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研究課題名(和文) Experimental study on photochemistry of water and CO molecules on silicate dust

研究課題名(英文) Experimental study on photochemistry of water and CO molecules on silicate dust

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研究成果の概要(和文)：氷星間塵上での化学プロセスは、星間分子雲における化学進化において重要な役割を果たす。一方、氷に覆われる前の星間塵上で、どのように化学種が進化するのか全くわかっていない。本研究では、初期星間分子雲に存在するケイ酸塩鉱物上での分子生成に関する実験をおこなう。10Kに冷却されたアモルファスケイ酸塩表面上に作製されたH<sub>2</sub>O、およびH<sub>2</sub>OとCOの混合氷への真空紫外光(VUV)照射による分子組成変化を明らかにする。氷へのVUV照射で、わずかにH<sub>2</sub>Oが消失した。また、H<sub>2</sub>O/CO混合氷へのVUV照射では、光化学反応生成物は確認できなかった。これらはケイ酸塩表面で特有の反応だと考えられる。

研究成果の学術的意義や社会的意義

These results contribute to the development of the astrochemistry field. Chemical evolution on bare cosmic dust is still an open question that scientists are always concerned about in the world. So, the present results can give one of the explanations for chemical processes on bare cosmic dust.

研究成果の概要(英文)：Chemical processes of molecules on cosmic ice dust play a significant role for chemical evolution in dense molecular clouds. In contrast, it remains totally unknown how molecules evolve on bare cosmic dust where ice mantles are not formed yet. The present study is to investigate the formation of primitive molecules on silicate dust analogs in dense clouds. In particular, the study is focusing on the photolysis of water and photochemical reactions of H<sub>2</sub>O/CO on amorphous silicate at 10 K. We confirmed that a small amount of water was lost from the amorphous silicate surface due to destruction by UV photons at 10 K. Additionally, the photochemical reaction of water/CO binary was not effective on amorphous silicate at 10 K.

Another study involving the chemistry of phosphine (PH<sub>3</sub>) on amorphous indicated that PH<sub>3</sub> was lost from the surface due to chemical desorption via exposure to H atoms. The present study will contribute to better understand the initial stage of chemical evolution in MCs.

研究分野：Astrochemistry

キーワード：Astrochemistry Molecular clouds Photochemistry

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Formulas C-19, F-19-1, Z-19 (common)

### 1. 研究開始当初の背景

Interstellar molecular clouds (MCs) are the birthplace of stars and planets in space. MCs are composed of many gaseous species and solid components so-called cosmic dust. Recently, more than 200 species have been detected in the interstellar medium (ISM) and their chemical reactions mostly take place in MCs whose typical temperature is as low as 10 K. Previous studies experimentally demonstrated that the formation of some molecules that are main components of MCs such as water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), ammonia (NH<sub>3</sub>), and methanol (CH<sub>3</sub>OH) can be produced by non-energetic surface reactions or energetic processes such as photolysis on cosmic dust at 10 K [1,2]. In fact, in previous studies, chemical reactions of species were typically studied on dust analogs covered with water ice; however, cosmic dust is just a bare silicate at the initial stage of dense clouds. It is totally unknown whether those processes occur on bare silicate dusts or not.

### 2. 研究の目的

The purpose of the present study is to study chemical processes on bare silicate dust to interpret the chemical evolution at the initial stage of cosmic dust. To investigate the chemical processes on bare silicate dust, I would like to mainly focus on the photolysis of water and water/carbon monoxide on bare silicate as low temperatures. In addition, I would like to study physico-chemical behavior of a phosphorus (P)-bearing molecule, phosphine (PH<sub>3</sub>), on silicate dusts. The chemistry of PH<sub>3</sub> on icy grains can interpret the presence of PH<sub>3</sub> gas in the dense, cold, and quiescent regions of molecular clouds is due to the chemical desorption of PH<sub>3</sub> on the icy surface as well as the deuterated isotopologues of phosphine, in particular PH<sub>2</sub>D, could be detected in future astronomical observations by telescopes that target PH<sub>3</sub> and rich deuterium-rich environments.

### 3. 研究の方法

I used an Apparatus for Surface Reaction in Astrophysics (ASURA) system to perform all experiments of the study. The ASURA system is composed of a vacuum chamber with the basic pressure of 10<sup>-10</sup> tor, multiple turbo molecular pumps, an aluminum (Al) reaction substrate which is covered with amorphous silicate (Mg<sub>2</sub>SiO<sub>4</sub>) with the thickness of 10-30 nm, which were prepared by magnetron sputtering to sintered polycrystalline Mg<sub>2</sub>SiO<sub>4</sub>. The surface temperature was controlled between 5 and 300 K. Compact amorphous solid water (c-ASW) was prepared by vapor deposition of H<sub>2</sub>O via a capillary plate and maintained at 110 K. The thickness of the c-ASW was estimated to be approximately 30 monolayers (MLs).

Firstly, water or water/CO binary layers deposited on Mg<sub>2</sub>SiO<sub>4</sub> were exposed to UV photons at 10 K.

Chemical processes of photolysis processes would be monitored in-situ by using a Fourier-Transform Infrared Spectroscopy (FTIR).

After completing chemical processes, the surface temperature will be heated up to high temperatures. Remaining reactants and products desorbed from the surface will be detected via quadrupole mass spectrometers (QMS) located very closed to the reaction substrate.

Secondly, I performed experimental and computational studies on chemistry of  $\text{PH}_3$  via studying the chemical desorption processes and H-D substitution reactions on  $\text{PH}_3$  on  $\text{Mg}_2\text{SiO}_4$  at 10 K [3,4]. A thin layer of  $\text{PH}_3$  desorbed on  $\text{Mg}_2\text{SiO}_4$  was exposed to H (or D) atoms at 10 K. I expect that  $\text{PH}_3$  reacts with H atoms and desorbs from the silicate substrate following reactions:  $\text{PH}_3 + \text{H} \rightarrow \text{PH}_2 + \text{H}_2$  and/or  $\text{PH}_2 + \text{H} \rightarrow \text{PH}_3$ . During exposure process, the chemical desorption of  $\text{PH}_3$  and products are recorded by FTIR at 10 K. Products of the reaction between  $\text{PH}_3$  and H (or D) atoms are detected by QMS.

#### 4. 研究成果

Firstly, I performed the photolysis of water and water/CO binary ices on  $\text{Mg}_2\text{SiO}_4$  at 10 K.  $\text{H}_2\text{O}$  decreased with increasing photon exposure time due to destruction by the following reactions:

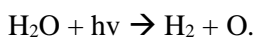
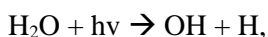


Figure 1 displays the decrease of  $\text{H}_2\text{O}$  by exposure to UV photons on  $\text{Mg}_2\text{SiO}_4$  at 10 K. The effect of dissociation of  $\text{H}_2\text{O}$  on silicate substrate depended on the binding energy between  $\text{H}_2\text{O}$  and the reaction  $\text{Mg}_2\text{SiO}_4$  surface at low temperatures.

The photodissociation of  $\text{H}_2\text{O}$  on silicate substrate was less significant compared to that on  $\text{H}_2\text{O}$  ice. This could be due to the effect of absorption of  $\text{H}_2\text{O}$  on silicates. In addition, the photochemical reaction of water/CO binary ice on silicate substrate is also affected on the silicate substrate. There were no products detected by both FTIR during the photolysis processes at 10 K as well as QMS after completing exposure to UV photons on the surface, which is inconsistent with previous studies where thick water/CO binary ice layers were exposed to UV photons at low temperatures [5,6]. Therefore, the present results imply that amorphous silicate substrate could suppress a progress of photochemistry of species at low temperatures.

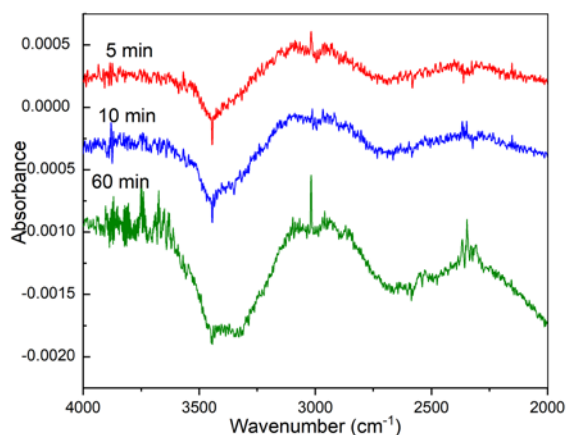


Figure 1: Variations in the difference spectra of  $\text{H}_2\text{O}$  after exposure to UV atoms for 5, 10, and 60 minutes at 10K.

Figure 2 displays the initial  $\text{PH}_3$  and variation in the difference spectra of  $\text{PH}_3$  focusing on the P-H stretching band after exposure to H atoms for up to 120 minutes at 10 K. The intensity of  $\text{PH}_3$  reduced with the exposure times of H atoms on the icy surface. After exposure to H atoms in 2 hours, 50 % of solid  $\text{PH}_3$  was lost from the icy surface. The decrease of  $\text{PH}_3$  by exposure to H atoms on icy surface should result from the chemical desorption following the reactions:  $\text{PH}_3 + \text{H} \rightarrow \text{PH}_2 + \text{H}_2$  and/or  $\text{PH}_2 + \text{H} \rightarrow \text{PH}_3$ .

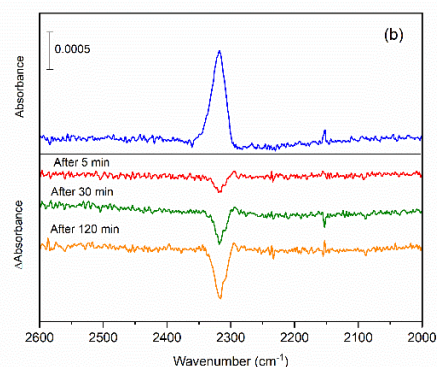


Figure 2: Variations in the difference spectra of the solid  $\text{PH}_3$  after exposure to H atoms for 5, 30, and 120 minutes at 10K. The initial P-H stretching band (blue) is shown as a reference.

We performed experimental studies on the reactions of  $\text{PH}_3/\text{PD}_3$  with D/H atoms at low temperatures. We confirmed that, at 10 K on icy surfaces, H-D substitution reactions of  $\text{PH}_3$  and D-H substitution reactions of  $\text{PD}_3$  occurred following reactions with D and H atoms, respectively. Those reaction related H or D-abstraction reactions have activation barriers; therefore, quantum tunneling should play a role at low temperatures, while the radical-radical reactions are barrierless. Figure 3 summarized the chemical pathways of H-D substitution reactions on  $\text{PH}_3$  and D-H substitution reactions on  $\text{PD}_3$  on the icy surface at 10 K.

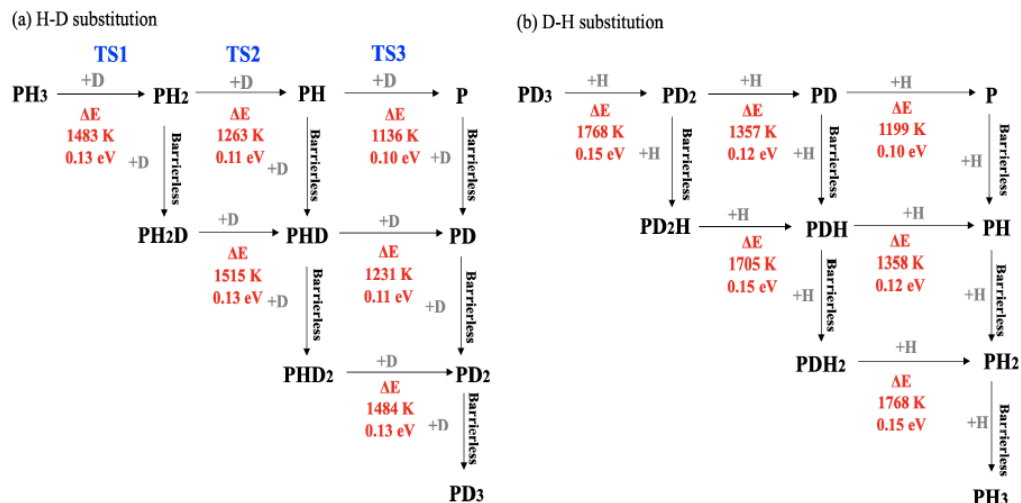


Figure 3: Chemical network of (a) H-D substitution reactions of  $\text{PH}_3$  and D atoms and (b) D-H substitution reactions of  $\text{PD}_3$  with H atoms on icy surface.

The present study demonstrates that the chemical desorption of phosphine is very effective regardless of the ice structure. It contributes to better understand chemistry of phosphine as well as P-bearing species in the ISM.

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5. 主な発表論文等

〔雑誌論文〕 計3件（うち査読付論文 3件/うち国際共著 1件/うちオープンアクセス 1件）

1. 著者名 M. Tsuge, T. Nguyen, Y. Oba, T. Hama, A. Kouchi, N. Watanabe	4. 巻 760
2. 論文標題 UV-ray irradiation never causes amorphization of crystalline CO <sub>2</sub> : A transmission electron microscopy study	5. 発行年 2020年
3. 雑誌名 Chemical Physics Letters	6. 最初と最後の頁 137999 (6pp)
掲載論文のDOI (デジタルオブジェクト識別子) 10.1016/j.cplett.2020.137999	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 -

1. 著者名 T. Nguyen, Y. Oba, T. Shimonishi, A. Kouchi, and N. Watanabe	4. 巻 898
2. 論文標題 An Experimental Study of Chemical Desorption for Phosphine in Interstellar Ice	5. 発行年 2020年
3. 雑誌名 The Astrophysical Journal Letters	6. 最初と最後の頁 L52 (6pp)
掲載論文のDOI (デジタルオブジェクト識別子) 10.3847/2041-8213/aba695	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 -

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3. 雑誌名 Review of Scientific Instruments	6. 最初と最後の頁 124504(36pp)
掲載論文のDOI (デジタルオブジェクト識別子) 10.1063/5.0018926	査読の有無 有
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〔学会発表〕 計0件

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8 . 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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