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科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Multiscale modeling of radical diffusion and radical reactions on interstellar ices

研究課題名（英文）Multiscale modeling of radical diffusion and radical reactions on interstellar ices

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　3,300,000円

研究成果の概要（和文）：OH, CH3Oラジカルと氷表面の結合エネルギーを計算したところ，吸着サイトにより，それぞれ0.06-0.72eVおよび0.1-0.5eVという広い範囲の値をとることが分かった。OH-負イオンが氷表面に存在するとき，氷内部へのプロトンホールの移動が生じ，結果として負の電荷が流れることを計算で明らかにした。量子化学計算により，PH3＋DおよびOCS＋Hの反応の経路ごとの活性化エネルギーを求めた。本研究結果は，宇宙の氷星間塵表面で生じる化学進化の解明に向けた，重要な基礎データとなる。

研究成果の学術的意義や社会的意義
Computed radical adsorption and reactions on ices are vital in understanding mechanisms of formation of complex organic molecules in interstellar medium. The project involved collaborations with the researchers in Japan and Sweden. Thus, the project would be beneficial for astrochemistry research.

研究成果の概要（英文）：A range of binding energies was observed for OH radical (0.06-0.74 eV). (Phys. Rev. Lett. A, 2020, 102, 052822) OH anion on ice can be transported to ice bulk through the proton hole transfer, giving rise to a negative current (J. Phys. Chem. Lett. 2021, 12, 1, 704-710) A range of binding energies, 0.10-050 eV, was also observed for CH3O radical on ices. (J. Phy. Chem. A, 2021, 125, 1, 387-393) Quantum chemical calculations rationalized the radical reaction mechanisms on ices; PH3 + D (Astrophys. J. 2021. 198, 73), OCS + H (Astrophys. J. 2021, 922, 146) I have summarized the results in a review; W. M. C. Sameera et al., Astron. Space Sci. 2022. (Accepted). DOI: 10.3389/fspas.2022.890161

研究分野：地球惑星科学

キーワード：Radicals on ice surfaces　Binding energy　Reaction mechanisms　DFT　QM/MM

１．研究開始当初の背景

Quantitative mechanistic details of the radical reactions on ice grains at very low temperatures (e.g., 10 K) are required to understand the formation of the complex organic molecules (COMs) in the interstellar medium (ISM).[1] The primary radicals in the ISM, particularly H, OH, CO, HCO, CH_3O, CH_2OH, CH_3, NH, and NH_2 can be formed through photodissociation of the molecules in ice mantles or through surface reactions. Accumulation of primary radicals and molecules on the ice grain surfaces may occur at very low temperatures, generally at 10 K in dark clouds. H atoms may diffuse on the grain surfaces at 10 K, whereas the other radical species and molecules may diffuse at relatively high temperatures, and react when they encounter to form COMs. The radical processes on ices are challenging to characterize from laboratory experiments. Quantitative detail of the radical processes on ices can be obtained using computational methods.

２．研究の目的

I used quantum chemical calculations to determine the binding energy of radical species (OH, CH_3O, PH_2, PH, P, and HCO) on ices. Also, I have rationalized the radical reaction mechanisms (PH_3 + D and OCS + H) on the interstellar ices. Computed properties were compared with the experimental results.

３．研究の方法

Local minima and transition states on the ground state potential energy surfaces were calculated using density functional theory (DFT) or two-layer Our own N-layered Integrated molecular Orbital and molecular Mechanics (ONIOM) method. DFT was used for ONIOM high-level, while the AMOEBA09 polarizable force field was used for ONIOM low-level using the SICTWO interface. Vibrational frequency calculations were performed to confirm the nature of the stationary points (i.e., no imaginary frequency for LM and one imaginary frequency for TS) and to calculate zero-point energies. Connectivity between the LM was confirmed by performing IRC calculations. Excited-state potential energy surfaces were calculated using the time-dependent DFT method. Ice cluster models were used to replicate ice surfaces.

４．研究成果

Binding energy of radicals on ices

Binding energies of the radicals on ices are a primacy interest to the astrochemistry field. Thus, I have calculated the binding energies of the radical species on ices. The computed binding energies are sensitive to the dangling hydrogen (*d*-H) or dangling oxygen (*d*-O) at the binding site (Fig. 1). A range of binding energies was

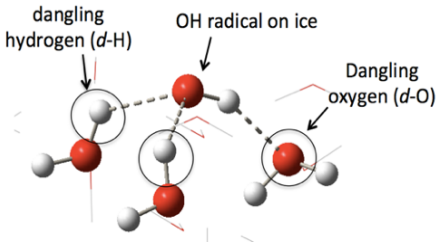

Fig. 1. Dangling hydrogen (*d*-H) or dangling oxygen (*d*-O).

observed for each radical; OH (0.06–0.74 eV),[2] CH_3O (0.10-0.50 eV),[3] PH_2 (0.13-0.21 eV),[4] PH (0.10-0.19 eV),[4] P (0.07-0.16 eV)[4] and OCSH (0.19-0.46 eV).[5] Therefore, the distribution of dangling atoms on ice plays a very important role. Thus, we proposed that a more realistic astrochemical model could be achieved by using a distribution of binding energies instead of a single value.

We have combined quantum chemistry and laboratory experiments to understand how OH radical behaves on ice.[2] Our experiments created OH radicals on ice by photodissociation of H_2O at interstellar conditions. Computed ground and excited-state potential energy surfaces of the OH radical on water suggested that one-photon absorption of the OH-$(H_2O)_n$ complex leads to OH desorption (Fig. 2). Excited OH can be entered into a dissociation channel through the conical intersection near the excited state minima, leading to the OH desorption from the ice surface.

If an OH radical on ice meets an electron, an OH anion can be formed. Then, the OH anion reacts with a water molecule on the ice surface, and the OH anion is transmitted in ice bulk through the proton hole transfer, giving rise to the negative current. This phenomenon was confirmed by quantum chemical calculations and laboratory experiments.[6] If the OH anion meets an organic molecule trapped in ice, COMs may be formed in ice bulk.

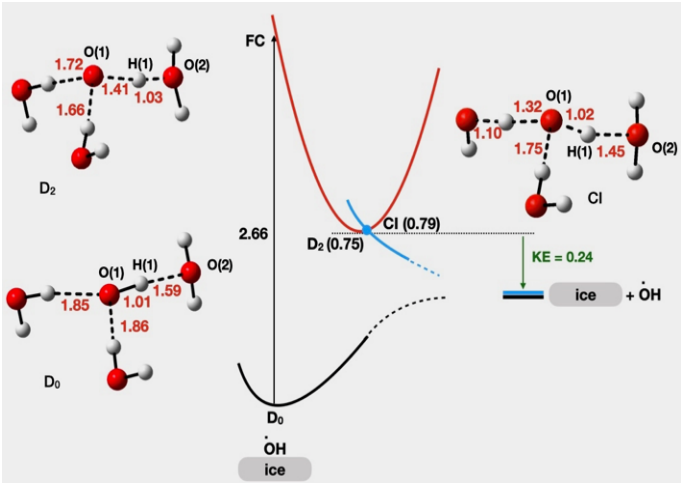

Fig. 2. Ground and excited state potential energy surfaces of the OH-$(H_2O)_n$ complex.

Radical reactions on ices.

OCS + H: A number of S-bearing species, including OCS, have been detected in the ISM. According to laboratory experiments, the reaction of OCS with H atoms on amorphous solid water (ASW) at 10 K gives rice to H_2S, CO, H_2CO, and CH_3OH as the major product. I have performed quantum chemical calculations to rationalize the reaction mechanisms. Calculated potential energy surfaces are shown in Figure 3a.

According to DFT calculations, the reactions between OCS and H on ASW showed three reaction paths. The lowest energy path gives rise to OCS-H, where the computed reaction barrier is 0.21 eV. Then, OCS-H reacts with the second H atom, and three barrierless reaction paths were found. Among them, OCS-H + H → CO + H_2S reaction path gives rise to the most stable products. Other possible products, HC(O)SH and H-OCSH, were relatively unstable. Therefore, CO and H_2S are the major products, while HC(O)SH is the minor product. The calculated reaction mechanisms are in

agreement with the experimental data. This study gives important mechanistic insights to understand the evolution of S-bearing species in the ISM.

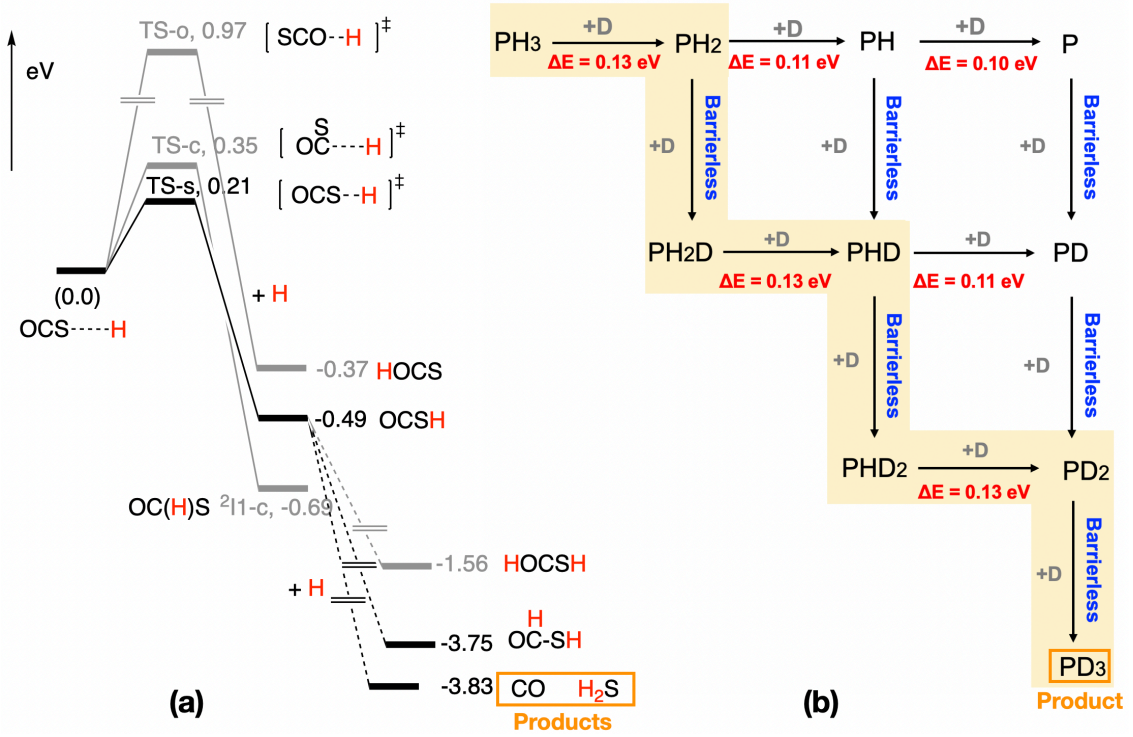

Fig3. (a) Potential energy surfaces for OCS + H reaction on ASW. (b) Reaction pathways for the PH_3 + D reaction on ASW.

PH_3 + D: Phosphine (PH_3) is an important molecule in the ISM. The chemistry of PH_3 in the ISM is vital in understanding the origin and chemical evolution of the phosphorus-bearing species. Experimental studies were performed for the PH_3 + D reaction on ASW at low temperatures. According to the experimental data, PD_3 is formed on ASW. Also, PH_2D and PHD_2 were detected, but their concentration is relatively low compared to PD_3. The mechanism of the reaction PH_3 + D reaction on ASW was rationalized from quantum chemical calculations. The computed reaction mechanism is shown in Figure 3b. PH_3 + D reaction on ASW yields PD_3, where step-wise dehydrogenation is occurred. Computed reaction paths explained the mechanism for the formation of PD_3 that goes through the experimentally observed PH_2D and PHD_2 intermediates. My findings give important mechanistic insights into understand chemical networks that include phosphine in the ISM

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５．主な発表論文等

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掲載論文のDOI（デジタルオブジェクト識別子） 10.3389/fspas.2022.890161	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 －

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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 該当する

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〔産業財産権〕

〔その他〕

Astrophysical Chemistry/Ice&Planetary Science
http://www.lowtem.hokudai.ac.jp/astro/index.html

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

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			
スウェーデン	University of Gothenburg			