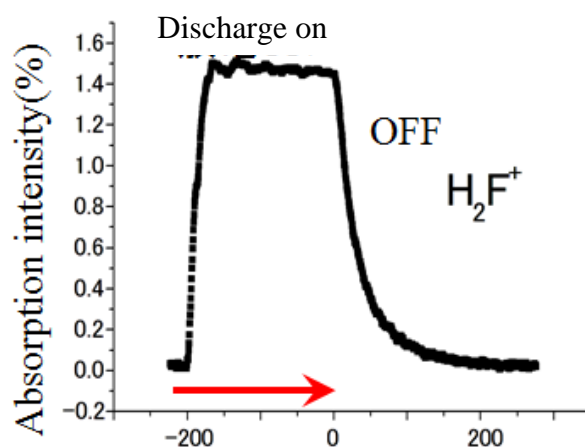

Fig.1 Time profile of the H_2F^+ line for ion-electron recombination study

[1] K. Kawaguchi, R. Fujimori, T. Amano, and F. Matsushima, Herschel OT2 (2013).
[2] R. Fujimori, K. Kawaguchi, and T. Amano, *ApJ. Letters* **729**, L2 (2011).
[3] T. Amano, F. Matsushima, T. Shiraishi, C. Schnozuka, R. Fujimori, and K. Kawaguchi, *J. Chem. Phys.* **137**, 134308 (2012).
[4] D. A. Neufeld, and M. G. Wolfire, *ApJ*, **706**, 1594 (2009).

Laboratory Spectroscopy of 1,2,3-butatriene cation $H_2CCCCH_2^+$ as a Candidate for a Diffuse Interstellar Band Carrier

M. Araki, S. Uchida, Y. Matsushita, and K. Tsukiyama

Department of Chemistry, Faculty of Science Division I, Japan

The diffuse interstellar bands (DIBs) were first discovered in the optical absorption spectra on stars in about 1920. Carbon chain molecules were suggested as candidates for DIB carriers in 1977 by Douglas [1]. Although large number of carbon chain molecules have been tested based on this suggestion, DIBs have not been identified yet. In this study, an emission spectrometer with hollow-cathode glow discharge and extended negative glow discharge systems produced a spectrum including the 4905 Å band from 2-butyne $H_3C-C\equiv C-CH_3$ as the precursor. Photoelectron spectroscopy of H_2CCCCH_2 [2] indicated that the simple carbon chain molecule $H_2CCCCH_2^+$ (1,2,3-butatriene cation) produces a $^2B_{3u}-X^2B_{2g}$ electronic transition at 4905 Å. However, the 4905 Å band does not match the reported DIBs. If the assignment of the 4905 Å band to $H_2CCCCH_2^+$ is true, it becomes doubtful as to whether carbon chain molecules are carriers of DIBs.

We confirmed the assignment of the band by using chemical and physical investigations [3]. The chemical behavior of the band was tested using several kinds of precursors in the discharge. Physical investigation by electrode switching indicated that the origin of the 4905 Å band has a positive charge. The accompanying bands at around 4905 Å were analyzed by the double-minimum torsional potential mode as shown in Figure 1. All of the investigations and the analysis gave the consistent results with the assignment. Therefore the observed 4905 Å band was surely assigned to $H_2CCCCH_2^+$. This cation does not correspond to the currently-known DIBs, even though this is one of the basic unsaturated carbon chain molecules. A question about carbon chain molecules as carriers of DIBs may be raised.
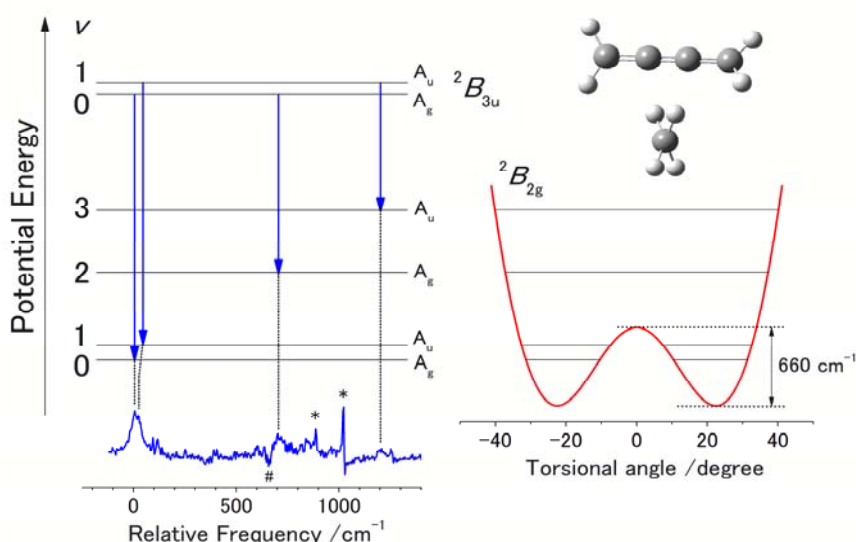

Figure 1: The observed vibronic bands of the $^2B_{3u}-X^2B_{2g}$ electronic transition of $H_2CCCCH_2^+$ (left). The vibrational structure and the obtained double-minimum torsional potential (right).

References

[1]   A.E. Douglas, 1977, Nat 269, 130.
[2]   F. Brogli, *et al.*, 1974, Chem. Phys. 4, 107.
[3]   M. Araki, S. Uchida, Y. Matsushita, & K. Tsukiyama, 2014, Journal of Molecular Spectroscopy 297, 51.

Atomic-scale insights of the chemistry occurring in the interstellar medium. Clues from quantum chemical methods

A. Rimola[1]

[1]*Departament de Química, Universitat Autònoma de Barcelona, Catalonia, Spain*

The existence of cosmic molecules is of great relevance due to due their connection with the chemical evolution steps occurring in the universe [1,2]. A key role of this chemical evolution is played by gas-grain processes, which involve in part the interaction of gaseous molecules with dust particles and the subsequent chemical reactivity. The current knowledge of these gas-grain processes is mostly based on spectroscopic observations, helped by laboratory experiments and astrochemical models. This combination has been fruitful to determine some important phsyico-chemical properties, such as the chemical activity of the gas-grain interactions [3,4]. However, this approach cannot provide atomic-scale information such as the precise mechanistic steps of the reactions or the exact role played by the grains, a serious limitation to fully understand the basic physical and chemical steps that lead to the chemical complexity in space. This information gap can be filled in by using theoretical calculations based on quantum mechanical approaches [5]. In this talk, examples on how these theoretical calculations can contribute to interstellar-related chemical studies from providing an atomistic interpretation of the gas-grain processes will be presented. In particular, results obtained from simulations devoted to the formation of H_2 through H recombination on bare olivine surfaces (Figure 1a) [6] and to the formation of interstellar H_2CO and CH_3OH through H additions to CO on water ice particles (Figure 1b) [7] will be shown. Results will provide both structural details of the systems involved and energetic data of the reactions, which in turn can be used as input parameters in astrochemical modelling studies. Estimates of tunneling contributions by calculating both tunneling crossover temperatures and transmission coefficients will also be presented.
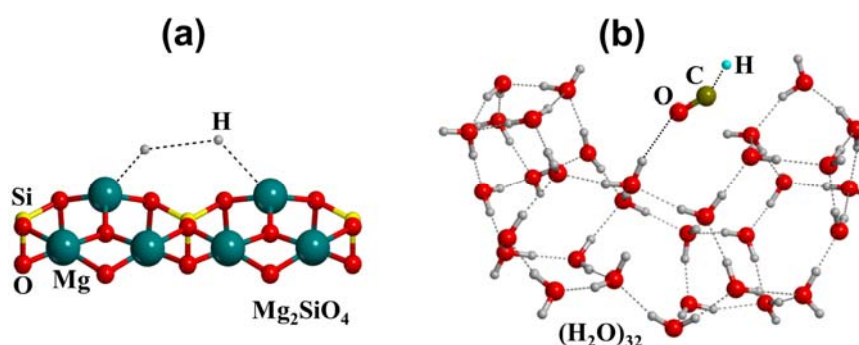

Figure 1: Transition state of (a) H_2 formation from H recombination on a Mg-rich olivine surface model and (b) HCO formation from H addition to CO on a water ice particle model.

References

[1]   A.G.G.M. Tielens, 2013, Rev. Mod. Phys. 85, 1021.
[2]   P. Caselli, & C. Ceccarelli, 2012, A&AR 20, 1.
[3]   L. Colangeli, T. Henning, J.R. Brucato, et al. 2003, A&AR 11, 97.
[4]   T. Hama & N. Watanabe, 2013, Chem. Rev. 113, 8783.
[5]   S.T. Bromley, T.P.M. Goumans, E. Herbst, A.P. Jones & B. Slater, 2014, Phys. Chem. Chem. Phys. 16, 18623.
[6]   J. Navarro-Ruiz, M. Sodupe, P. Ugliengo & A. Rimola, 2014, Phys. Chem. Chem. Phys.16, 17447.
[7]   A. Rimola, V. Taquet, P. Ugliengo, N. Balucani & C. Ceccarelli, submitted to A&A.

Molecular collisions for astrophyics: Theory and experiments

Laurent Wiesenfeld[1]

[1] *Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France*

&

CNRS, IPAG, F-38000 Grenoble, France

In order to retrieve actual molecular abundances from astrophysical observations of molecular spectral lines, knowledge of the rotational levels excitation schemes is essential, in order to go beyond the Local thermodynamical Equilibrium approximation. Actual excitation results of a trade-off between photon excitation and collisional excitation by the main constituents of the interstellar gas, molecular hydrogen, and, to a lesser extent, atomic hydrogen and helium. These rates are almost always obtained from theoretical investigations, by computing classical or quantum dynamics of the interaction of molecules with these colliders.

Many types of molecules are observed and consequently, many collisions have been studied recently, like hydrides [1], water and its isotopomers [2], organic molecules [3]. Also, conditions for absorption against the cosmic background or masing have been examined.

In order to assess the quality of the computations, a systemic comparison with experiments is being undertaken. Observables are mainly integral or differential cross-sections [4], as well as pressure broadening cross sections [5].

All comparisons show an agreement between theory and experiments, thereby validating the quality of the Potential Energy Surfaces and the quantum scattering computations.

References

[1] Mathieu Lanza, Yulia Kalugina, Laurent Wiesenfeld and François Lique, 2014 J. Chem. Phys., 140, 064316
(2) A. Faure, L. Wiesenfeld, Y. Scribano and C. Ceccarelli,2012 Mon. Not. R. Astron. Soc. 420, 699–704.
[3] L. Wiesenfeld‹ and A. Faure, 2013, Mon. Not. R. Astron. Soc., 432, 2573-8.
[4] C.-H. Yang, G. Sarma, D. H. Parker, J. J. ter Meulen, and L. Wiesenfeld, 2011, J. Chem. Phys, 134, 204308.
[5] Brian Drouin and Laurent Wiesenfeld,2012, Phys. Rev A86, 022705.

Progress in Chemical Simulations with Gas and Surface Chemistry

E. Herbst[1]

[1]*Department of Chemistry, University of Virginia, United States*

Astrochemistry is undergoing a period of growth spurred on by a generation of new and more powerful telescopes. Analysis of both current and future data requires, in my view, better and more detailed chemical simulations for diverse sources in both our galaxy and others. A few examples of the need for better simulations will be given. I will then talk about our research program in developing improved gas-grain chemical simulations The grain surface chemistry will be emphasized because this field of chemistry is still much less certain than gas-phase chemistry for a variety of reasons. Following a history of techniques used to mimic surface/ice chemistry in interstellar sources, I will concentrate on the most detailed stochastic method used to date: the continuous-time random-walk approach [1]. But not only must the chemistry be treated better, the physics must also be improved, and I will discuss our preliminary efforts to develop models including both gas-grain chemistry and 3D magnetohydrodynamics. Initial calculations show that there is a severe problem in the treatment of molecular hydrogen in interstellar ices. A possible resolution of this problem will be discussed [2]. Despite all of these improvements, it may well be that chemical simulations will not be able to keep up with the overwhelming number of data in the ALMA age, and I discuss several alternatives.

References
[1]   Q. Chang, & E. Herbst, 2014, ApJ 787, 135.
[2]   U. Hincelin, Q. Chang, & E. Herbst, 2014, A&A, submitted.

Investigation of ^{13}C isotopic fractionation of HC$_5$N in TMC-1

K. Taniguchi,[1, 2] S. Takano,[2, 3] H. Ozeki,[1] N. Sakai,[4] S. Yamamoto,[4]
F. Nakamura,[3, 5] and Z45 group

[1]*Department of Environmental Science, Faculty of Science, Toho University, Japan*
[2]*Nobeyama Radio Observatory, NAOJ, Japan*
[3]*Department of Astronomical Science, School of Physical Science, The Graduate University*
for Advanced Studies, Japan
[4]*Department of Physics, Faculty of Science, The University of Tokyo, Japan*
[5]*Devision of Theoretical Astronomy, NAOJ, Japan*

Around 180 molecules have been detected in the interstellar medium (ISM) or circumstellar shells until now, and approximately 40 % of the molecules in space are classified into carbon-chain molecules. Therefore, it is important for astrochemistry to study these molecules. The formation mechanisms of some of the carbon-chain molecules, which are abundant in the ISM, have been studied by observations of ^{13}C isotopic fractionation of these molecules (N. Sakai *et al*. summarized [1]), including HC$_3$N [2], which is the shortest carbon-chain molecule of cyanopolyynes. This observation aims at clarifying the formation mechanism of HC$_5$N, which is the second shortest carbon chain of cyanopolyynes.

We used the 45m telescope of Nobeyama Radio Observatory, and conducted observation in 2014 March and April. We used the Z45 receiver, which is the low noise receiver at 45 GHz region, and analyzed by a smoothed bandpass calibration method [3]. The observed source was the cyanopolyyne peak in Taurus Molecular Cloud -1 (TMC-1) (R.A. = 4^h 41^m 42^s.29, Decl. = 25° 41' 27".0, J2000). Normal species and five ^{13}C isotopologues of HC$_5$N were measured using the $J = 16 - 15$ rotational transition at 42 GHz region. We got the spectra with the signal-to-noise ratio between 12 and 14.5 (Fig.1).

There is no clear ^{13}C isotopic fractionation among the five ^{13}C isotopologues of HC$_5$N. From these observational results, we concluded that the growth of the carbon chain of HC$_3$N, which was considered as one of the most possible formation mechanisms of HC$_5$N, HC$_7$N and so on, may not be an important formation mechanism of HC$_5$N, because ^{13}C isotopic fractionation of HC$_5$N does not clearly reflect that of HC$_3$N. We think at the present stage that HC$_5$N is presumably formed by reaction with nitrogen atom [4], not with CN radical as in the case of HC$_3$N. Therefore, cyanopolyynes are probably not mainly produced by the sequential carbon-chain growth of the shorter member.

Figure 1: The spectra of five ^{13}C isotopologues of HC$_5$N

References

[1] N. Sakai *et al*., *J. Phys. Chem. A*, **117(39)**, 9831 (2013). [2] S. Takano *et al*., *Astron. Astophys.*, **329**, 1156 (1998). [3] H. Yamaki *et al*., *PASJ*, **64**, 118 (2012). [4] A. J. Markwick *et al*., *ApJ*, **535**, 256 (2000).
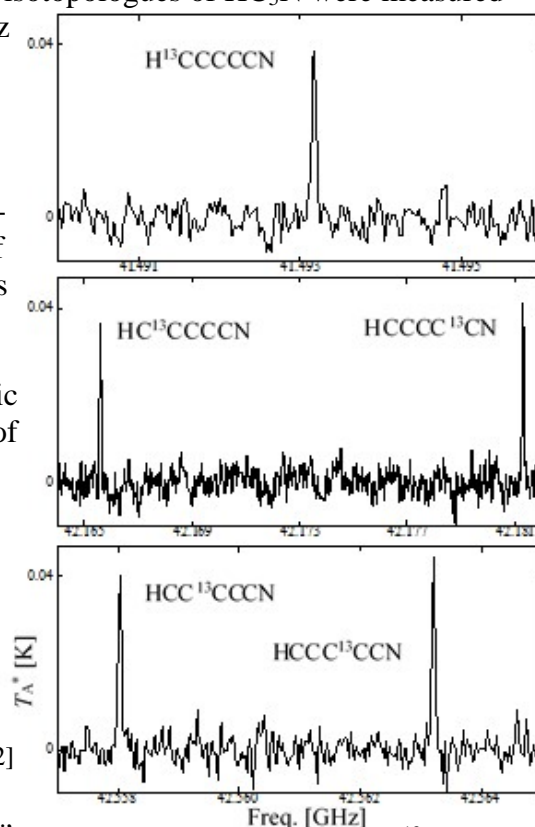
DNC/HNC Ratio in the IRDC clump G34.43+00.24 MM3

T. Sakai,[1] N. Sakai,[2] K, Furuya,[3] Y. Aikawa,[4] T. Hirota,[5,6]
J. B. Foster,[7] P. Sanhueza,[5,8] J. M. Jackson,[8] and S. Yamamoto[2]

[1]*Graduate School of Informatics and Engineering, The University of Electro-Communications, Japan*
[2]*Department of Physics, Graduate School of Science, The University of Tokyo, Japan*
[3]*Leiden Observatory, Netherlands*
[4]*Department of Earth and Planetary Sciences, Kobe University, Japan*
[5]*National Astronomical Observatory of Japan, Japan*
[6]*Department of Astronomical Sciences, Graduate University for Advanced Studies, Japan*
[7]*Department of Astronomy, Yale University, USA*
[8]*Institute for Astrophysical Research, Boston University, USA*

In cold molecular clouds, deuterium is known to be fractionated into molecules, except for HD. The equilibrium deuterium fractionation ratios of molecules depend on temperature, where lower temperature leads to higher deuterium fractionation ratios. Sakai et al. (2012) observed the DNC/HNC ratio toward 16 clumps, including the infrared dark clouds (IRDCs) and high-mass protostellar objects (HMPOs), by using the Nobeyama Radio Observatory 45 m telescope. Sakai et al. found that the DNC/HNC ratio of some IRDCs is lower than that of the HMPOs, although the temperature of the IRDCs is lower than that of the HMPOs. In order to investigate the origin of the low DNC/HNC ratio of the IRDCs, we have observed the IRDC clump G34.43+00.24 MM3, which has the lowest DNC/HNC ratio in the sample of Sakai et al. (2012), in the DNC J=3-2 and HN13C J=3-2 lines with the Atacama Large Millimeter/submillimeter Array. Then, we have found that the DNC emission is stronger than the HN13C emission toward most parts of this clump. The DNC/HNC ratio averaged within the 15"x15" area around the phase center is derived to be higher than 0.08. This ratio is much higher than that in the previous single-dish observation (~0.003). It seems likely that the DNC and HNC emission observed with the single-dish telescope traces lower density envelopes, while that observed with ALMA traces higher density and highly deuterated regions. We have compared the observational results with the model calculation results in order to investigate the behavior of DNC and HNC in the dense cores. Taking these results into account, we have reinterpreted the previous single-dish survey results.

References

[1]   Sakai, T., Sakai, N., Furuya, K., Aikawa, Y., Hirota, T., Yamamoto, S. 2012, ApJ, 747, id. 140

Optically thick H<small>I</small> in the local interstellar medium: An alternative to "dark gas"

Y. Fukui,[1]

[1]*Department of physics, Nagoya University, Japan*

Hydrogen is the main element in the Universe and it is of fundamental importance to understand the behavior of atomic and molecular hydrogen. The 21cm line of atomic hydrogen is generally assumed to be optically thin in text books on astronomy. This implies that the HI intensity is exactly proportional to the total HI gas column density. A comparison between HI intensity and dust opacity obtained by *Planck*, however, shows a poor correlation within 200 pc of the sun, which is inconsistent with optically thin HI if the dust properties are uniform in the local space. We have found that the HI gas at the highest dust temperature obeys the optically thin limit, whereas most of the HI gas at lower dust temperature shows lower intensity than expected from the dust opacity, suggesting significantly high optical depth of the HI line. We present a new method to calculate HI spin temperature T_s and HI opacity by coupling the two equations of radiation transfer and HI opacity based on the *Planck* dust properties. The results show that 70% of the local HI gas has T_s=15 – 40 K and HI optical depth of 0.5 – 2.0 for typical N_{HI} column density around 10^{21} cm^{-2}. Typical density of the HI is then calculated to be ~100 cm^{-3}, which lies between those of the classical HI and CO gas. We argue that such cold dense HI gas is a possible alternative as the dark gas candidate which has been often debated as CO-free H_2 gas.

Distributions of molecules in the circumnuclear disk and surrounding starburst ring in the Seyfert galaxy NGC 1068 observed with ALMA

S. Takano,[1,2] T. Nakajima,[3] K. Kohno,[4,5] N. Harada,[6] E. Herbst,[7]
Y. Tamura,[4] T. Izumi,[4] A. Taniguchi,[4] and T. Tosaki[8]

[1]*Nobeyama Radio Observatory, National Astronomical Observatory of Japan, Japan*
[2]*Department of Astronomical Science, The Graduate University for Advanced Studies (SOKENDAI), Japan*
[3]*Solar-Terrestrial Environment Laboratory, Nagoya University, Japan*
[4]*Institute of Astronomy, The University of Tokyo, Japan*
[5]*Research Center for Early Universe, School of Science, The University of Tokyo, Japan*
[6]*Max Planck Institute for Radio Astronomy, Germany*
[7]*Department of Chemistry, University of Virginia, USA*
[8]*Department of Geoscience, Joetsu University of Education, Japan*

We report distributions of several molecular transitions including shock and dust related species (^{13}CO $J = 1$-0, $C^{18}O$ $J = 1$-0, ^{13}CN $N_J = 1_J$-0_J, CS $J = 2$-1, SO $N_J = 2_3$-1_2, HNCO $J_{Ka,Kc} = 5_{0,5}$-$4_{0,4}$, HC$_3$N $J = 11$-10, 12-11, CH$_3$OH $J_K = 2_K$-1_K, and CH$_3$CN $J_K = 6_K$-5_K) in the nearby Seyfert galaxy NGC 1068 observed with ALMA [1]. The central ~1 arcmin (~4.3 kpc) of this galaxy was observed in the 100 GHz region with an angular resolution of ~4" x 2" (290 pc x 140 pc) to study the effects of an active galactic nucleus and its surrounding starburst ring on molecular abundances. We present images (e.g., Fig. 1) and report a classification of molecular distributions into three categories: (1) molecules concentrated in the circumnuclear disk (CND), (2) molecules distributed both in the CND and the starburst ring (CS and CH$_3$OH), and (3) molecules distributed mainly in the starburst ring (^{13}CO and $C^{18}O$). In the starburst ring, the relative intensity of CH$_3$OH at each clumpy region is not consistent with those of ^{13}CO, $C^{18}O$, or CS. This is probably caused by the unique formation mechanisms of CH$_3$OH.
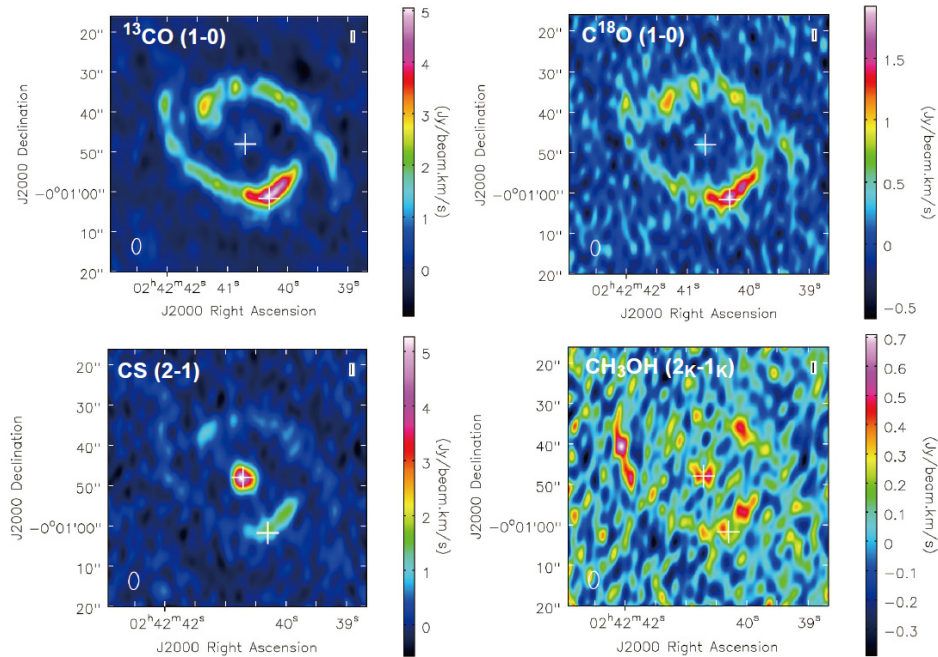

Figure 1: Images of integrated intensity of ^{13}CO, $C^{18}O$, CS, and CH$_3$OH. The central position and the ^{13}CO $J = 3$–2 intensity peak at the south-west position in the starburst ring [2] are indicated with white crosses.

References   [1]   S. Takano et al., 2014, PASJ 66, 75.   [2]   T. Nakajima et al., PASJ submitted.

Variations in the CO_2/H_2O ice abundance ratios in nearby galaxies

M. Yamagishi[1], H. Kaneda[1], S. Oyabu[1], D. Ishihara[1], T. Onaka[2], T. Shimonishi[3], K. Furuya[4], Y. Aikawa[3], T. Suzuki[5]

[1]*Graduate school of science, Nagoya University, Japan*
[2]*Graduate school of science, The University of Tokyo, Japan*
[3]*Graduate school of science, Kobe University, Japan*
[4] *Leiden Observatory, Leiden University, The Netherlands*
[5] *SRON, The Netherlands*

Absorption features due to interstellar ices are observed in near- and mid-infrared spectra. Among various parameters about ices, we focus on a CO_2/H_2O ice abundance ratio which effectively reflects the ice-forming interstellar environment. In past studies, CO_2/H_2O ratios show large variations from object to object in our Galaxy. The cause of the variations is, however, still under debate. In this study, we examine variations in CO_2/H_2O ratios in nearby galaxies based on the AKARI near-infrared (2.5-5.0 μm) spectra for 1031 regions in 158 galaxies. The CO_2/H_2O ratios in the galaxies are in a range of 0.05-0.30. In the dataset, we find a positive correlation between the CO_2/H_2O ratios and the Brα/PAH 3.3 μm ratios which depend on the massive star-forming activities. Furthermore, we find a positive correlation between the CO_2/H_2O ratios and the specific star formation rates of the galaxies, which depend on the evolutionally stage of the galaxies. These results suggest that CO_2/H_2O ratios are high in active star-forming regions in young galaxies. It is possible that cosmic-ray induced UV photons due to the massive star-forming activities contribute to the CO_2 formation. Finally, effects of cosmic-ray on the CO_2/H_2O ratio are examined by using a gas-grain chemical model. We also show initial results of the model calculations.
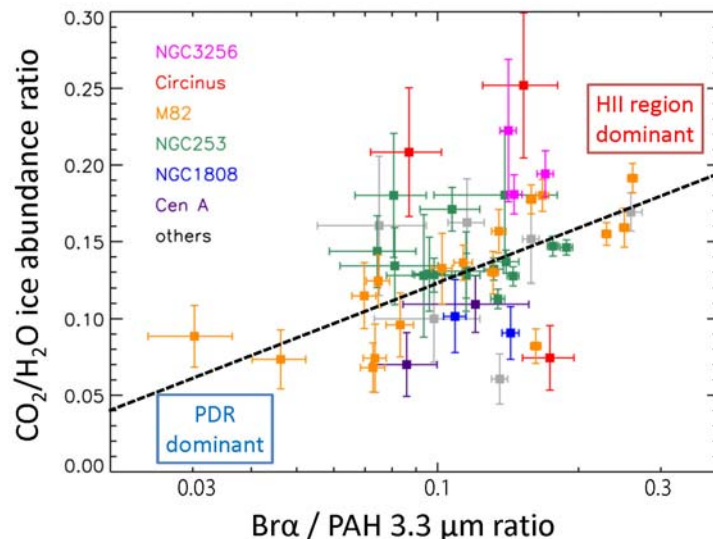
Figure 1: CO_2/H_2O ice abundance ratios plotted against the Brα/PAH 3.3 μm ratios for all the regions where H_2O and CO_2 ices are detected. The dashed line represents the best-fit relation in M82.

Experiments for ionic cluster formation using an ion drift-tube with selected-ion injection

Y. Nakai[1], H. Hidaka[2], N. Watanabe[2] and T. M. Kojima[3]

[1] *RIKEN Nishina Center for Accelerator-Based Science, Japan*
[2] *Institute of Low Temperature Science, Hokkaido University, Japan*
[3] *Atomic Physics Laboratory, RIKEN, Japan*

Ion-induced nucleation has been regarded as one of important processes for gas-phase nucleation. It is because a free-energy barrier on fine-particles growth decreases by attractive polarization forces between ions and atoms/molecules, as shown in the liquid drop model. Ionic cluster formation, particularly, is a key subject; it is an early stage of the ion-induced nucleation and governs the reactions on the subsequent stages.

The ionic cluster formation has been widely studied from various views of points. However, in many of experimental researches, the formation processes were triggered in a reactant gas including both parent molecules of core ions and ligand molecules using discharge, a pulsed electron beam, radiation sources, and so on. In such a situation, various ionic species can be produced with desired core ions. Therefore, initial ionic reactions were not well defined, generally. For elimination of reactions by undesired ions, we developed an experimental apparatus based on an ion drift-tube with selected-ion injection [1-4], where only specific ions are injected to a reaction cell.

The ions are extracted from an ion source and mass-selected using a Q-pole mass analyzer. Then, the ions are decelerated and injected into a gas filled in the drift tube. The ions are drifted with an average velocity defined by the electric field and the number density of the molecules in the drift tube. They concurrently react with molecules and ionic clusters are grown. Finally, produced ionic clusters are extracted from the drift tube. The masses of the extracted ionic clusters are analyzed with another Q-pole mass analyzer. Thus far, we have performed experiments for hydration of protons and NO^+ ions near room temperatures. In this symposium, we will exhibit our experimental apparatus and some of results for reaction equilibria of proton hydration.

References

[1]   H. Böhringer and F. Arnold, 1983, Int. J. Mass Spectrom. and Ion Phys. 49, 61.
[2]   T. M. Kojima et al., 1992, Z. Phys. D: At., Mol. Clusters 22, 645.
[3]   H. Tanuma et al., 2000, Rev. Sci. Instrum. 71, 2019.
[4]   Y. M. Ibrahim, et al, 2005, J. Am. Chem. Soc. 127, 7053.

Formation of H_3O^+ hydrate by NO^+ injection into drift tube filled with H_2O/buffer gases: separation between the contributions of two formation pathways by the drift time measurements
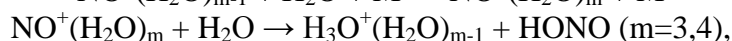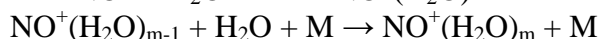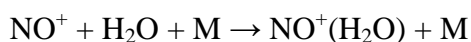
H. Hidaka,[1] Y. Nakai,[2] T. M. Kojima,[3] and N. Watanabe[1]

[1]Institute of Low Temperature Science, Hokkaido University, Japan
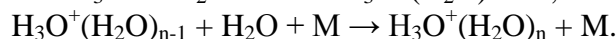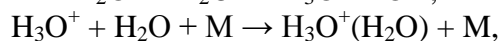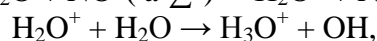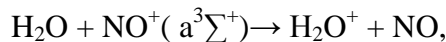*[2]Nishina Center for Accelerator-Based Science, RIKEN, Japan*
[3]Atomic Physics Laboratory, RIKEN, Japan

H_3O^+ hydrate, $H_3O^+(H_2O)_n$, is known to exist in the terrestrial ionosphere in quantities. As one of the important formation-pathway, $H_3O^+(H_2O)_n$ formation by the accompanying release of nitrous acid (HONO) from $NO^+(H_2O)_m$ which is formed by the successive hydration of NO^+:

$$NO^+ + H_2O + M \rightarrow NO^+(H_2O) + M$$
$$NO^+(H_2O)_{m-1} + H_2O + M \rightarrow NO^+(H_2O)_m + M$$
$$NO^+(H_2O)_m + H_2O \rightarrow H_3O^+(H_2O)_{m-1} + HONO \ (m=3,4),$$

has been often proposed and indeed studied in flow-tube experiments[1,2].

However, in those experiments, the parent NO^+ ions were produced by conventional electron impact method and thus contained the metastable NO^+. Since the ionization energy to the lowest metastable state of $NO^+(a^3\sum^+)$ is 15.66eV[3], H_2O in the ground state having the ionization energy of 12.65 eV can be ionized by the charge exchange with the metastable NO^+ ions. If the charge-exchange reaction occurs, the new formation pathway of $H_3O^+(H_2O)_n$ may open as follows:

$$H_2O + NO^+(a^3\sum^+) \rightarrow H_2O^+ + NO,$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH,$$
$$H_3O^+ + H_2O + M \rightarrow H_3O^+(H_2O) + M,$$
$$H_3O^+(H_2O)_{n-1} + H_2O + M \rightarrow H_3O^+(H_2O)_n + M.$$

The above processes are not appropriate in atmospheric environments. Therefore, in order to study the formation pathway of $H_3O^+(H_2O)_n$ via $NO^+(H_2O)_m$ alone, the formation of $H_3O^+(H_2O)_n$ through the charge-exchange reaction must be separated in the experiment.

Using a newly-developed ion drift-tube with selected-ion injection, we tried to separate the contribution of metastable NO^+ on the $H_3O^+(H_2O)_n$ formation. In our experiment, the NO^+ beam including the metastable NO^+ was injected in the H_2O/buffer gas filled drift-tube and the products were mass-analyzed by the quadrupole mass spectrometer. Furthermore, the drift time for the mass-selected $H_3O^+(H_2O)_n$ was also measured, which provides the chemical-reaction history of products experienced. That is, when measuring the drift-time spectrum of $H_3O^+(H_2O)_n$, the spectrum consists of two peaks depending on the different origins, $NO^+(H_2O)_m$ or H_2O^+ from the metastable NO^+. By varying the abundance of metastable NO^+, the origins of two peaks were identified, respectively.

References
[1]   N. Eyet, et al., 2011, J. Phys. Chem. A 115, 7582.
[2]   F. C. Fehsenfeeld, M. Mosesman, & E. E. Ferguson, 1971, J. Chem. Phys. 55, 2120.
[3]   D. L. Albritton, A. L. Schmeltekkopf, & T. F. Morgan, 1979, J. Chem. Phys. 71, 3271.

On the Radiolysis of Ethylene Ices by Energetic Electrons and Implications

Li Zhou,[1] Ralf I. Kaiser[2]

[1] Chemistry Department, Nanchang University, Nanchang , China, 330031
[2] Department of Chemistry, University of Hawaii, Honolulu, Hawaii, US, 96822

The investigation of the chemical evolution of the largest satellite of Saturn Titan offers a unique opportunity to understand the origin and chemical evolution of the Solar System especially of proto-Earth. In Titan's atmosphere, nitrogen (N_2, 98.4%) and methane (CH_4) are the dominating constituents with hydrocarbons such as acetylene (C_2H_2), ethylene (C_2H_4), diacetylene (C_4H_2), etc., several cyanides (HCN, HCCCN, C_2N_2), carbon dioxide (CO_2), carbon monoxide (CO), and water (H_2O) being present in trace amounts. The gaseous molecules might also agglomerate to aerosol particles and sequester to Titan's surface. In a pioneering study, Sagan and Thomas outlined that energetic cosmic ray particles can penetrate deep into the lower atmospheric layers. These energetic particles could incorporate part of their kinetic energy into chemical reaction and thus process simple organics in Titan's lower atmosphere. In a more recent study, Molina-Cubero et al. derived an energy deposition on Titan's surface of 4.5×10^9 $eVcm^{-2}s^{-1}$. However, the radiation processing of these simple organics by energetic electrons is not well understood. To shed light on this matter and to gain a comprehensive picture on the hydrocarbon chemistry, we present data on the interaction of ionizing radiation, in form of energetic electrons, with solid ices of acetylene, ethylene, and ethane (C2-ices) at temperatures between 10 and 70 K. We will also investigate to what extent the radiation processing can lead to the formation of polymer-like macromolecules, which could present building blocks of Titan's organic aerosol layers, via heterogeneous chemistry.

L. Zhou, W. Zheng, R.I. Kaiser, A. Landera, A. M. Mebel, M. C. Liang, Y.L. Yung, *Cosmic-Ray Mediated Formation of Benzene on the Surface of Saturn's Moon Titan.* ApJ 718, 1243-1251 (2010).
L. Zhou, S. Marry, M. Abplanalp, A.Turner, R.I. Kaiser, On the radiolysis of Ethylene ices by energetic electrons and Implications to the Extraterrestrial Hydrocarbon Chemistry. ApJ 790, 38, 1-10 (2014).

Hydrogen atom desorption from water ice by 157 nm irradiation at 8-130 K

A. Yabushita[1] and M. Yamazaki[2]

[1] Department of Molecular and Material Sciences, Kyushu University, Japan
[2] Department of Molecular Engineering, Kyoto University, Japan

Interstellar grains typically consist of silicates or carbonaceous cores and are covered predominantly by water ice. In a diffuse cloud, the ice mantle is subjected to vacuum-ultraviolet (VUV) irradiation [1]. Photodissociation of H_2O molecules yielding H + OH fragments is the major channel in the gas phase photolysis for 105–185 nm. The excess energy over and above that required to break the HO–H bond appears predominantly as product translation:

$$H_2O(ads) + h\nu \rightarrow H^* + OH, \Delta H = 5.6 \text{ eV} \tag{1}$$
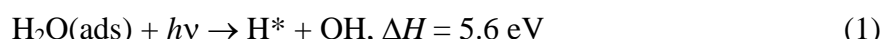
where H* represents a highly translationally excited H photoproduct with a few eV. Energetic hydrogen atoms could drive chemical reactions that are endothermic, or possess activation energy barriers.

In an ultrahigh vacuum chamber, amorphous solid water (ASW) and polycrystalline ice (PCI) films were prepared on a cooled platinum substrate [2]. A water ice film was photodissociated at 157 nm with a pulsed laser. Resonance-enhanced multiphoton ionization was used to probe H atom photoflagments. Translational energy distributions of H atoms were obtained by analyzing the time-of-flight (TOF) mass spectra of H atoms.

TOF spectra of H atoms from photodissociation of ASW and PCI ice films were measured at 8 K. Both of them could be characterized by a combination of three (fast(A, T_{trans} = 4750 K), medium(B, T_{trans} = 625 K), and slow(C, T_{trans} = 100 K) different Maxwell-Boltzmann energy distributions. Each TOF spectrum consists of the same three components, but contributions of each component are different.

TOF spectra were measured in the range of 8-130 K. The average translational temperatures of the component (A) and (B) didn't change, but that of the component C increased with substrate temperatures above 90 K. Integrated H signal intensities of the component (A) and (B) were nearly constant in the range of 8-70 K. Molecular dynamics simulation shows the H atom photodesorption probability in the top four monolayers does not depend on ice temperature at 10, 20, 30 and 90 K [3]. These results imply that the component (A), (B) and (C) come from the topmost H_2O layer, some layers just below the topmost H_2O layer and the deeper monolayers, respectively (Fig. 1).
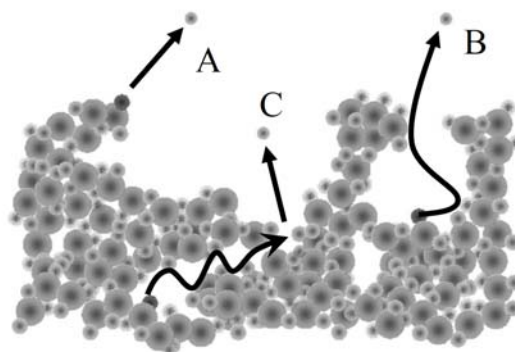

Fig. 1　Desorption mechanisms for hydrogen atoms from photodissosiation of water ice

References
[1] A. Yabushita, T. Hama, & M. Kawasaki, 2013, J. Photochem. Photobiol. C. 16, 46
[2] A. Yabushita, D. Kanda, N. Kawanaka, M. Kawasaki, M. N. R. Ashfold, 2010, J. Chem. Phys. 125, 133406
[3] C. Arasa, S. Andersson, H. M. Cuppen, E. F. van Dishoeck, & G.-J. Kroes, 2010, J. Chem. Phys. 132, 184510

Photo-induced synthesis of interstellar organic matter: Volatile compounds and texture of organic residues

S. Tachibana[1], T. Hama[2], Y. Endo[1], L. Piani[1], H. Yurimoto[1] and A. Kouchi[2]

[1]*Department of Natural History Sciences, Hokkaido University, Jaoan*
[2]*Low Temperature Institute, Hokkaido University, Japan*

Various organic compounds, discovered in the interstellar medium, are the products of photo-induced low-temperature chemistry in dense clouds. These organic compounds are one of the precursors of the solar system, and are preserved in solar-system small bodies (comets and asteroids). Investigation of extraterrestrial organic matter has shown that organic matter with enrichment of D and 15N could be originated in low-temperature environments, but it is not clear how low-temperature dense-cloud organic matter evolve in the early solar system before incorporation into small bodies.

In order to simulate the photo-induced synthesis of interstellar organic matter and its subsequent thermal evolution, a new experimental apparatus, PICACHU (Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University), was developed. In the presentation, we report (1) in-situ analyses of volatile species sublimated from UV-irradiated ice during with increasing temperature and (2) laser- and atomic-force microscope observation of microtexture of organic residues.
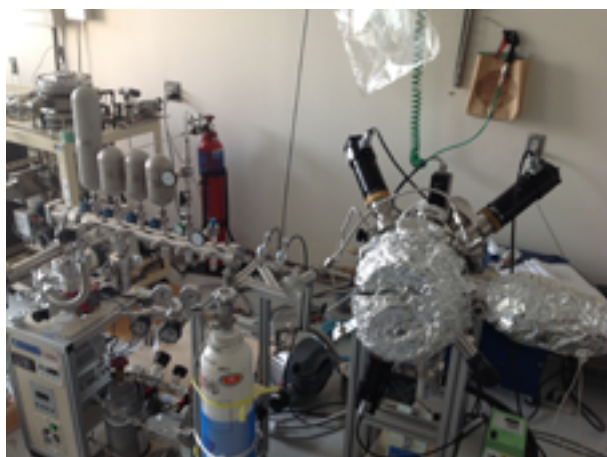

Figure 1: PICACHU, Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University.

Reproductive experiment of organic formation by catalytic reactions in the solar nebula

Y. Kimura,[1] N. Watanabe,[1] A. Tsuchiyama, [2] H. Nagahara, [3] and A. Kouchi[1]

[1]*Institute of Low Temperature Science/Hokkaido University, Japan*
[2] *Division of Earth and Planetary Sciences, Kyoto University, Japan*
[3] *Department of Earth and Planetary Science, The University of Tokyo, Japan*

At the transition phase from molecular cloud to the solar system, organic molecules on the surface of cosmic dust particles experienced environmental changing in wide range, i.e., increasing temperature and pressure. Then, some molecules released from the surface of dust and the others reacted to be more complex organic molecules by assistance of catalytic dust. ALMA is able to detect distribution profiles of sublimated molecules into gas phase in both of molecular cloud and extrasolar nebula with high spatial resolution and high sensitivity. Recent high-resolution proves are also able to analyze the fine composition of meteorite and stardust samples and finding many kinds of organic materials. These organics may contributed to the primordial organic system of the Earth. Unfortunately, however, there is no real evidence about the process of organic formation in a solid phase. Although some experimental studies have been performed using dust analogues, the elementary steps in molecular evolution in the environment from molecular clouds to nebulae are still uncertain.

Catalytic reactions such as the Fischer-Tropsch type and Haber-Bosch type reactions produce organic molecules efficiently on the surface of dust including iron at temperature above 573 K [1,2]. Recently, we developed a new experimental system to test the catalytic chemical reactions in the early nebula environment [lower temperature (100-500 K) and pressure (10^{-3}-10^{0} Pa)] using a substrate of magnesium silicate or iron. Figure 1 shows a photo of the system, which has a temperature controllable substrate made of gold. Silicate or iron with a thickness of submicron is deposited onto the substrate and used as a substrate for the catalytic reaction experiment. Molecules on the substrate are detected by a Fourier-transform infrared spectrometer (FT-IR). Released molecules into the gas phase detect by quadrupole mass spectrometers (Q-MSs). Here, we will show the preliminary results of the project.

Figure 1: Photo of the newly developed system for catalytic reaction experiment. This system has differential pumping system, a temperature-controlled substrate (26-800 K), FT-IR, two Q-MSs and gas flow controller.

References

[1]   H. G. M. Hill, & J. A. Nuth, 2003, Astrobiology 3, 291.
[2]   J. A. Nuth, N. M. Johnson, & S. Manning, 2008, ApJ 673 L225.

High precision measurement of isotopic composition of amino acids
by LC x GC/C/IRMS

Y. Takano, Y. Chikaraishi, and N. Ohkouchi

Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Nitrogen isotopic composition of amino acids has been widely applied to biochemical and geochemical studies in an attempt to trace nitrogen source and transformation processes. For accurate isotope analysis of individual amino acids, we validated a preparative method involving the isolation of underivatized amino acids by ion-pair chromatographic separation and confirmed the consistency of nitrogen isotope composition. Ion-pair reversed-phase liquid chromatography coupled with electrospray ionization mass spectrometry (LC/ESI-MS) and gas chromatography/ combustion coupled with isotope ratio mass spectrometry (GC/C/IRMS) were conducted for the purpose of separation of underivatized amino acids and nitrogen isotopic analysis, respectively. Firstly, we confirmed the resolution of proteinogenic and non-proteinogenic amino acids by the preparative ion-pair LC separation. Diagnostic product ions determined by mass spectrometry can support the rapid identification of individual amino acids in screening analyses. Secondly, we observed no dependency on nitrogen isotopic composition for the injection amount of underivatized amino acids and even for different chemical formula including neutral, acidic, sulfur-containing, heterocyclic, and aromatic species. The present method and strategy of LC coupled with GC/C/IRMS (i.e., LC x GC/C/IRMS) are useful for the high precision determination of the nitrogen isotopic composition of amino acids, in conjunction with an appropriate pre-treatment of chromatographic procedures.
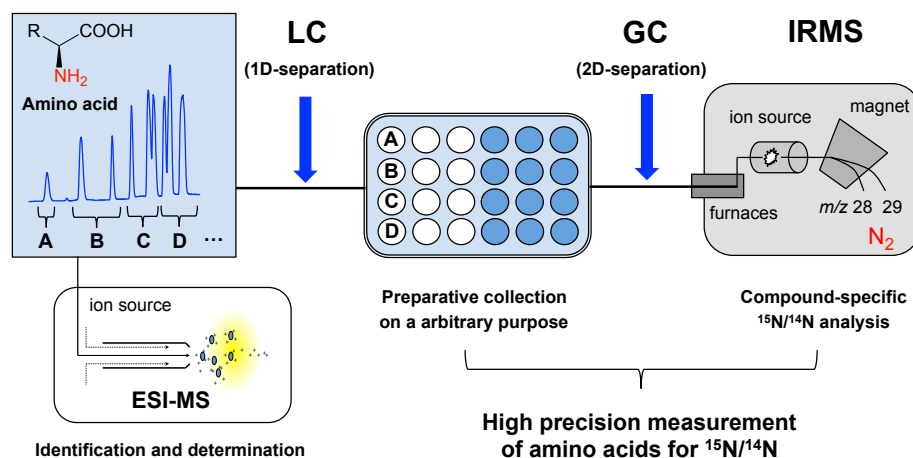
Figure 1: Scheme and developed system of liquid chromatography x gas chromatography/ combustion/ isotope ratio mass spectrometry (LC x GC/C/IRMS) for precise compound-specific isotope analysis (CSIA) and enantiomer-specific isotope analysis (ESIA) of amino acids.

References

[1] Takano et al., 2009. *Anal. Chem.*, **81**, 394-399.
[2] Chikaraishi et al., 2010. *Earth, Life, and Isotopes* (Kyoto Univ Press), 367-386.
[3] Takano et al., 2010. *Rapid Comm. Mass Spectrometry* **24**, 2317-2323.

Formation of clathrate hydrate from amorphous ice during warming

R. Netsu, T. Ikeda-Fukazawa

Department of Applied Chemistry, Meiji University, Japan

Water molecules are condensed on dust grains in interstellar molecular clouds and protester nebulae. The water exists as amorphous ice in the cold clouds and is transformed into various structures depending on thermal conditions and compositions with various deposited molecules. Blake *et al*. [1] proposed the presence of CO_2 clathrate hydrate in cometary ice. From the results using the transmission electron microscopy (TEM) and fourier transformed infrared spectroscopy (FT-IR), they showed the phase transition of vapor deposited amorphous ice including CO_2 and CH_3OH into type-II clathrate hydrate at around 120 K.

Clathrate hydrates are inclusion compounds consisting of water molecules and a variety of guests molecules. Most clathrate hydrates form one of two distinct crystallographic structures, type-I and –II, depending on the sizes and shapes of the guest molecules. The cubic unit cell of type-I clathrate hydrate contains 46 water molecules in a framework of two dodecahedral and six tetrakaidecahedral cages, and that of type-II clathrate hydrate contains 136 water molecules in a framework of 16 dodecahedral and eight hexakaidecahedral cages. The structure of CO_2 clathrate hydrate formed under a high pressure condition is type-I [2]. For the hydrate from the vapor deposited amorphous ice [1], the structure is type-II due to the help-gasses effect of CH_3OH. For the CO_2 clathrate hydrate grown epitaxially on a hydrate in low pressure conditions, the structure depends on the structure of the hydrate as the substrate [3]. In order to investigate the formation mechanisms of pure CO_2 clathrate hydrate in low pressure conditions, we analyzed infrared spectra of vapor deposited amorphous ice including CO_2 during the warming.

The gas mixtures of H_2O and CO_2 with 1:1 in $H_2O:CO_2$ were deposited with 10±8 μm/min onto a substrate of oxygen-free copper at 43 K. After the deposition, the substrate was warmed from 43 to 160 K with a rate of 1-4 K/min. During the warming, the infrared spectra were measured at intervals of 2 K using Shimadzu IRPrestige-21.

The results show that the spectral features change during the warming. From the analysis of the wave numbers of the O–H stretching modes of H_2O and the C–O asymmetric stretching modes of CO_2, significant changes were found at around 100 K. The wave numbers of the O–H stretching modes increase as the temperature increases at temperatures above 100 K, whereas those decrease in lower temperatures. The wave numbers of the C–O asymmetric stretching modes change significantly at around the temperature, and become almost constants at temperatures above 100 K. Furthermore, a remarkable gas release and exothermic temperature rise were also observed. The results suggest the crystallization of amorphous ice at around 100 K. The spectral feature of the C–O asymmetric stretching modes (i.e., the wave numbers, widths, and intensity ratio of two peaks) indicates that the crystal is the type-I clathrate hydrate. From the extrapolating the equilibrium line of the phase diagram of the H_2O-CO_2 system to our thermal condition, we propose the formation of CO_2 clathrate hydrate from the vapor deposited amorphous ice in vacuo.

References
[1]   D. Blake, L. Allamandola, S. Sandford, D. Hudgins, & F. Freund, 1991, Science 254, 548 .
[2]   T. Ikeda, S. Mae, O. Yamamuro, T. Matsuo, S. Ikeda, & R. M. Ibberson, 2000, JPC A 104, 10623 .
[3]   F. Fleyfel, & J. P. Devlin, 1991, JPC 95, 3811 .

Crystallization mechanism of silicate formed from supersaturated vapor investigated by *in-situ* IR measurement

S. Ishizuka[1, 2], Y. Kimura[2]

[1]*Department of Earth Science, Tohoku University, Japan*
[2]*Institute of Low Temperature Science, Hokkaido University, Japan*

We have developed a new experimental apparatus, named Free-flying *In-situ* infrared measurement of Nucleating nanoparticle Experimental (FINE) system, by which we can monitor dust imitated nanoparticles forming via homogeneous nucleation from evaporated vapor [1]. In the present study, we monitored crystallinity of Mg-bearing silicate (forsterite) formed from hot mixed vapor of Mg, SiO and O_2.

As shown in Figure 1, we found that just nucleated nanoparticles have less crystallized structure and crystallization proceeding as particles cool. Interestingly, crystallization occurred in a gas atmosphere at ~500 K, which is significantly lower than previously known crystallization temperature at 1000 K for amorphous silicate [2]. We concluded that, in our experiment, crystallization proceeded from supercooled nano "droplets", in which activation energy for crystallization is effectively reduced compared with that for crystallization from amorphous. Here we report the brand new crystallization mechanism and possibility that crystalline silicate formed from supercooled nano "droplets" in astronomical environment.
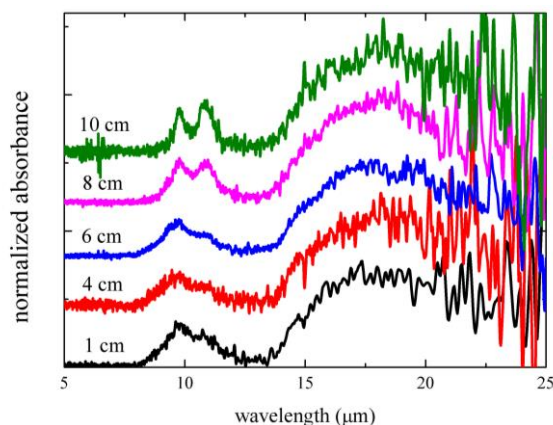

Figure 1: IR spectra measured at different height from evaporation source at 2300 ± 100 K. Focusing on silicate 10 μm band, just nucleated nanoparticles show broad feature attributable to less crystallized magnesiosilica and, in contrast, cooled nanoparticles show sharp crystalline feature. Crystallization effectively proceeded in 6-10 cm region where is estimated to be cooler than 500 K [3].

References

[1] S. Ishizuka, Y. Kimura & I. Sakon, 2014, ApJ, submitted

[2] Koike, C., et al. 2010, ApJ, 709, 983

[3] C. Kaito, 1991, Kemuri no Himitsu (only in Japanese), Kyouritsu Shuppan.

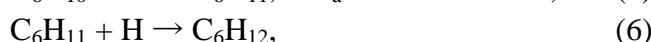# Hydrogen atom addition reactions to solid benzene by quantum tunnelling and its strong structure dependence

Tetsuya Hama,[1] Hirokazu Ueta,[1] Akira Kouchi,[1] Naoki Watanabe,[1] and Hiroto Tachikawa[2]

[1]*Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan*
[2]*Division of Materials Chemistry, Hokkaido University, Sapporo, Japan*

Aromatic and aliphatic hydrocarbons are abundant in the interstellar medium, and they carry a number of infrared features. Benzene (C_6H_6), the simplest aromatic hydrocarbon, has been detected in circumstellar environments such as post-asymptotic giant branch objects. Recent experimental studies reported that aromatic hydrocarbons such as C_6H_6 and naphthalene ($C_{10}H_8$) are efficiently produced in cold interstellar clouds via gas-phase reactions [1]. One might expect that the formation of saturated hydrocarbon can be easily achieved in these regions considering the overabundance of hydrogen in the interstellar medium. However, an activation barrier of about 20 kJ mol^{-1} generally exists for hydrogenation of aromatic hydrocarbon in order to break the aromaticity. At typical interstellar grain temperatures, i.e., at $T{\sim}10$–50 K, C_6H_6 weakly adsorbs on the surface of interstellar dust grain through van der Waals forces, which should only acts as an inert surface. Therefore, Hydrogen (H) atoms cannot add to the C_6H_6 by overcoming the activation barrier.

The present study shows that H atoms can efficiently add to C_6H_6 molecules on the surface of amorphous C_6H_6 at 10–50 K by quantum tunneling to form the cyclic saturated hydrocarbon, cyclohexane (C_6H_{12}).

$$C_6H_6 + H \rightarrow C_6H_7, \qquad E_a = 15.5 \text{ kJ mol}^{-1}, \qquad (1)$$
$$C_6H_7 + H \rightarrow C_6H_8, \qquad (2)$$
$$C_6H_8 + H \rightarrow C_6H_9, \qquad E_a = 6.3 \text{ kJ mol}^{-1}, \qquad (3)$$
$$C_6H_9 + H \rightarrow C_6H_{10}, \qquad (4)$$
$$C_6H_{10} + H \rightarrow C_6H_{11}, \qquad E_a = 10.5 \text{ kJ mol}^{-1}, \qquad (5)$$
$$C_6H_{11} + H \rightarrow C_6H_{12}, \qquad (6)$$

Here, E_a represents the activation barrier in the gas phase. The radical–radical recombination reactions (2), (4), and (6) should be barrier-less. We also report that the surface structure strongly determined the hydrogenation efficiency; hydrogenation was completely suppressed on a crystalline C_6H_6 surface.
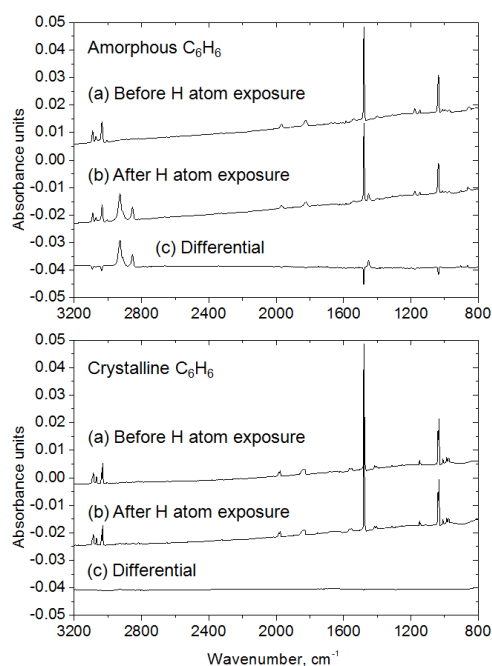

Fig.1 Infrared absorption spectra over the range of 3200–800 cm^{-1} for (upper panel) amorphous solid C_6H_6 and (lower panel) the crystalline C_6H_6 of 6×10^{15} molecules cm^{-2} at 20 K: (a) before and (b) after cold H atom exposure for 180 min. (c) differential spectra upon H atom exposure on the two surfaces ((b) − (a)).

References

[1] Jones et al., 2010, PNAS 108, 452.

H-D Substitution Reactions of Solid Ethanol with Atomic Deuterium via Quantum Tunneling at Low Temperatures

K. Osaka,[1] Y. Oba,[1] A. Kouchi,[1] and N. Watanabe[1]

[1]*Institute of Low Temperature Science, Hokkaido University, Japan*

It has been recently revealed that surface reactions on interstellar dust play an important role in enrichment of deuterated species observed in molecular clouds as compared with the cosmic D/H ratio. Previous experimental studies demonstrated that molecules such as formaldehyde, methanol, and methylamine can be deuterated by surface reactions with deuterium (D) atoms at very low temperatures [1-3]. This process most likely consists of the radical formation through H abstraction by D atoms (e.g., $CH_3OH + D \rightarrow CH_2OH + HD$) and the following D addition to the radical to form deuterated isotopologues (e.g., $CH_2OH + D \rightarrow CDH_2OH$). In molecular clouds, there are certainly more complex organic molecules than CH_3OH. For example, ethanol (CH_3CH_2OH) has been observed toward Sgr B2 (ethanol/methanol ~ 0.02 – 0.2) [4]. The correlation between such complex organic molecules and their reactivities with D atoms is still not experimentally investigated.

Here, we studied H-D substitution reactions of CH_3CH_2OH solid, which has more substituent groups than CH_3OH. The obtained results were compared with a previous theoretical study. The present study provides important insights into reactivity of other astronomical molecules with D atoms. Experiments were performed using the Apparatus for SUrface Reations in Astrophysics (ASURA), which mainly consists of a main chamber, and an atomic source chamber. Pure solid CH_3CH_2OH (10 K) was exposed to cold D atoms (100 K). Subsequently the change in the composition of ethanol was measured using FT-IR *in situ*.

H-D substitution occurred in the ethyl group but were negligible in the hydroxyl group, which is consistent with the methanol case [2]. We also found that the D-H substitution reaction on CD_3CD_2OD also occur when solid CD_3CD_2OD was exposed to H atoms at 10 K. We will further discuss the temperature dependence of each reaction at 10-30 K and the difference of reactivity for each functional group.

References

[1]   N. Watanabe & A. Kouchi,, 2008, Prog. Surf. Sci. 83, 439
[2]   A. Nagaoka, N. Watanabe, & Akira Kouchi, 2007, J. Phys. Chem. A 111, 3016
[3]   Y. Oba, *et al.*, 2014, Meteoritics & Planetary Science 49, 117
[4]   M. Ikeda, *et al.*, 2001, ApJ 560, 792

Hydrogen addition reactions of simple aliphatic hydrocarbons (C$_2$H$_2$ and C$_2$H$_4$) ~ clue to the formation mechanism of cometary C$_2$H$_6$~

H. Kobayashi,[1] N. Watanabe,[2] H. Hidaka,[2] T. Hama,[2] Y. Watanabe,[1] and H. Kawakita[1]

[1]*Koyama Astronomical Observatory, Kyoto Sangyo University, Japan*
[2]*Institute of Low temperature Science, Hokkaido University, Japan*

Comets are thought as remnants of planetesimals formed in the early solar nebula. Their nuclei consist of volatile ices and dust grains that were formed in the pre-solar molecular cloud and probably chemically altered in the proto-planetary disk. Although the outline of evolution from a molecular cloud to the disk is basically understood, detailed chemical processes are still in debate. To investigate the links between proto-planetary disk and the molecular cloud, we focused on cometary ethane (C2H6) which is considered to form through the hydrogen addition reactions on the cold grain surfaces. C2H6 and accetylene (C2H2), the parent molecule of the C2H6, have been observed in multiple comets since 1996 and their abundances relative to water (the major component of cometary ices) is ~0.001 with some variations [1]. Such variation might be caused by the difference in the mixing ratios between the materials originated in the molecular cloud and the disk-processed materials. C2H6 has never been detected in molecular cloud thus we evaluate experimentally the hydrogenation processes to form the C2H6 from C2H2 (C2H2 -> C2H3 -> C2H4 -> C2H5 -> C2H6). In the previous experimental studies [2], it was concluded that the reaction from C2H4 to C2H6 is considerably rapid than the reactions from C2H2 to C2H4 and it would be a reason for the absence of C2H4 in comets. To investigate those reactions quantitatively in realistic conditions of molecular clouds, we performed the laboratory measurements of hydrogen addition reactions of C2H2 and C2H4 on amorphous solid water.

The experiments were conducted by using laboratory setup for surface reaction in interstellar environment (LASSIE) at Institute of Low Temperature Science, Hokkaido University [3]. Atomic hydrogen used for the reactions were produced by the dissociation of hydrogen molecules in micro-wave induced plasma. The kinetic temperature of hydrogen atoms were ~120K and the H-atom flux was ~10^{13} cm^{-2}s^{-1}. The samples of pure solid C2H2, C2H4 and those on ASW were produced on the substrate located in the center of the main chamber at 10K and 20K. Infrared absorption spectra of the ices were measured by FTIR before and during the exposure of H-atom.

Although our measurements show basically the same trend as shown in the previous studies, the difference in reaction rates for C2H2 and C2H4 was found to be much less than that previously reported. We will discuss the temperature and thickness dependence of the time constant for the sample ices in the poster.

References
[1]   M. J. Mumma & S. B. Charnley, 2011, Annu. Rev. Astro, Astrophys. 49, 471.
[2]   K. Hiraoka, T. Takayama, A. Euchi, H. Handa, & T. Sato, 2000, ApJ, 532, 1029
[3]   N. Watanabe & A. Kouchi. 2002. ApJ, 571, L173

Nitrogen isotopic fractionation of ammonia by adsorption on grain surface: An experimental approach to understand ^{15}N-enriched organic matters in extraterrestrial materials

H. Sugahara, Y. Takano, N. O. Ogawa, Y. Chikaraishi, and N. Ohkouchi

Department of Biogeochemistry, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), JAPAN

Nitrogen isotopic composition of the solar system objects show a variation in the range of minus hundreds to plus thousands permil in $\delta^{15}N$ value (‰, normalized as vs. Air). The bulk $\delta^{15}N$ values of the solar system, which are inferred from the analysis of the solar wind samples returned by Genesis mission, exhibit around -400‰ and those of the protosolar nebula are considered as similar values [1]. The bulk $\delta^{15}N$ values of Jupiter atmosphere are also similar to those of the solar wind [2]. Conversely, the terrestrial planets (Venus, Earth, and Mars) show much more positive values ranging from -40 to $+350$‰ [3, 4]. Primitive solar system materials, such as chondrites, comets, and interplanetary dust particles (IDPs) also show various degrees of ^{15}N-enrichment up to $+1500$‰ in the bulk $\delta^{15}N$ value [5, 6]. Furthermore, anomalously high ^{15}N-enrichments, as called hot spots, are frequently found within a single material and their highest $\delta^{15}N$ values reach as high as $+5000$‰ [7]. However, only a few models can explain the considerable $\delta^{15}N$ diversity in the interstellar medium (ISM) [e.g., 8] and likely isotopic discrimination processes have never been well understood.

In the study, we shed light on an adsorption of ammonia on grain surface as a potential mechanism for ^{15}N-discrimination in ISM. Adsorption is an interaction between gaseous molecules and grain surface and may be a first step for grain surface chemistry to form more complicated organic matter. We focused on ammonia in this study, because it is one of major carrier forms of nitrogen in ISM and also a high-active chemical as a precursor for nitrogen-involving organic matters. As a potential model for the ^{15}N-discrimination through adsorption process on grain surface, we enclosed ammonia gas into vacuumed glass vials together with several absorbent materials. We determined the difference in $\delta^{15}N$ value between the initial ammonia gas and the absorbed one.

References

[1] B. Marty, M. Chaussidon, R.C. Wiens, A.J.G. Jurewicz, & D.S. Burnett, 2011, Science 332, 1533 .

[2] M.M. Abbas, A. LeClair, T. Owen, B.J. Conrath, F.M. Flasar, V.G. Kunde, C.A. Nixon, R.K. Achterberg, G. Bjoraker, D.J. Jennings, G. Orton, & P.N. Romani, 2004, APJ 602, 1063 .

[3] J.H. Hoffman, R.R. Hodges, M.B. McElroy, T.M. Donahue, & M. Kolpin, 1979, Science 205, 49 .

[4] K.J. Mathew & K. Marti, 2001, JGR 106, 1401 .

[5] L. Bonal, G.R. Huss, A.N. Krot, K. Nagashima, H.A. Ishii, & J.P. Bradley, 2010, GCA 74, 6590 .

[6] J. Manfroid, E. Jehin, D. Hutsemékers, A. Cochran, J.-M. Zucconi, C. Arpigny, R. Schulz, J.A. Stüwe, & I. Ilyin, 2009, A&A 503, 613 .

[7] G. Briani, M. Gounelle, Y. Marrocchi, S. Mostefaoui, H. Leroux, E. Quirico, & A. Meibom, 2009, PNAS 106, 105222 .

[8] S.D. Rodgers & S.B. Charnley, 2008, Mon.Not.R.Astron.Soc.385, L48 .

Infrared characteristics of carbonaceous materials irradiated by nitrogen plasma

K. Sato,[1] I. Sakon,[1] T. Onaka,[1] T. I. Mori,[1] M. Hammonds,[1] S. Kimura,[2] and S. Wada

[1]*Department of Astronomy, Graduate School of Science, the University of Tokyo, Japan*
[2]*The Center for Instrumental Analysis, The University of Electro-Communications, Japan*

Recent observations have discovered buckminsterfullerene (C_{60}) in planetary nebulae (PNe) [1][2]. In addition to the emission from C_{60}, the spectra also show broad emission plateau in the 6-9 micron region in three PNe [3]. This feature is thought to be carried by mixtures of aromatic/aliphatic hydrocarbons [2][3]. However, we have limited knowledge on the chemical and evolutionary relation among C_{60} and other carbonaceous dust such as polycyclic aromatic hydrocarbons and hydrogenated amorphous carbons, which has to be examined based on not just observational studies but also laboratory experiments.

We have performed the experiments to investigate the infrared characteristics of the laboratory-synthesized materials after irradiating nitrogen plasma to C_{60} as an initial step. This experiment aims to investigate the infrared characteristics of nitrogen-bearing carbonaceous materials.

Figure 1 shows the infrared absorption spectra of the synthesized materials in our experiments with different irradiation time. Each spectrum shows a feature at about 6.3 micron and another feature whose peak position varies from 8.1 to 8.3 micron depending on the irradiation time. Features peaking at those wavelengths can be contributed by aromatic and aliphatic C-C and C-N bonds [4][5]. In this presentation, we discuss the effect of nitrogen/carbon ratio and aliphatic/aromatic bond ratio on the infrared spectra of the nitrogen-bearing carbonaceous materials synthesized in our experiments.
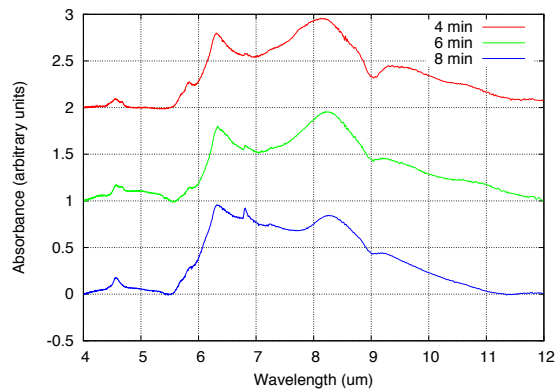

Figure 1: The infrared absorption spectra of the materials synthesized with different irradiation time. The continuum is subtracted. The small bump at 9 micron is an artifact due to the spectral structure of a silicon substrate.

References
[1]   J. Cami, J. Bernard-Salas, E. Peeters, & S. E. Malek, 2010, Science, 329, 1180.
[2]   D. A. García-Hernández, A. Manchado, P. García-Lario, et al., 2010, ApJ, 724, L39.
[3]   J. Bernard-Salas, J. Cami, E. Peeters, et al., 2012, ApJ, 757, 41.
[4]   L. J. Allamandola, A. G. G. M. Tielens, & J. R. Barker, 1989, ApJS, 71, 733.
[5]   "The Sadtler Handbook of Infrared Spectra", Sadtler Research Laboratories, 1978.

Detectability of Prolate Symmetric-Top Molecules in Diffuse Clouds by a "Hot-Axis Effect"

M. Araki,[1] S. Takano,[2] N. Kuze,[3] T. Oyama,[1] K. Tsukiyama[1]

[1]*Faculty of Science Division I, Tokyo University of Science, Japan*
[2]*Nobeyama Radio Observatory and the Graduate University for Advanced Studies (Sokendai), Japan*
[3]*Faculty of Science and Technology, Sophia University, Japan*

The aim of this study is to detect prolate symmetric-top molecules in diffuse clouds by observations of absorption lines by a "hot-axis effect." Molecules in low excitation temperatures in diffuse clouds can be detected by only absorption. A prolate symmetric-top molecule, such as CH_3CN and CH_3CCH, has a special advantage to detect absorption lines. The K rotation (rotation around the red dotted lines in Figure 1) is excited by collisions in a high kinetic (collisional) temperate and is not cooled by radiation. On the other hand, the J rotation is cooled well by radiation due to a permanent dipole moment and the low radiative temperature as shown in Figure 1. As a result, the special advantage is that the $J = K$ rotational levels have population concentrations as shown in Figure 2. We call the population concentrations a "hot-axis effect." Absorption lines of the $J + 1 \leftarrow J (= K)$ and $\Delta K = 0$ transitions indicated by the red arrows in Figure 2 can be strong. To calculate the population concentrations, both of radiation and collisions should be considered simultaneously. In the case of a linear molecule the equation for rotational distribution by radiation and collisions was derived by Oka *et al*. [1]. Recently Araki *et al*. derived the equation in the case of a symmetric-top molecule having the hot-axis effect [2]. Using the equation the population concentrations of CH_3CN and CH_3CCH were calculated and the intensities of absorption lines were estimated. Therefore it is suggested that the absorption lines enhanced by the hot-axis effect can be the powerful probe of the molecules in diffuse clouds.
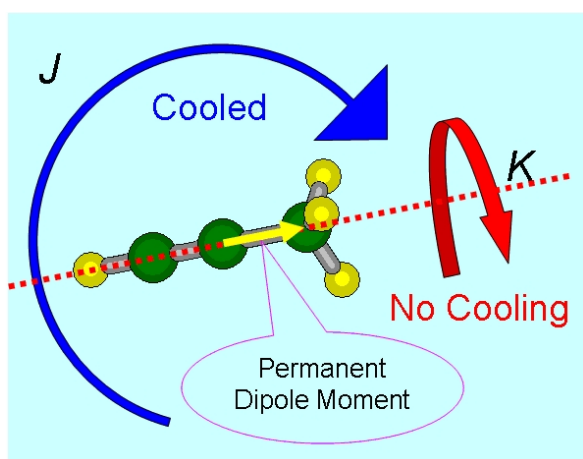

Figure 1: Hot-axis effect for a prolate symmetric top molecule. The red dotted line is the hot axis.
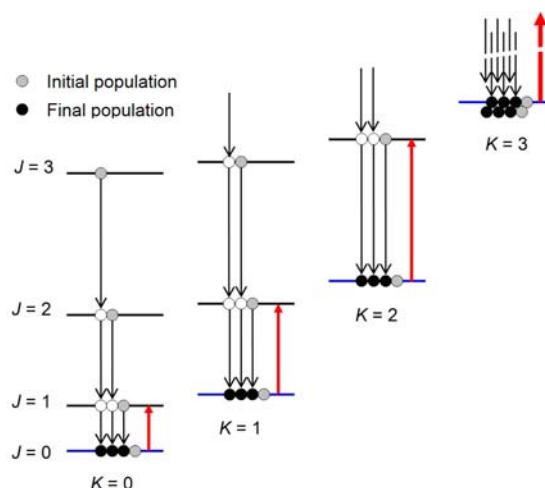

Figure 2: Population concentrations at the $J = K$ levels for a prolate symmetric top molecule. The emissions are drawn by the black arrows. The $J = K$ levels are descried by the blue bars and the strong absorptions are by the red arrows.

References

[1]   Oka *et al*., 2013, ApJ, **773**, 42.
[2]   Araki *et al*., 2014, AJ, in press.

Laser Spectroscopic Study of CaH in the UV region

K. Watanabe, K. Kobayashi, F. Matsushima, and Y. Moriwaki
Department of physics, University of Toyama, Japan

The electronic transitions of CaH were found in the Sun and M dwarfs [1, 2]. The transitions of CaH in the stellar atmospheres changes depending on the gas pressure, therefore CaH bands can be used to determine luminosity and surface gravity of cool stars [3-5]. Spectroscopic studies on CaH began in the 1920's [6], and many studies have been carried out since then. Bernath's group observed transitions of CaH in the IR and visible regions and identified $A^2\Pi$, $B^2\Sigma^+$, $E^2\Pi$ states [7-10]. Bell et al. extensively assigned $D\ ^2\Sigma^+$-$X\ ^2\Sigma^+$ bands in the UV region [11]. In their study, the change in the previous vibrational assignments of the $D\ ^2\Sigma^+$ state was suggested and interactions between $B\ ^2\Sigma^+$, $C\ ^2\Sigma^+$, and $D\ ^2\Sigma^+$ were discussed to explain the irregular vibrational spacing of the $D\ ^2\Sigma^+$ state. The ab initio calculations have shown that $B\ ^2\Sigma^+$ and $D\ ^2\Sigma^+$ of CaH has complex potential curves [12, 13]. Due to the avoided crossing, it is suggested that the $B\ ^2\Sigma^+$ has an interesting double minimum potential. We have carried out a laser induced fluorescence (LIF) study of transitions in this UV region (360 - 430 nm). We have produced CaH by the laser ablation of a calcium target in the hydrogen gas environment.

The several bands of $D\ ^2\Sigma^+$-$X\ ^2\Sigma^+$ of CaH was observed and CaH production was confirmed. In addition, extra bands were observed. Figure 1 shows the part of the spectra showing one of the extra band. By using the combination differences of CaH, the lower state was confirmed to be the vibrational ground state of $X\ ^2\Sigma^+$state. We will discuss the upper state of this band.
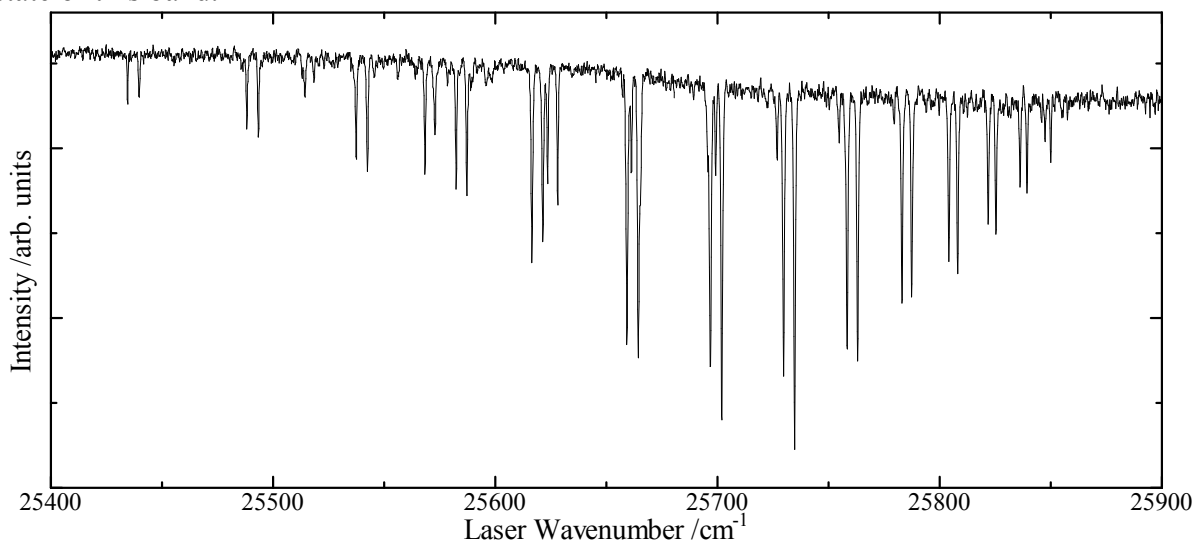

Figure 1: Part of the CaH spectra identified in this work.

References
[1]   C. M. Olmsted, Astrophys. J. 27, 66(1908).
[2]   A. Eagle, Astrophys. J. 30, 231(1909).
[3]   J. R. Mould, Astrophys. J. 207, 535(1976).
[4]   J. R. Mould et al. ,Mon. Not. Roy. Astron. Soc. 181, 625(1977).
[5]   B. Barbuy et al. , Astron. Astrophys. Suppl. 101, 409(1993).
[6]   R. S. Mulliken, Phys. Rev. 25, 509(1925).
[7]   A. Shayesteh et al. ,J. Mol. Struct. 695-696, 23(2004).
[8]   R. S. Ram et al. , J. ,Mol. Spectrosc. 266, 86(2011).
[9]   Gang Li et al. , J. Quant. Spectrosc. Rad. Transfer, 113, 67(2012).
[10]   A. Shayesteh, et al. J. Mol. Struct. 288, 46(2013).
[11]   G. D. Bell et al. Physica Scripta, 20, 609(1979).
[12]   P. F. Weck and P. C. Stabcil, J. Chem. Phys. 118, 9997(2003).
[13]   H. Martin, J. Chem. Phys. 88, 1797(1988).

High Resolution Spectroscopy of the $^2A_2 - \widetilde{X}\,^2B_1$ Electronic Transition of Phenoxy Radical as a Candidate of Diffuse Interstellar Bands Carrier

Y. MATSUSHITA, M. ARAKI, K. NIWAYAMA and K. TSUKIYAMA

Faculty of Science Division I, Tokyo University of Science, Japan

Diffuse Interstellar Bands (DIBs) still haven't been identified, although several hundreds of bands have been detected [1]. To identify DIBs, we observed the laboratory absorption spectra of the $^2A_2 - \widetilde{X}\,^2B_1$ electronic transition of the phenoxy radical C_6H_5O by cavity ring down spectroscopy. The radical was produced by pulsed discharge with a hollow cathode (inside diameter: 2 cm) using a gas mixture of anisole $C_6H_5OCH_3$ (0.1 Torr) and herium (0.4 Torr) in a cell. The optical cavity in the cell was formed with two high-reflectivity mirrors ($R >$ 99.99 %). Laser pulses transmiting the cavity were detected with a photomultiplier tube and ring down curves were acquired with an oscilloscope. The three absorption bands having the large intervals about 500 cm^{-1} were measured in the $5700-6200$ Å region and were assigned to the $^2A_2 - \widetilde{X}\,^2B_1$ electronic transition as shown in Figure 1 because the origin band of the electronic transition was reported at around 6200 Å in matrix [2] and the measured three bands were assigned to the 1-0, 2-0, and 3-0 bands of the ν_{11} mode by comparing with the frequencies obtained by a quantum chemical calculation (B3LYP/cc-pVTZ). The three bands include the two shoulder peaks at the lower-wavenumber side as shown in Figure 2. The shoulder peaks can not be assigned to the hot bands of the ν_{11} mode due to the large intervals from the main band ($\nu_{11} = 2$-0). The relative intensity of the shoulder peaks were tested in a dry-ice temperature. Decreasing of the relative intensity suggested that the peaks are attributed to the hot bands of the lowest vibrational mode (ν_{20}).
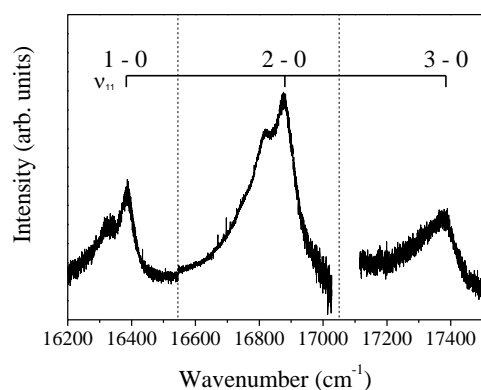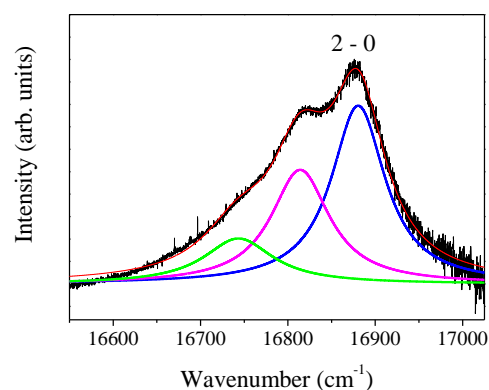

Figure 1: Absorption spectra of the phenoxy radical

Figure 2: The 2-0 band and the shoulder peaks of the $^2A_2 - \widetilde{X}\,^2B_1$ electronic transition of the phenoxy radical

References

[1] Heger M. L., *Lick Obs. Bull.* **10**, 141 (1922)

[2] Radziszewski *et al.*, *J. Chem. Phys.* **115**, 9733 (2001)

Stability of Glycine and Interstellar Carbonaceous Dust Analogs under UV Irradiation and Electron Bombardment

B. Maté, I. Tanarro, M. A. Moreno, M. Jiménez-Redondo,
V. J. Herrero, V. Timón and R. Escribano[1]

[1]*Instituto de Estructura de la Materia IEM-CSIC, Serrano 123, 28006 Madrid , Spain*

The formation and survival of molecules in extraterrestrial environments is a subject of considerable interest. For example, the stability of organic molecules under the high radiation flux and low temperature conditions found at the surfaces of many solar system objects is a key question in astrobiology. Even harsher conditions exist in the interstellar medium (ISM). Dust grains in the ISM are frequently simulated by means of hydrogenated amorphous carbon (HAC) particles generated in the lab [1].

Further to our previous work on glycine [2], we present here our investigation on the stability of glycine and HAC particles under irradiation with UV photons (~165 nm) and with 2 keV electrons, aiming to simulate the effects of cosmic rays present in different regions of the interstellar medium. The evolution of the samples is monitored with infrared spectroscopy.

In addition, we discuss theoretical calculations that add some light to the adsorption process of glycine at the surface of carbonaceous materials.
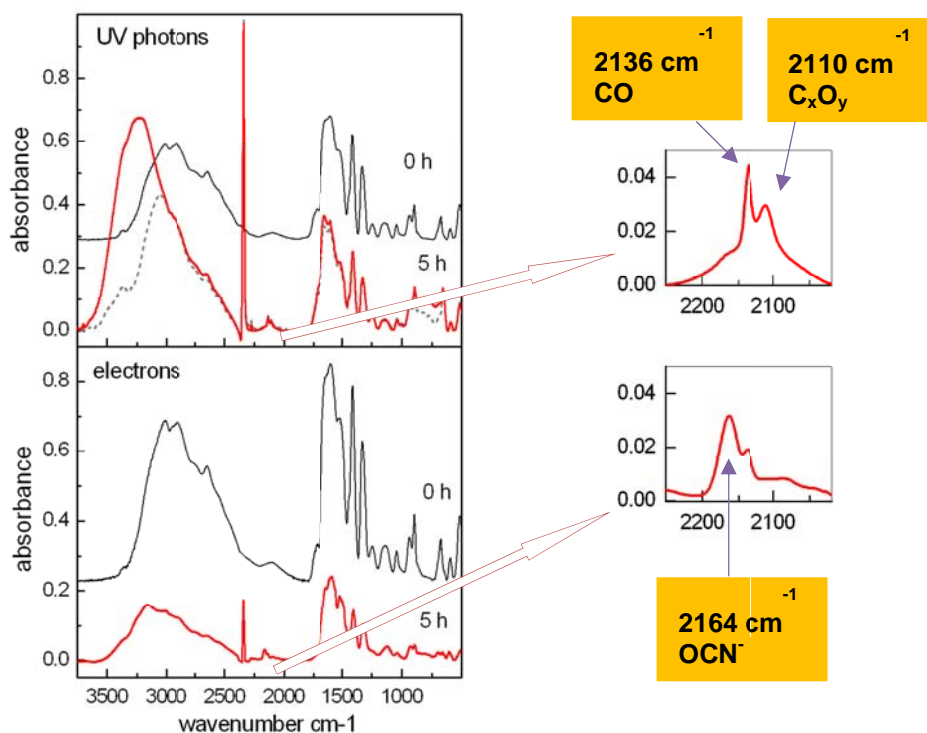

Figure 1: IR spectra of amorphous glycine deposited at 25 K. Top: 600 nm deposit before (black) and after (red) 5 hours processing by UV photons. Bottom: 900 nm sample, before (black) and after (red) 5 hours bombardment with 2.0 keV electrons. Right panel: detail and assignments of C-O stretching region.

References

[1]   Y. J. Pendleton & L. J. Allamandola, Ap. J. Supp. Ser. 2002, 138:75.
[2]   B. Maté et al., 2011, Phys. Chem. Chem. Phys. 13, 12268.

Infrared activation of the breathing mode of methane

R. Escribano, O. Gálvez, V.J. Herrero, B. Maté, V. Timón, M.A. Moreno

Instituto de Estructura de la Materia, IEM-CSIC, Serrano 123, 28006 Madrid, Spain

The breathing mode of methane, an in-phase stretching and shrinking of all four C-H bonds where the C atom and the charge distribution remain undisturbed, is inactive in the infrared spectrum of gas-phase or of pure solid methane. However, in low-temperature methane/water mixtures, like those generated to model astrophysical ices, a small but distinguishable feature has been observed in IR spectra, at the expected frequency of this vibration. Hodyss et al. [1] were the first to report this observation, which was subsequently confirmed by Gálvez et al. [2]. Although weak in general terms, the strength of this anomalous band could be large enough to allow detection in astrophysical or atmospheric field observations, thus providing a direct evidence of the presence of a form of methane in direct interaction with water.

We have built theoretical models that mimic experimental samples of CH_4/H_2O mixtures in an attempt to understand this effect, and to find out if, and when, this activation is predicted. Our results for a number of quantum chemical models turn out to be diverse, ranging from no activation at all to the prediction of some very strong features in specific cases.

For our calculations we have used several modules of the Materials Studio package, namely Amorphous Cell, Adsorption Locator, and CASTEP, which allow building models for amorphous solids for specific values of density and temperature and predicting their vibrational spectra. We have considered two amorphous water (ASW) models, of densities 0.7 g cm^{-3}, to simulate low-density ASW, and of 0.94 g cm^{-3}, for more compact water solids. Methane molecules were added to these amorphous structures at 30 K, in CH_4/H_2O ratios varying between 1/20 and 1/8.
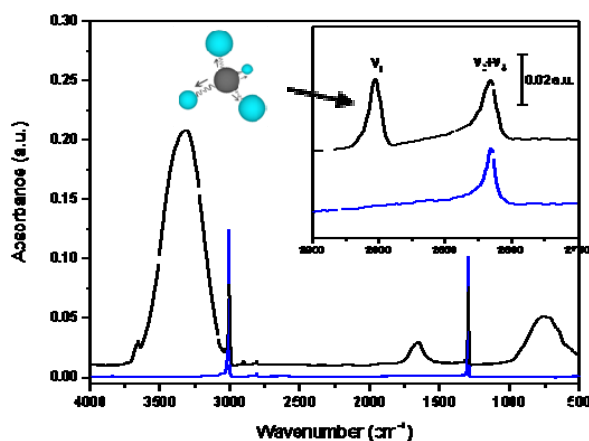

Figure 1: IR spectra of a 1:3 CH_4:H_2O mixture deposited at 14 K (black, above), and of pure CH_4 (blue, below). Inset: enlargement of the breathing mode region; the band is forbidden for pure CH_4, but it becomes as strong as a the $\nu_2+\nu_4$ combination band for the mixture.

References

[1]   R. Hodyss et al. "Photochemistry of methane-water ices", 2008, Icarus, 200, 338.
[2]   O. Gálvez et al. "Spectroscopic effects in CH_4/H_2O ices", 2009, Ap. J. 703:2101

Structures of surface and grain boundary of amorphous ice

Y. Kumagai and T. Ikeda-Fukazawa

Department of Applied Chemistry, Meiji University, Japan

In interstellar molecule clouds, the elements such as hydrogen, oxygen, carbon, and nitrogen, deposit on dust grains, and amorphous H_2O ice and various molecules (e.g., CO, CO_2, NH_3, CH_4, H_2CO, and so on) are formed [1]. Because the molecules undergo chemical evolutions through various processes on the surface of amorphous ice, the structure and properties of amorphous ice surface is one of the important factors govern the chemical evolutions of organic molecules in molecular clouds.

For crystal ice, the quasi-liquid layer exists on its surface [2]. The dangling motion of the free O-H bond which exists at the surface causes the surface melting [3]. The impurities adsorbed on the surface have effects to promote the dangling motion [4]. Although there are various studies on structure and properties of ice crystal, the surface properties of amorphous ice are less understand because of its complicated structure. In order to investigate the structures of surface and grain boundary of amorphous ice, we performed molecular dynamics (MD) calculations of amorphous ice.

The MD calculations were performed using an atom-atom potential model, KKY potential model with the program MXDORTO [5]. Using a system consisting of 2760 water molecules, an infinite surface was simulated by replicating the cell in the directions parallel to the surface using periodic boundary conditions. The amorphous structure with 1.03 g cm^{-3} in density was prepared by quenching of a liquid water phase from 290 to 10 K. For the simulations of the sintering process, two amorphous ice layers with about 40 Å in thickness were arranged with 10-20 Å in intervals.

The results show that the surface layer with low density exists in amorphous ice. The surface layer has high amplitude of thermal vibration of water molecules in comparison with bulk state, because the water molecules in the layer form a few of hydrogen bonds with weaker strength. Furthermore, the sintering processes were calculated to investigate the structure of grain boundary formed from adsorption of two surfaces. In the case that the initial interval of the two layers is 10 Å, the layers gradually move and are sintered within 100 ps. The sintering is not observed in the cases that the intervals of the layers are greater than 15 Å for our simulated time scale (~180 ps). The density of the boundary between the layers increases during the sintering, and becomes a constant at around 100 ps. The reached density was slightly lower than the value of bulk. The present results suggest the existence of the boundary with low density between amorphous ice grains. The structures of surface and interface might have important implications for adsorption, diffusion, and chemical reaction in interstellar amorphous ice.

References
[1]   A. Kouchi, T. Yamamoto, T. Kuroda, & J.M. Greenberg, 1994, A. & A. 290, 1009.
[2]   M. Faraday, 1859, Philos. Mag. 17, 162.
[3]   T. Ikeda-Fukazawa & K. Kawamura, 2004, J. Chem. Phys. 120, 1395.
[4]   T. Ikeda-Fukazawa & K. Kawamura, 2006, Chem. Phys. Lett. 417, 561.
[5]   K. Kawamura, MXDORTO, Japan Chemistry Program Exchange, No.029.

A Theoretical Study of H_2 Adsorption on Ice XI Surfaces

Y. Kunisada, and N. Sakaguchi

Center for Advanced Research of Energy and Materials,
Faculty of Engineering, Hokkaido University, Japan

In the evolution of molecules in space, it is assumed that physicochemical processes mainly proceed on cosmic dust grains.[1] Because of low temperature character of interstellar medium in space, only exothermic reactions can proceed in the gas phase. On the other hand, in the case of surface reactions in dense clouds, heat of formation can be effectively released to surfaces. Thus, various kinds of reactions can occur on surfaces. Therefore, in order to understand evolution of molecules in space, it is important to know the environmental temperature, i.e. gas and surface temperature, at the time of physicochemical processes.

One of the ways to investigate the environmental temperature at the time of physicochemical processes is a measurement of nuclear spin temperature of H_2 in space. Since protons are fermions, the total wave function of H_2 must be anti-symmetric with respect to the exchange of two nuclei. According to this anti-symmetry requirement for the total nuclear wave function, H_2 are classified as *ortho* and *para* species, i.e., *ortho* H_2 and *para* H_2 have total nuclear spin $I=1$ and 0, respectively. In the case of isolated H_2 molecule, *ortho-para* (o-p) H_2 conversion occurs quite slowly because such nuclear spin conversion is strictly forbidden. Corresponding o-p H_2 conversion time is 2.0×10^{21} s.[2] Thus, nuclear spin temperature of H_2 may conserve the environmental temperature at the time of H_2 formation processes. But it has been reported that o-p H_2 conversion can be enhanced on ice surfaces.[3-5] Therefore, it is important for interpretation of nuclear spin temperature of H_2 to reveal the accurate o-p H_2 conversion rate. In order to investigate o-p H_2 conversion rate, we have to clarify the interaction between H_2 and ice surfaces.

In this study, we investigated the adsorption properties of H_2 on ice surfaces with the aid of the first principles calculations based on density functional theory. We focused on the H_2 adsorption on ice XI surfaces to consider the effect of ferroelectric properties of crystalline ice surfaces. Moreover, we took the van der Waals interaction into consideration with the non-local correlation functional vdW-DF [6] to treat H_2 adsorption states on ice XI surfaces accurately.

At first, we investigated the adsorption energy of H_2 on ice XI surfaces. In this study, we adopted the 2x1 ice XI surface super cell with 12x12x32 grids as adsorption configurations. We calculated the adsorption energy at each grids point. We found that the hollow site is the most stable adsorption site. In the workshop, we will also show the quantum and isotope effect on adsorption and diffusion properties.

References
[1] T. Hama, & N. Watanabe 2013, Chem. Rev. 113, 8783.
[2] K. Pachucki, & J. Komasa, 2008, Phys. Rev. A 77, 030501(R).
[3] N. Watanabe, Y. Kimura, A. Kouchi, T. Chigai, T. Hama, & V. Pirronello, 2010, ApJ, 714, L233.
[4] T. Hama, K. Kuwahata, N. Watanabe, A. Kouchi, Y. Kimura, T. Chigai, & V. Pirronello, 2012, ApJ, 757, 185.
[5] T. Sugimoto, & K. Fukutani, 2011, Nature Phys. 7, 307.
[6] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, & B. I. Lundqvist, 2004, Phys. Rev. Lett. 92, 246401.

Solving the Schrödinger equations of interstellar molecules

H. Nakashima[1] and H. Nakatsuji[1]

[1]Quantum Chemistry Research Institute (QCRI), Japan

Schrödinger equation is the most fundamental equation in quantum mechanics and it governs most of phenomena in molecular science including space chemistry of interstellar molecules. In spite of that importance, however, the exact solutions of this equation have not been able to be solved for over 80 years. Recently, Nakatsuji was successful to propose a new general theory, the free complement (FC) method, for solving this equation [1] and theory was also extended to solving the relativistic Dirac equation [2]. In the tests with a few electron systems, the extremely accurate results could be obtained [3] and the stringent tests of the exactness of the obtained wave functions indicate how accurately the FC wave function can provide close to the exact solutions [4]. With different from ordinary quantum chemistry, the FC method is based on the idea that the exact wave function should be obtained by a functional of the Hamiltonian. Therefore, the adequate wave functions are automatically generated by the system's Hamiltonian itself and this feature is significant for space chemistry that appears the various unusual situations and environments.

We have applied the present method to various atoms and molecules [5] and also interstellar species with the environments of space. In the latter case, the following situations are rather significant: the accurate excited states and theoretical spectra, non Born-Oppenheimer (non-BO) calculations which include the quantum effect of nuclear motion [6], solving the relativistic Dirac equation [2], and atoms and molecules in an extreme environment such as under the strong magnetic fields [7]. For example, the non-BO calculations can provide the vibronic and rotational states including all the quantum effects of electron and nuclear motion, whose theoretical results are directly comparable with the observations and/or experimental results. For the last topic, the Universe's strongest magnetic field was observed on Magnetar object surface in space and the quantum mechanical calculations in magnetic fields become realistically important.

Thus, the present method indicated a high potentiality to be helpful for doing space chemistry in Schrödinger accuracy. We now continue to develop the methods and computational algorithms to be more easily applicable to more general atoms and molecules.

References
[1]   H. Nakatsuji, 2000, J. Chem. Phys. 113, 2949. H. Nakatsuji, 2004, Phys. Rev. Lett. 93, 030403. H. Nakatsuji, 2005, Phys. Rev. A 72, 062110.
[2]   H. Nakatsuji & H. Nakashima, 2005, Phys. Rev. Lett. 95, 050407.
[3]   H. Nakashima & H. Nakatsuji, 2007, J. Chem. Phys. 127, 224104. Y. Kurokawa, H. Nakashima, & H. Nakatsuji, 2008, Phys. Chem. Chem. Phys. 10, 4486.
[4]   H. Nakashima & H. Nakatsuji, Phys. Rev. Lett. 2008, 101, 240406.
[5]   H. Nakatsuji, H. Nakashima, Y. Kurokawa, & A. Ishikawa, 2007, Phys. Rev. Lett. 99, 240402. H. Nakatsuji, 2012, Acc. Chem. Res. 45, 1480. H. Nakatsuji & H. Nakashima, 2014, TSUBAME e-Science J. 11, 24 (2014).
[6]   Y. Hijikata, H. Nakashima, & H. Nakatsuji, 2009, J. Chem. Phys. 130, 024102. H. Nakashima, Y. Hijikata, & H. Nakatsuji, 2013, ApJ 770, 144. H. Nakashima & H. Nakatsuji, 2013, J. Chem. Phys. 139, 074105.
[7]   H. Nakashima & H. Nakatsuji, 2010, ApJ 725, 528. A. Ishikawa, H. Nakashima, & H. Nakatsuji, 2012, Chem. Phys. 401, 62.

Collision dynamics of PAH clusters with charged particles

M. Nakamura[1] and A. Ichimura[2]

[1]*College of Science and Technology, Nihon University, Japan*
[2]*Institute of Space and Astronautical Science, JAXA, Japan*

The polycyclic aromatic hydrocarbon (PAH) molecules are believed to be abundant in interstellar space. The collisions dynamics of charged particles with PAH clusters would play an important role in the chemical evolution in molecular clouds. Recently, there have been experimental studies for the collision of ions with PAH molecules and PAH clusters [1,2]. In the present work, we make an analysis for the experimental observation. In the collision with singly and doubly charged ^{3}He ions, doubly charged clusters of anthracene and coronene were detected for cluster size $n \geq 15$. To analyze the origin of this *appearance size*, we propose a stacked structure model [3]. In the model, it is assumed that a PAH cluster takes a layer structure of planar molecules. (See Fig. 1) The appearance sizes are calculated for doubly charged clusters of benzene, anthracene and coronene by the present model [3] and by the conventional liquid drop model [4]. They are shown in Table 1 together with experimental results [1-2,5]. For benzene cluster, the liquid drop model gives a considerably good agreement with the experiment [5] while the stacked structure model does not at all. For anthracene and coronene clusters, both models conspicuously underestimate the appearance sizes in comparison with the experimental results [1-2]. The origin of this discrepancy is discussed. The result was partly reported in [3].
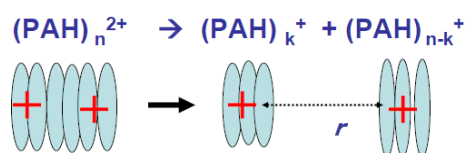

Fig. 1: Stacked structure model for stability for fragmentation of doubly charged PAH cluster.

Table 1. Appearance sizes of doubly charged clusters.

constituent	experiment	stacked structure model	liquid drop model
benzene	23	9	18
anthracene	15	6	6
coronene	15	3	3

References

[1] A. I. S. Holm *et al*., Phys. Rev. Lett. **105**, 213401 (2010) ; P. Rousseau et al., Nucl. Instr. Phys. Res. B **279**, 140 (2012)
[2] H. A. B. Johansson *et al*., Phys. Rev. A **84**, 043201 (2011)
[3] M. Nakamura and A. Ichimura, *Physica Scripta* T **156**, 014063 （2013）
[4] O. Ehct *et al*., Phys. Rev. A **38**, 3236 (1988)
[5] M. Y. Hahn *et al*., J. Chem. Phys. **88**, 4242 (1988)

Chemical Reactions in Protoplanetary Disks and Possibility of Detecting H₂O Snowline using Spectroscopic Observations

S. Notsu,[1] H. Nomura,[2] and D. Ishimoto[1,2]

[1]*Department of Astronomy, Graduate School of Science, Kyoto University, Japan*

[2]*Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan*

In the hot inner part of protoplanetary disks, H_2O evaporates from the dust surface into gas. On the other hand, it freezes on the dust surface in the cold outer part of the disks. H_2O snowline is the line which divides the two different regions [1]. H_2O ice enhances the solid material in the cold outer part of a protoplanetary disk, which promotes the formation of cores of gaseous planets. We can also regard H_2O snowline as the dividing line between formating regions of rocky planets and gas giant planets. In the case of disks around solar-mass T-tauri stars. it is considered that the H_2O snowline exists at a few AU from the central star. Therefore, it is difficult to detect H_2O snowline of exoplanetary systems by imaging observations, since their spacial resolution is insufficient.

In contrast, H_2O emissions from protoplanetary disks are detected by recent observations of Spitzer and Herschel telescope. Zhang et al. (2013) [2] estimated the position of H_2O snowline by using the intensity ratio of different H_2O lines, but the result depends on the model of temperature distribution in the protoplanetary disk. In this work we propose the method of detecting H_2O snowline more directly by analyzing the velocity profiles of H_2O line spectra which will be obtained by high dispersion spectroscopic observations in near future.

First, we calculate chemical reactions using a self-consistent physical model of protoplanetary disks and investigate abundance distribution of H_2O gas and the position of H_2O snowline. As a result we confirmed that the abundance of H_2O is high not only in the inner region of H_2O snowline near the equatorial plane but also in the hot surface layer of outer disk.

Second, we calculate the velocity profiles of H_2O emission lines from protoplanetary disk, and found that we can obtain the information of H_2O snowline through investigating the profiles of some emission lines which have small Einstein A coefficient and large excitation energy. The wavelengths of the useful H_2O emission lines range from mid-infrared to submillimeter. We also discuss the possibility of future observations.

References
[1]   C. Hayashi,1981, Progress of Theoretical Physics Supple-ment 70, 35
[2]   K. Zhang, K. M. Pontoppidan, C. Salyk, et al. 2013,ApJ 766, 82
[3]   C. Walsh, T.J. Millar, & H. Nomura, 2010, ApJ 722, 1607

Chemistry in protoplanetary disks with the effects of the grain growth

D. Ishimoto,[1,2] H. Nomura,[2] C. Walsh,[3] and T. J. Millar[4]

[1]*Department of Astronomy /Kyoto University, Japan*
[2]*Department of Earth and Planetary Science, Institution/Tokyo Institute of Technology, Japan*
[3]*Leiden Observatory /Leiden University, Netherlands*
[4]*School of Mathmatics and Physics /Queen's University Belfast, UK*

Planetesimals are thought to be formed in protoplanetary disks as a result of grain growth, but many uncertainties are still remained in this process. So observations of disks in transient period which has large grain are good for understanding planetesimal formation. Observational instruments are developed recently like ALMA, and theoretical study of these disks become important.

In this study, we calculate the chemistry and radiative transfer to investigate the influences of the grain growth on chemical structure of protoplanetary disks. In the case of large grains, FUV radiation can penetrate near the midplane because of the low opacity, and that changes the gas temperature. As a result, most molecules are abundant near the midplane compared with the case of small grains.

The results of calculations of radiative transfer are shown in Figure 1. Line of CO3-2 is optically thick even in the case of small grain, so in the case of large grains, intensity of CO3-2 line is not much different from the case of small grain. On the other hand, intensity of CN3-2 line change greatly with the case of small grains and large grains. Line of CN3-2 is optically thin in the case of small grain, but CN are abundant in the high density region(midplane) in the case of large grains, so CN3-2 line is changed to optically thick.
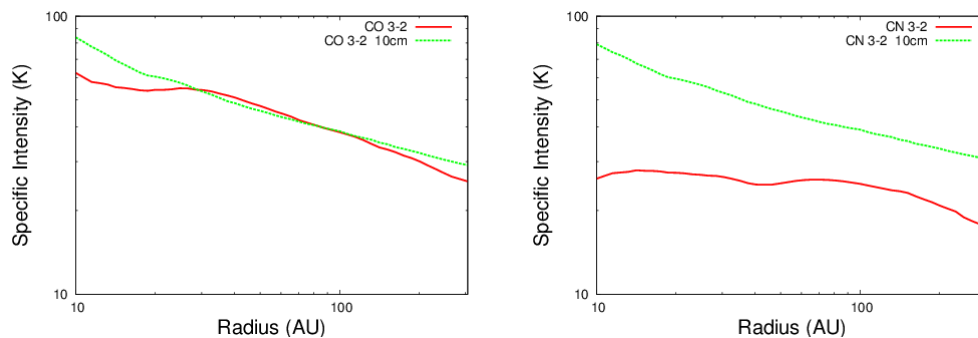

Figure 1: Specific intencity as a function of radius; red line indicates the case of small grain, and green line indicates large grain; (Left): CO 3-2, (Right): CN 3-2

Time and Space Variation of the Organic Particles in the Proto-Solar Disk

M. Numata,[1] and H. Nagahara[1]

[1]*Department of Earth and Planetary Science, The University of Tokyo, Japan*

It is one of the critical problems of planetary science whether organic materials formed in molecular cloud were the origin of the organic materials of the planets and small objects. Nakano et al. (2003) suggested that organic materials in meteorite parent bodies were not derived from molecular clouds, because the compositional variation of the C and N contents of heated organic analogs does not agree with that of carbonaceous chondrites. On the other hand, organic grains must have experienced temperatures change according to the radial transport in the protoplanetary disk, which would have been resulted in compositional change and mixing of various organics in the protoplanetary disk.

In this study, we investigate the temporal and spatial change of distribution and chemical composition of organic particles in the proto-solar disk by taking the experimental results by Nakano et al. (2003) into consideration. We calculate the viscous disk evolution of the model by Ciesla (2010a) and location of individual particles position simultaneously. The temperature that each particle experienced is estimated on the basis of radial temperature distribution and the chemical composition of individual particles is obtained by applying the results of heating experiments on analog organic materials by Nakano et al. (2003).

The temporal change of organic particle distribution is shown in Fig. 1, which shows that particles initially located in the outer region drift inward with logarithmic decay, and that organic particles were stably present in the inner region after 10^6 year. Figure2 shows the C contents of the particles corresponding to Figure1, where the vertical value of ~40 wt% represents the initial value at the molecular cloud. The composition of organics changes with time and space, and the total amount of C decreases with distance. On the other hand, due to the radial transport, the inner region tends to be occupied with primitive organics with time. Planetesimals formed at 2-3 AU at the early stage of the disk evolution would have contained organics that were thermally processed to various degrees, whereas, those formed at the later stage would have contained organics that retained primitive chemical composition originated from the molecular cloud.
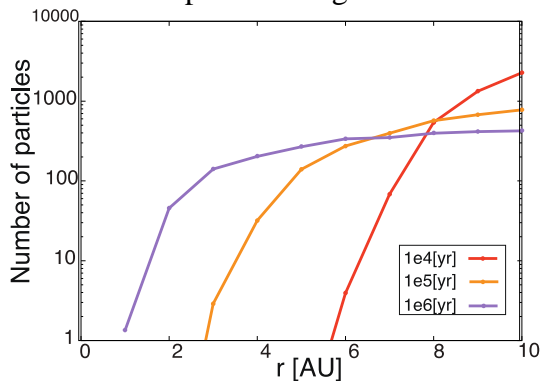

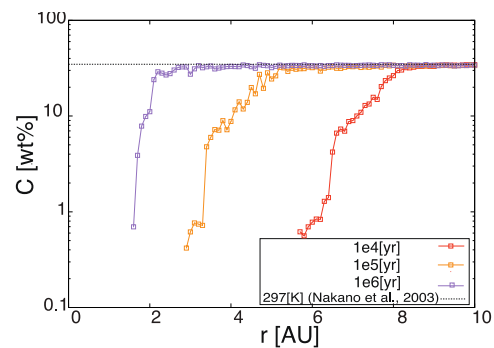Figure 1: Time-space variation of organic matterr distribution

Figure 2: Time-space variation of composition of organic material

References

F. Ciesla, 2010a, Icarus 208, 455; F. Ciesla, 2010b, ApJ 723, 514; F. Ciesla, 2011, ApJ 740, 1; Nakano et al., 2003 ApJ 592, 1252

Chemistry in a Forming Protoplanetary Disk

Yuri Aikawa[1], Haruaki Yoneda[1], Kenji Furuya,[2] and Yusuke Tsukamoto[3]

[1]*Department of Earth and Planetary Sciences, Kobe University, Japan*
[2]*Leiden Observatory, Netherland (JSPS Fellow)*
[3] *Department of Physics, Nagoya University, Japan*

Sun-like stars are formed by the gravitational collapse of dense cloud cores. Due to the angular momentum conservation, circumstellar disks are naturally formed, which will be a birth place of planetary systems. While various molecules, including organics, are detected in presetellar and protostellar cores, how they are incorporated to disks and then to planetary systems remains an open question. In this presentation, we report results of our chemical models starting from prestellar cores to protoplanetary disks. Using the 3D radiation hydrodynamics model of Tsukamoto et al (2013), we investigate if and how the molecules in the cloud core are chemically modified in the process of disk formation.

References
[1]   Tsukamoto, Y. and Machida, M. N. 2013, MNRAS 428, 1321

A Multi-Transition Study of Molecules toward NGC 1068 based on High-Resolution Imaging Observations with ALMA

T. Nakajima,[1] S. Takano,[2,3] K. Kohno,[4,5] N. Harada,[6] E. Herbst,[7]
Y. Tamura,[4] T. Izumi,[4] A. Taniguchi,[4] and T. Tosaki[8]

[1] Solar-Terrestrial Environment Laboratory, Nagoya University, Japan
[2] Nobeyama Radio Observatory, National Astronomical Observatory of Japan, Japan
[3] Department of Astronomical Science, The Graduate University for Advanced Studies (SOKENDAI), Japan
[4] Institute of Astronomy, The University of Tokyo, Japan
[5] Research Center for Early Universe, School of Science, The University of Tokyo, Japan
[6] Max Planck Institute for Radio Astronomy, Germany
[7] Department of Chemistry, University of Virginia, USA
[8] Department of Geoscience, Joetsu University of Education, Japan

We present 0.8-mm band molecular images and spectra obtained with the Atacama Large Millimeter/submillimeter Array (ALMA) toward one of the nearest galaxies with an active galactic nucleus (AGN), NGC 1068. Distributions of CO isotopic species (^{13}CO and $C^{18}O$) J=3-2, CN N=3-2 and CS J=7-6 are observed toward the circumnuclear disk (CND) and a part of the starburst ring with an angular resolution of ~1.3"×1.2". The physical properties of these molecules and shock-related molecules such as HNCO, CH_3CN, SO, and CH_3OH detected in the 3-mm band [1] were estimated using rotation diagrams under the assumption of LTE [2]. The rotational temperatures of the CO isotopic species and the shock-related molecules in the CND are, respectively, 14-22 K and upper limits of 20-40 K. Although the column densities of the CO isotopic species in the CND are only from one-fifth to one-third of that in the starburst ring, those of the shock-related molecules are enhanced by a factor of 3-10 in the CND. We also discuss the chemistry of each species, and compare the fractional abundances in the CND and starburst ring with those of Galactic sources such as cold cores, hot cores, and shocked clouds in order to study the overall characteristics.
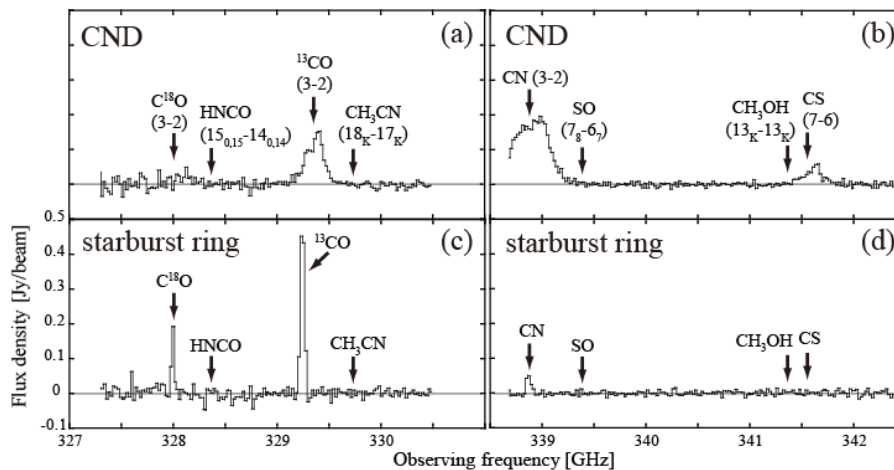
Figure 1: The top spectra (a) and (b) are at the central continuum position (in the CND), and the bottom spectra (c) and (d) are at the position of the ^{13}CO J=3-2 intensity peak in the starburst ring

References
[1]   S. Takano, et al., PASJ, 66, 75 (2014)
[2]   T. Nakajima, et al., submitted to PASJ.

Distribution of Molecules in Spiral Arm of M51

Yoshimasa Watanabe,[1] Nami Sakai,[1] Yuri Nishimura,[1] Kazuo Sorai,[2]
and Satoshi Yamamoto[1]

[1]*Depertment of Physics, The University of Tokyo, Japan*
[2]*Department of Physics, Hokkaido University, Japan*

Recently, chemistry of external galaxies has attracted more attention of astronomers than before, because various molecular species become readily detected in nearby galaxies owing to rapid increase of sensitivity in radioastronomical observations. In general, chemical compositions observed toward external galaxies are `average' chemical compositions of a number of giant molecular clouds (GMCs). The GMC-scale chemical compositions are mostly in chemical equilibrium, and mainly depend on structures and environmental conditions of GMCs. Therefore, they cannot directly be discussed on the basis of astrochemical concepts established in nearby molecular clouds in our Galaxy. If the physical meaning of the GMC-scale chemical compositions is adequately established by observational and theoretical studies, we can make use of it as a new tracer to diagnose external galaxies.

With this motivation, we have carried out the spectral line survey toward the spiral arm of M51 with the IRAM 30 m telescope and detected 13 molecular species (Watanabe et al. 2014). The excitation temperatures of the molecules are estimated to be less than 10 K toward P1. Therefore, most of detected molecules would reside in a cold (~10 K) and widespread molecular gas, although a part of molecular emissions may also come from the hot molecular gas. Based on this spectral line survey, we conducted mapping observation of CH_3OH, CS, CN, HNCO, $C^{18}O$ and ^{13}CO with the CARMA interferometer. These molecules are successfully imaged with sufficient signal-to-noise ratios. Although the CO isotopologues traces spiral arm structure, we can see significant difference of the other distributions from molecule to molecule. These differences would be originated from the environment around GMCs or the dynamics in the spiral arm such as cloud-cloud collisions.

References

[1]   Watanabe, Y. et al. ApJ, 788, 4

The spatial distribution of shock/dust-related molecules in the nearby starburst galaxy NGC 253 observed with ALMA

T. Izumi,[1] K. Kohno,[1,2] Y. Tamura,[1] A. Taniguchi,[1] S. Takano,[3,4]
T. Nakajima,[5] T. Tosaki[6], N. Harada[7], and E. Herbst[8]

[1]*Institute of Astronomy, The University of Tokyo, Japan*
[2]*Research Center for Early Universe, School of Science, The University of Tokyo, Japan*
[3]*Nobeyama Radio Observatory, National Astronomical Observatory of Japan, Japan*
[4]*Department of Astronomical Science, The Graduate University for Advanced Studies
(SOKENDAI), Japan*
[5]*Solar-Terrestrial Environmental Laboratory, Nagoya University, Japan*
[6]*Department of Geoscience, Joetsu University of Education, Japan*
[7]*Max Planck Institute for Radio Astronomy, Germany*
[8]*Department of Chemistry, University of Virginia, USA*

We present spatial distributions of typical dense gas tracers (CS J=2-1, 7-6), shock/dust-related molecules (HNCO $J_{Ka,Kc}$=$5_{0,5}$-$4_{0,4}$, CH_3OH J_K=2_K-1_K, and CH_3CN J_K=6_K-5_K) and 3 mm continuum emission in the central kpc region of the nearby starburst galaxy NGC 253, obtained with Atacama Large Millimeter/submillimeter Array (ALMA) cycle 0 observations. The achieved sensitivity was ~ 0.5 mJy per 30 pc beam, at a velocity resolution of 10 km s^{-1}. We found that CS emission is concentrated toward the very nuclear region, whereas CH_3OH and HNCO are more prominent in the "super bubble" (expanding bubble probably caused by super(hyper)novae) region [1] than in the nucleus. The existence of the expanding bubble is also confirmed in the channel map and the position-velocity diagram of CS, i.e., dense gas is also expanding. From our results, the abundances of CH_3OH and HNCO would be enhanced in the super bubble region likely due to shocks. In addition, we found shock/dust-related molecules are faint at the peak position of the 3 mm continuum emission. The initially high dust temperature would restrain the formation of these species there [2].
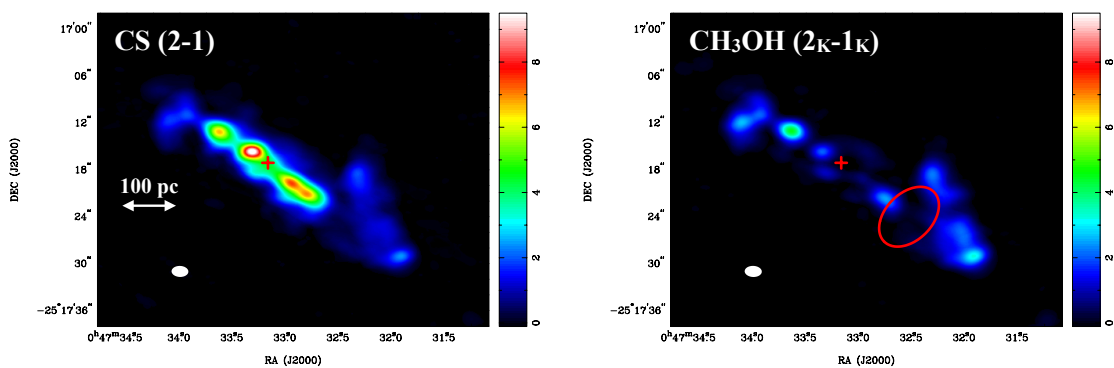
Figure 1: Integrated intensity maps of CS (left) and CH_3OH (right) in the central ~ 0.5 kpc × 1 kpc region of NGC 253. The central cross and the white ellipse in both panels indicate the peak position of the 3 mm continuum emission and the synthesized beams, respectively. In the right panel, the red ellipse indicates the location of the "super bubble" [1]. The CH_3OH emission is more prominent at the rim of the bubble. The color scales are in the unit of Jy beam^{-1} km s^{-1}.

References
[1]   K. Sakamoto, et al., 2006, ApJ, 636, 685
[2]   T. Nakajima, et al., 2014, submitted to PASJ

A Substellar-Mass Protostar and its Outflow of IRAS 15398-3359 revealed by Subarcsecond-Resolution Observations of H$_2$CO and CCH

Y. Oya,[1] N. Sakai,[1] T. Sakai,[2] Y. Watanabe,[1] T. Hirota,[3] J.E. Lindberg,[4,5] S.E. Bisschop,[4,5] J.K. Jørgensen,[4,5] E.F. van Dishoeck,[6,7] and S. Yamamoto[1]

[1]*Department of Physics, The University of Tokyo, Japan*
[2]*Department of Communication Engineering and Informatics, Graduate School of Informatics and Engineering, The University of Electro-Communications, Japan*
[3] *National Astronomical Observatory of Japan, Japan*
[4] *Center for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen, Denmark*
[5] *Niels Bohr Institute, University of Copenhagen, Denmark*
[6] *Leiden Observatory, Leiden University, The Netherlands*
[7] *Max-Planck-Institut f ̈ur Extraterrestrische Physik, Germany*

Subarcsecond (0".5) images of H$_2$CO and CCH line emission have been obtained in the 0.8 mm band toward the low-mass protostar IRAS 15398-3359 in the Lupus 1 cloud as one of the Cycle 0 projects of the Atacama Large Millimeter/Submillimeter Array (ALMA). We have detected a compact component concentrated in the vicinity of the protostar and a well-collimated outflow cavity extending along the northeast-southwest axis. The inclination angle of the outflow is found to be about 20º, or almost edge-on, based on the kinematic structure of the outflow cavity. This is in contrast to previous suggestions of a more pole-on geometry. The centrally concentrated component is interpreted by use of a model of the infalling rotating envelope with the estimated inclination angle, and the mass of the protostar is estimated to be less than 0.09 Msun. Higher spatial resolution data are needed to infer the presence of a rotationally supported disk for this source, hinted at by a weak high-velocity H$_2$CO emission associated with the protostar. Although IRAS 15398-3359 and L1527 are both the warm-carbon-chain chemistry sources, their physical properties in the vicinity of the protostar are found to be much different from each other. Thus, Chemical variation of the protostellar envelope do not originate from the present physical structure.

Abundance Anomaly of the ^{13}C Isotopic Species of c-C$_3$H$_2$

K. Yoshida,[1] T. Tokudome,[1] N. Sakai,[1] Y. Watanabe,[1] S. Takano,[2] B. Lefloch,[3] and S. Yamamoto[1]

[1]*Department of Physics, The University of Tokyo, Japan*
[2]*Nobeyama Radio Observatory and the Graduate University for Advanced Studies (Sokendai), Japan*
[3]*Institut de Planétologie et d'Astrophysique de Grenoble, France*

It has been reported that the ^{12}C/^{13}C ratios of several carbon-chain molecules in cold clouds are significantly higher than the interstellar elemental ^{12}C/^{13}C ratio of 60-70 [1]. For example, the [CCS]/[^{13}CCS] ratio is reported to be 230±130 [2], and the [CCH]/[^{13}CCH] ratio is reported to be higher than 250 [3] in the cold starless core TMC-1 (Cyanopolyyne Peak; CP). In addition, two or more ^{13}C species of a single molecular species have different abundances. For Instance, Takano et al. [4] found that the relative abundance ratio of H^{13}CCCN, HC^{13}CCN, and HCC^{13}CN is 1.0 : 1.0 : 1.4 in TMC-1 (CP).

We recently found the similar anomaly for c-C$_3$H$_2$ toward low-mass star-forming region L1527. Many lines of c-C$_3$H$_2$ and its ^{13}C species detected in the spectral line surveys with the NRO 45 m and the IRAM 30 m telescopes enable us to derive the ^{12}C/^{13}C ratios for the two ^{13}C species accurately.

For c-C$_3$H$_2$, attempting to fit these lines by one rotational temperature and one column density was not successful. We found systematic residuals in the fit. Then, we employ the two component model, assuming inner warm and outer cold regions. We calculated the ^{12}C/^{13}C ratio and found a systematic difference of the anomaly between them; the anomaly is mitigated in the inner region. This is the first indication of the variation of the ^{12}C/^{13}C ratio along star formation. This result suggests that the anomaly can be used as a new diagnostic tool for physical and chemical evolution of protostellar cores.
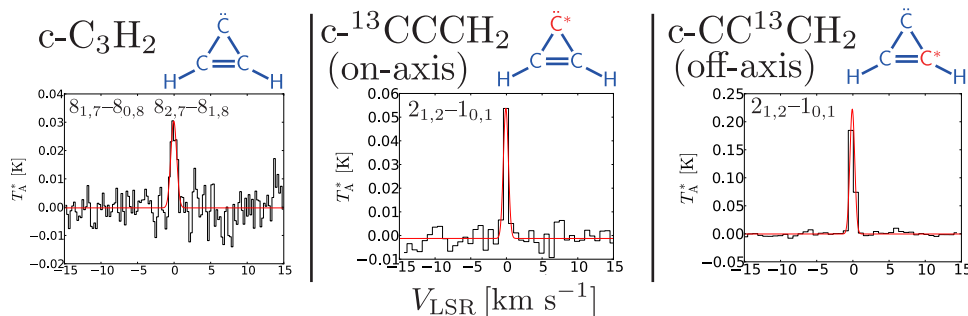

Figure 1: Spectral lines of c-C$_3$H$_2$ and its ^{13}C species observed toward L1527.

References

[1] Lucas, R. & Liszt, H. 1998, A&A, 337, 246.
[2] Sakai, N. et al, 2007, ApJ, 663, 1174.
[3] Sakai, N. et al. 2010, A&A, 512, A31.
[4] Takano, S. et al. 1998, ApJ, 329, 1159.

Origin of Methanol in the Starless Core, Taurus Molecular Cloud-1

T. Soma, N. Sakai, Y. Watanabe and S. Yamamoto

Department of Physics, the University of Tokyo, Japan

Methanol (CH_3OH) is one of fundamental saturated organic molecules, and is widely detected in star forming regions [1]. It is generally thought that CH_3OH is produced on dust grains and is liberated into the gas phase by various star formation activities (e.g. protostellar heating and outflow shocks). However, CH_3OH is also moderately abundant in cold dark clouds, and its origin is still controversial [2]. Non-thermal evaporation processes should play an important role.

To examine this we have conducted high spectral resolution observations of CH_3OH toward the cyanopolyyne peak of Taurus Molecular Cloud-1 (TMC-1 CP). The spectral line of CH_3OH toward TMC-1 CP is found to have a double-peaked profile separated by 0.4 km s^{-1}. Since the double-peaked profile is observed for the ^{13}C species of CH_3OH, it is not due to optical depth and/or self-absorption effects. The spectral line profile of CH_3OH is much different from those of $C^{34}S$, C_3S, and HC_7N observed toward this source. Statistical equilibrium calculations are carried out for the $1_{0,0} - 0_{0,0} A^+$, $2_{0,2} - 1_{0,1} A^+$ and $3_{0,3} - 2_{0,2} A^+$ lines of CH_3OH, and the H_2 density of the emitting region for the blue-shifted and red-shifted components are derived to be $(1.7 \pm 0.2) \times 10^4$ cm^{-3} and $(4.3 \pm 0.4) \times 10^4$ cm^{-3}, respectively. Although these densities are similar to or slightly lower than those found for the other molecules, CH_3OH is distributed differently. This has been confirmed by mapping observations of the CH_3OH $2_{0,2} - 1_{0,1} A^+$ and the $C^{34}S$ $J = 2 - 1$ lines around TMC-1 CP.

Non-thermal desorption from dust grains seems to be responsible for the gas-phase CH_3OH. The grain-surface origin of CH_3OH is further confirmed by the $CH_3OH/^{13}CH_3OH$ ratio. As for the desorption mechanism, weak shocks caused by accreting diffuse gas to the TMC-1 filament, photoevaporation caused by the cosmic-ray induced UV radiation, and desorption of excess reaction energy in formation of CH_3OH on dust grain are discussed.

References
[1]   Herbst, E., & van Dishoeck, E. F. 2009, ARA&A, 47, 427
[2]   Takakuwa, S., Mikami, H., Saito, M. et al. 2000, ApJ, 542, 367

Effects of Line Overlap in statistical equilibrium calculations of OH 18cm lines

Y. Ebisawa,[1] H. Inokuma,[1] Y. Watanabe,[1] N. Sakai,[1] H. Maezawa,[2] K. M. Menten,[3] and S. Yamamoto[1]

[1]*Department of physics, University of Tokyo, Japan*
[2]*Department of physics, Osaka Prefecture University, Japan*
[3]*MPIfR, Germany*

The 18 cm OH transition is the first spectral line of interstellar molecules detected in the radio wavelength region. It is the fine structure transition between the Λ-type doubling levels in the lowest rotational state ($J=3/2$, $\Omega=3/2$), and consists of four hyperfine components (1612, 1665, 1667, 1720 MHz). It is well known that the relative population of the hyperfine structure levels can attain values that deviate from LTE values. In our observation toward eastward of Heiles Cloud 2 (HCL2), we found a clear absorption feature of 1612 MHz component. In order to interpret this, we conducted statistical equilibrium calculations. As a result, we found that intensities of the four hyperfine components of OH are sensitive to the temperature (Fig.1 left). Therefore, they can be used as a good thermometer for quiescent molecular clouds.

However, we recently observed 1720 MHz absorption feature in the northwest of Taurus Molecular Cloud-1 (TMC-1) (Fig.1 right). In order to interpret this 1720 MHz absorption feature, we again conducted statistical equilibrium calculations considering the effect of Line Overlap. As a result, we found that thermal Line Overlap could cause 1720 MHz absorption feature when the column density of OH is high, the temperature is high, the linewidth is narrow and there is no velocity gradient in the cloud. We also found that the effect of Line Overlap is negligible as long as the column density of OH is not so high. Therefore, we can safely use four hyperfine components of OH as a thermometer if the column density of OH is not so high.

$n(H_2) = 10^4$ cm^{-3}, $N(OH) = 10^{14}$ cm^{-2}, $V = 1$ km/s
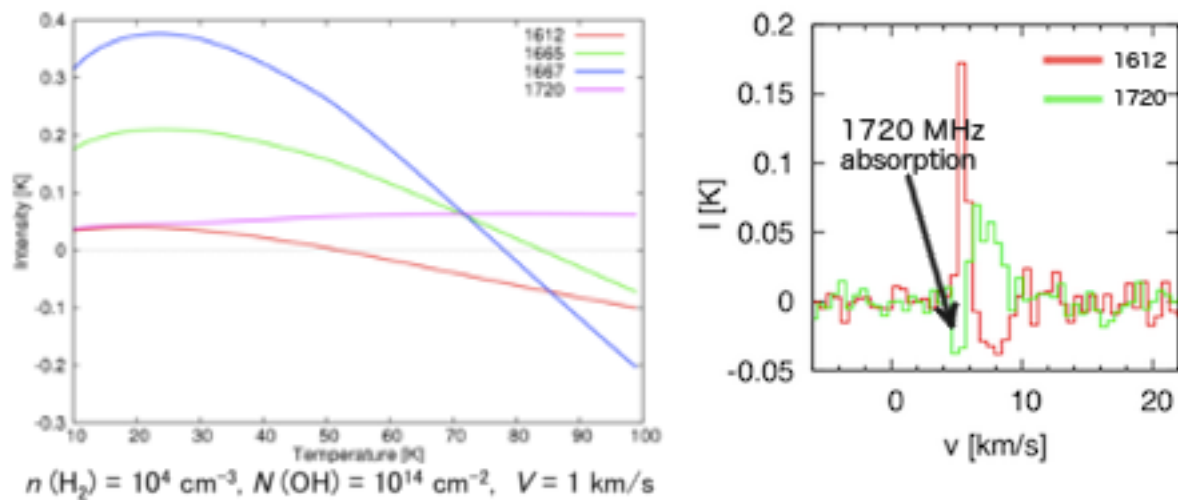
Figure 1: (left) Intensities of the four hyperfine components of OH as a function of temperature derived from the statistical equilibrium calculation. 1612 MHz line appears in absorption when the temperature is higher than 40 K. (right) Intensities of the 1612 MHz line and the 1720 MHz line observed in the northwest of TMC-1.The 1720 MHz line appears in absorption.

Spectral Line Survey toward Quienscent GMC in the LMC

Y. Nishimura,[1] T. Shimonishi,[2] Y. Watanabe,[1] N. Sakai,[1] Y. Aikawa,[2] A. Kawamura,[3] and S. Yamamoto[1]

[1]*The University of Tokyo, Japan*
[2]*Kobe University, Japan*
[3]*National Astronomical Observatory of Japan*

Spectral line survey observations of three giant molecular clouds in the Large Magellanic Cloud (LMC) have been conducted in the 3 mm band with the Mopra 22 m telescope. Spectral lines of fundamental species such as CN, CS, SO, HCN, HCO^+, and HNC are detected in addition to CO and ^{13}CO. Although the observed sources show different star-formation activities, chemical compositions averaged over a molecular-cloud scale (10 pc) with our telescope beam are found to be similar to one another. The observed chemical compositions are almost free from star formation activities and their feedbacks. Nitrogen-containing species are confirmed to be deficient in comparison with the Galactic molecular clouds due to a lower elemental abundance of nitrogen in the LMC. In spite of general resemblance of chemical abundances among the three sources, it is found that the CS/HCO^+ and SO/HCO^+ ratios are slightly higher in a quiescent molecular cloud. An origin of this trend is discussed in relation to possible depletion of sulfur along molecular cloud formation.

Study of Formation Processes and Chemical Conditions of L1544 Pre-stellar Core

N. Tanekura,[1] H. Maezawa,[1] and Y. Aikawa[2]

[1]Department of Physical Science, Osaka Prefecture University, Japan
[2]Department of Earth and Planetary Sciences, Kobe University, Japan

Dark cloud cores are star-forming sites. L1544 located in the eastern area of Taurus molecular complex is a well-known dense pre-stellar core accompanied by a 0.1pc-scale rotating and collapsing disk [1,2,3,4]. We have conducted observations of some molecular species such as SO, CS, CCS, HC_3N, N_2H^+, NH_3 and so on, toward the L1544 core with the NRO 45-m telescope. N_2H^+, NH_3 and SO increase at the late stages of chemical evolution of molecular clouds, whereas carbon chain molecules such as CCS and HC_3N increase in the early stages. We found that the distributions of SO and CCS show the anti-correlation, and the SO decreases at the center of the disk due to the depletion onto dust grains. These results are well consistent with the conventional time-dependent chemical models [2]. Additionally it was found that the maximum peak of SO exists in 0.1 pc northeast of the disk where N_2H^+ and NH_3 were not detected, and the line intensity of CCS was very faint (Fig.1). According to a time-dependent chemical model (density=2.0E+04 cm^{-3}, Av=8 mag), the chemical abundances observed in the SO-clump correspond to those of the molecular cloud in the early stage of chemical evolution (a few ten thousand years).

The parent cloud of L1544 core has blue and red-shifted velocity components [4]. The rotating/collapsing disk appears to be located along the interface region of the two components. On the other hand, the SO-clump adjacent to the disk belongs only to the blue-shifted one. This suggests that the encounter of the two clouds possibly induced the formation of the L1544 pre-stellar core with rotating/collapsing disk, and that the SO-clump is still a chemically and physically young clump left behind by the evolution and formation of the L1544 pre-stellar core. These observed results will be presented in this symposium.
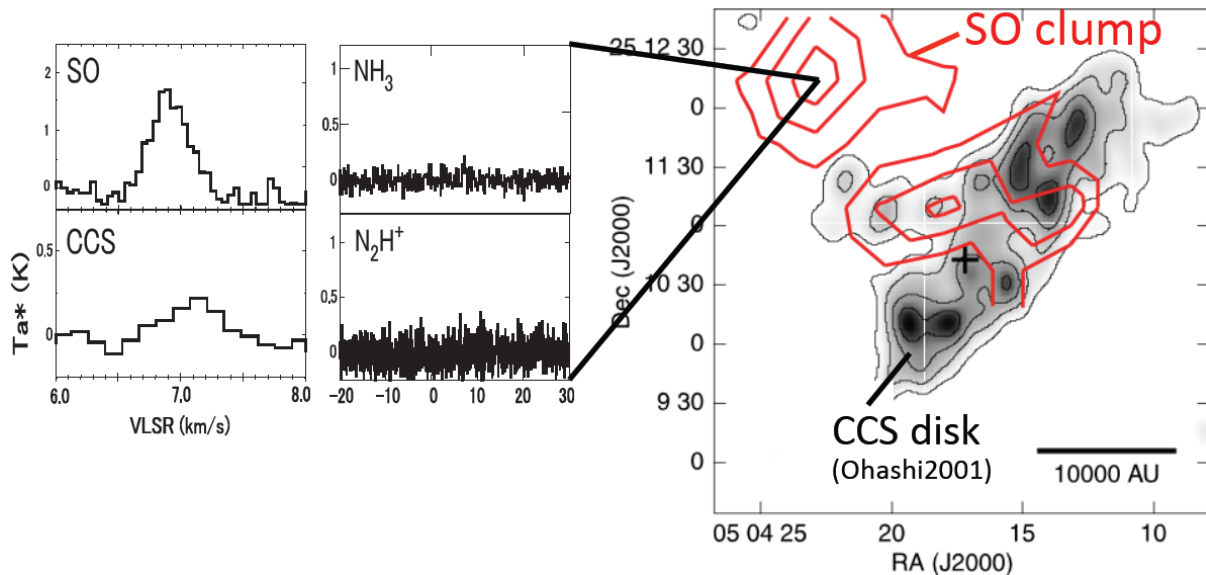

Figure 1: Integrated intensity map of SO ($J_N=3_2-2_1$) and the spectral lines observed toward the SO clump.

References

[1] Ohashi et al, ApJ, 518, L41 (1999). [2]Aikawa et al, ApJ, 620, 330 (2005). [3]Caselli et al, ApJ, 565, 331 (2002). [4]Tafalla et al, ApJ, 504, 800 (1998).

Processing of ices in a massive star-forming region

T. Shimonishi,[1] T. Onaka,[2] T. Mori,[2] M. Yamagishi,[3] and *AKARI*/IRC team

[1]*Graduate school of science, Kobe University, Japan*
[2]*Graduate school of science, The University of Tokyo, Japan*
[3]*Graduate school of science, Nagoya University, Japan*

Infrared absorption spectroscopy toward dense molecular clouds suggests that the bulk of heavy elements exist in the solid phase as ices and dust. Understanding the effect of star formation activities on properties of ices is one of the key issues for interstellar ice chemistry since chemical reactions in the solid phase play an important role in the chemical evolution of star- and planet-forming regions.

This study aims to clarify the effect of star formation activities on the chemical evolution of circumstellar and interstellar ices. For this purpose, spatial distribution of ices in a nearby high-mass star-forming region, Cepheus A, is spectroscopically mapped using the Infrared Camera (IRC) on board the *AKARI* satellite. This is the first spectroscopic mapping of circumstellar ices in a continuous 2—5 micron wavelength region. As a result of observations, infrared absorption bands due to major ice species such as H_2O, CO_2 and CO, are detected from various regions in Cepheus A (Figure 1). Based on the spectral fitting, column densities of each molecular species are derived to map the spatial distribution of ices. We find that ice column densities are centrally concentrated toward the high-mass protostellar object HW2 located in a central part of Cepheus A. This suggests that observed ices are located in the envelope of HW2. We also find that the column density ratio of CO_2/H_2O ices does not vary significantly within a 0.1 pc region around HW2, suggesting that the chemical compositions of ices are less affected by protostellar radiation. In this poster, we discuss the effect of radiation and jet from the protostellar object on the chemical and physical properties of circumstellar ices.
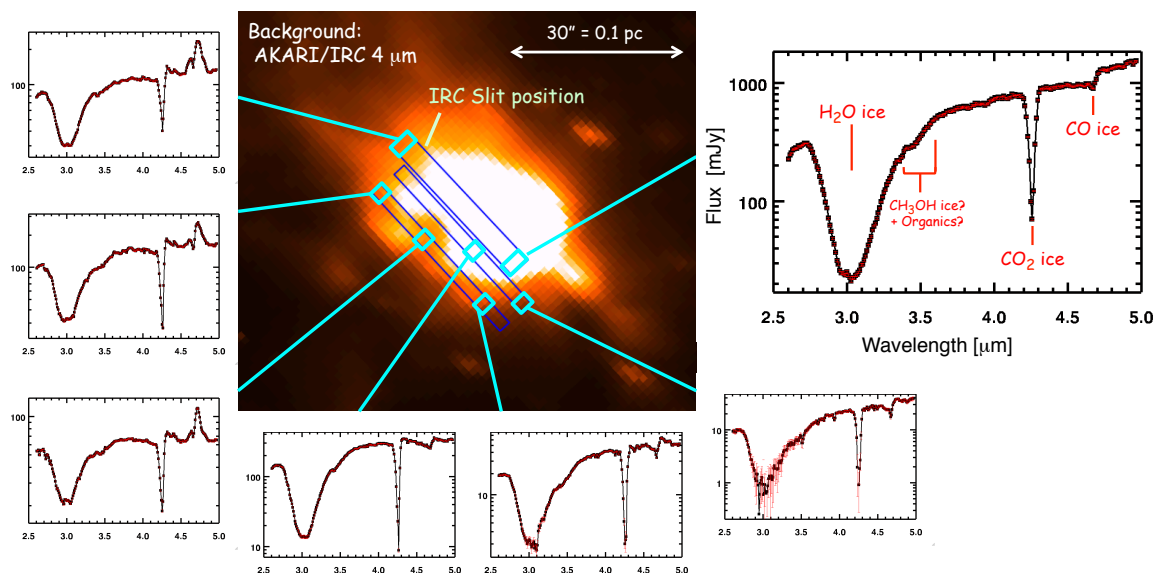

Figure 1: Examples of *AKARI*/IRC near-infrared spectra observed toward the Cepheus A region. The positions of detected ice absorption features are labeled in the upper right panel. The observed slit positions are shown by the blue rectangles in the central panel; the background is *AKARI*/IRC 4 micron image of Cepheus A.

3.3 micron feature variations in AKARI data

M. Hammonds, T. Mori, F. Usui, and T. Onaka

Department of Astronomy, University of Tokyo, Japan

Archived data from AKARI were analysed in the 2.5–5 µm region were analysed to investigate variations in the 3.3 µm PAH feature and related hydrocarbon emission bands. PAHs (and/or related carbonaceous molecular species) comprise a substantial fraction of the carbon budget in the Universe, making the study of their formation and evolution an important means of understanding the behaviour and lifecycle of carbon in our galaxy and beyond.

The data were investigated in the context of the interpretation that the 3.3 µm feature can be decomposed into two closely spaced sub-features at 3.28 µm and 3.30 µm[1,2], in order to explain the observed asymmetry and profile variation of the overall emission band. Our findings indicate that this feature is universally well described by these two components in data recorded using AKARI grism spectroscopy. The cause for these components is discussed in terms of the structure of the emitting molecular carriers, and their relative abundance in different astrophysical environments. Further, a correlation is found between the 3.28 µm sub-feature and the aliphatic hydrocarbon band at 3.4 µm, implying similar environmental conditions for the formation of these molecular carriers. Possible interpretations are discussed in terms of molecular stability and destruction pathways of carbonaceous interstellar species.
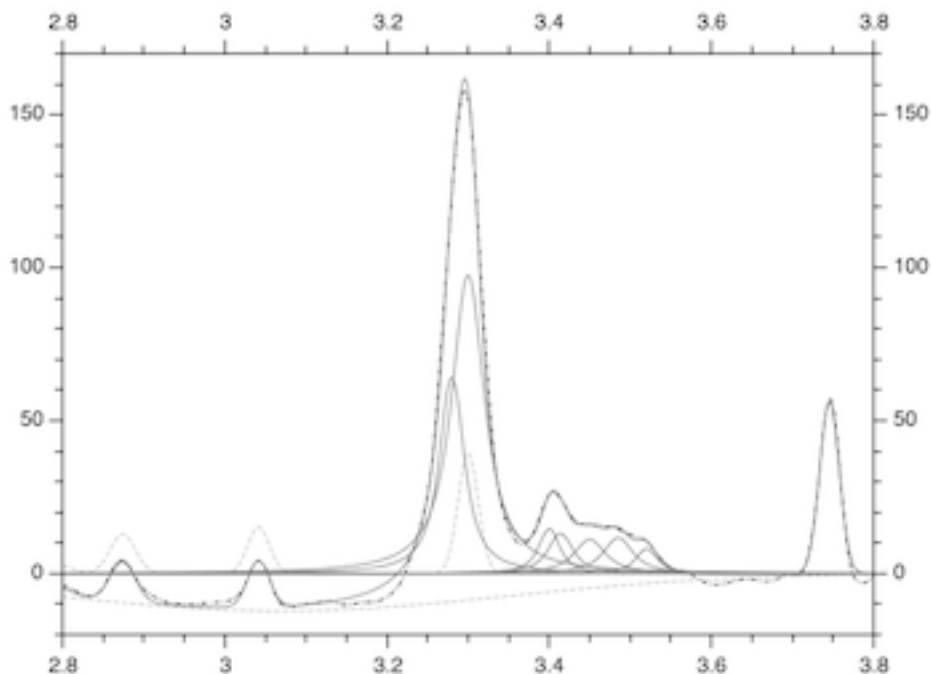

Figure 1: Spectroscopic fitting used in this work. Original data is shown as a solid gray line, and the overall fit is shown by the black dot-dashed line. Note the inclusion of two sub-features (shown in gray) to match the profile of the 3.3 µm band.

References

[1]   Song, I.-O., Kerr, T. H., McCombie, J., & Sarre, P. J. 2003, MNRAS, 346, L1
[2]   Candian, A., Kerr, T. H., Song, I.-O., McCombie, J., & Sarre, P. J. 2012, MNRAS, 426, 389