

Behaviour of radicals on interstellar dust analogues

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Abstract. Surface reactions of radicals play important roles in the formation of complex molecules on interstellar dust grains. Under interstellar conditions, because the coverage of adsorbates on dust is significantly low, surface reactions are often limited by precedent processes, namely, the adsorption and diffusion of reactants. Therefore, to appropriately incorporate dust surface reactions into chemical models, information on the adsorption and diffusion of radicals is crucial. However, it is not easy to follow the behaviour of radicals on surfaces by conventional experimental methods. To monitor radicals on interstellar dust analogues, we have recently succeeded in applying a combination of photostimulated desorption and resonance-enhanced multiphoton ionization methods. In this paper, we briefly review our recent experiments for clarifying radical behaviour on water ice, pure solid CO and diamond-like carbon.

Keywords. Radicals, detection method, ice.

1. Introduction

It is widely accepted that surface reactions on dust grains are necessary for the synthesis of abundant molecules such as H₂, H₂O, H₂CO and CH₃OH in molecular clouds. In fact, the formation of these molecules by surface reactions has been confirmed experimentally (for a review, see [Hama & Watanabe \(2013\)](#) and [Watanabe & Kouchi \(2008\)](#)). Most experiments have focused on hydrogenation reactions, and in typical experiments, reactants on dust analogues such as water ice were exposed to hydrogen atoms at low temperatures. The reaction rates and products were monitored by Fourier Transform Infrared Spectroscopy (FTIR) and occasionally with a temperature-programmed desorption (TPD) method. These experiments have revealed the reactivity and products for various hydrogenation reactions. However, information on the surface processes prior to reaction, namely, adsorption and diffusion, is scarce due to high hydrogen fluxes required in such experiments in which hydrogen atoms can immediately encounter reaction partners without long-distance diffusion on the surface. In contrast to such experiments, surface reactions on realistic dust grains require the adatoms to migrate for a long distance because the accretion rate of atoms is approximately once a day and thus the surface coverage of atoms should be very low. In such circumstances, reaction rates are often limited by diffusion. Therefore, to evaluate surface reactions quantitatively, the surface diffusion of atomic reactants needs to be clarified.

After a pioneer research by d'Hendecourt *et al.* ([d'Hendecourt *et al.* \(1982\)](#)), in recent years, the reactions of radicals heavier than hydrogen atom such as OH and HCO have attracted attention for the formation of complex organic molecules (COMs) on dust grains ([Garrod *et al.* \(2008\)](#)). Because the heavier radicals cannot migrate at low temperatures, the radical-radical reactions are considered to occur during warming-up in chemical models. Experiments to study the radical-radical reactions have also been launched. For

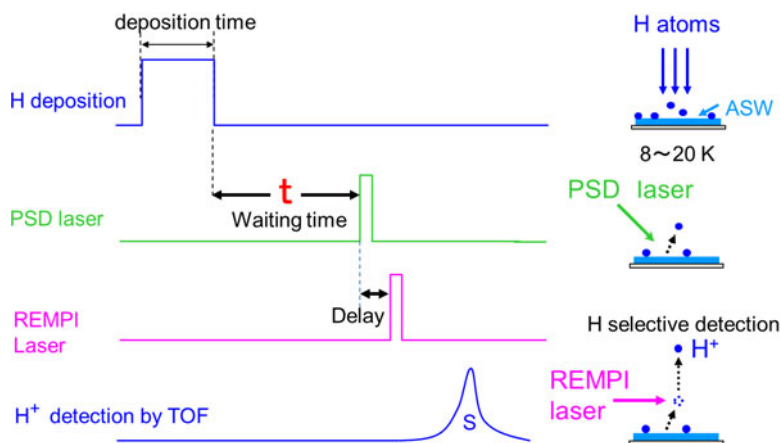


Figure 1. Timing chart of the PSD-REMPI method for the detection of H atoms on ice.

example, the formation of COMs has been observed in solids by the codeposition of H atoms and some molecules at approximately 10 K (e.g., Fedoseev *et al.* (2015)). In the codeposition experiments, a significant amount of radicals is produced by hydrogenation reactions during deposition, and thus, the average distance between radicals would be short enough to cause radical-radical reactions even at low temperatures. Because radical-radical reactions are normally barrier-less, the observation of COM formation at low temperatures in such experiments is reasonable. To incorporate these results into chemical models, the diffusion of heavier radicals should be quantified experimentally. However, there have been no experiments to detect surface radicals due to the intrinsic technical difficulties.

The activation energies for the surface diffusion of hydrogen atoms on ice were derived by conventional TPD experiments (Perets *et al.* (2005) and Matar *et al.* (2008)). In these experiments, H and/or D atoms were deposited onto the surface and then the TPD spectra of recombined H₂ were obtained during heating. To obtain the activation energy of hydrogen atoms, three free parameters (the activation energies for atomic diffusion, atomic desorption, and H₂ (HD, or D₂) desorption) were adopted to analyse the TPD spectra. Multi-parameter fittings often cause large uncertainties. Furthermore, the diffusion barriers should be widely distributed in height because ice has an irregular surface. Therefore, TPD experiments have disadvantages for determining the surface diffusion barriers. In fact, TPD experiments have provided contradictory results (Perets *et al.* (2005) and Matar *et al.* (2008)). Microscopic techniques such as STM, FEM, and AFM can be used to detect surface radicals. However, these methods are not applicable for radicals showing fast and long-distance diffusion. In addition, ice is not an electrical conductor. Although techniques for solids such as FTIR and EXAFS are often utilized for radical detection and NMR can follow radical diffusion, these methods are not surface sensitive. Therefore, we have developed a new methodology to detect radicals mainly on ice.

2. PSD-REMPI method

We have combined photostimulated desorption (PSD) and resonance-enhanced multiphoton ionization (REMPI) methods to monitor radicals from dust grain analogues (Watanabe *et al.* (2010), Hama *et al.* (2012), and Kuwahata *et al.* (2015)). As for picking up H atoms on ice, a typical procedure is shown in Figure 1. First, H atoms are prepared on ice at a given coverage. H-atom adsorbates are photodesorbed by unfocused weak PSD

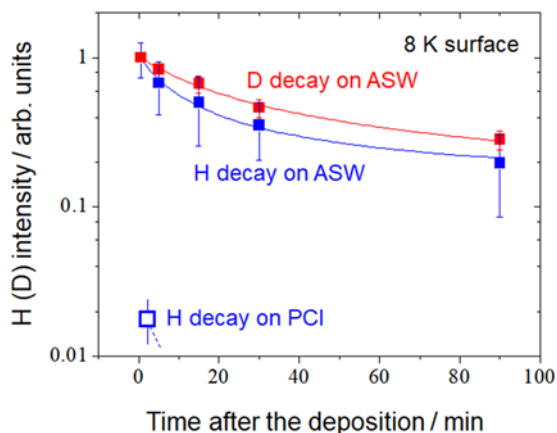


Figure 2. Attenuation of H and D atoms on amorphous solid water (ASW) and polycrystalline ice (PCI). Solid lines are fitting by equations of recombination.

laser radiation, typically at 532 nm, and subsequently selectively ionized by REMPI just above the surface. Ionized atoms are mass analysed by a time-of-flight method. In the experiments, the detected REMPI signal intensities were proportional to the coverage. Based on the delay time of the REMPI laser shot after the PSD laser and the distance between the surface and the focal position of the REMPI laser, the translational energy distribution of desorbed H atoms can be derived. As described later, the photodesorption mechanisms depend on the adsorbates. In the following sections, we show several experiments that demonstrate the behaviours of radicals on dust analogues by using the PSD-REMPI method.

3. Behaviour of H (D) atoms on ice

3.1. Activation energy of surface diffusion on ice

The basis of the experiments is as follows. When hydrogen atoms are present at a given coverage on ice at approximately 10 K, which is well below the mono-atomic desorption temperature, the attenuation rate of surface H-atom density is governed by H_2 recombination. Because recombination is itself a radical-radical barrier-less reaction in the physisorption system, it would be limited by the surface diffusion of H atoms. Therefore, following the decrease in the number density of H atoms on ice should provide information of the surface diffusion of H atoms (Watanabe *et al.* (2010) and Hama *et al.* (2012)).

Amorphous solid water was prepared as an ice dust analogue on an aluminium substrate at 10 K by vapour deposition of up to 40 monolayers (MLs). The H (D) atoms were produced by dissociation of H_2 (D_2) in a microwave-induced plasma and deposited on ice through a cold aluminium pipe to reduce the kinetic temperature. Controlling the H_2 gas flow rate and deposition time, the coverage of H atoms was set to be approximately 10^{-3} . The H-atoms on the surface were monitored by the PSD-REMPI method. Because both H atoms and H_2O molecules are transparent to photons at 532 nm, desorption should be induced by a mild desorption process such as phonon propagation from the substrate as opposed to an energetic photochemical process. In fact, the kinetic energy of desorbed H atoms was found to correspond to a temperature of about 30 K. By changing the time gap between the termination of H (D) atom deposition and the PSD-REMPI detection, we observed the attenuation of H (D) atoms on ice, as shown in Figure 2. As described above, the attenuation should be H_2 (D_2) diffusion-limited

recombination. Because the attenuation curves do not show a significant isotope effect, the surface diffusion is dominated by thermal hopping rather than tunnelling under the present experimental conditions. The attenuation curves are well reproduced by a diffusive recombination rate with at least three components of activation energies, <18 meV, 22 meV, and >30 meV (Hama *et al.* 2012). We also performed the same measurement for polycrystalline ice. The attenuation was too rapid to follow with the present experimental procedure, suggesting the occurrence of tunnelling diffusion. Thus, we employed a different procedure with the PSD-REMPI method.

3.2. Diffusion mechanism on polycrystalline ice and amorphous solid water: thermal or tunnelling

Polycrystalline ice consists of many pieces of single crystals. We propose that the H atoms migrate by tunnelling within a crystalline piece having rather periodic potentials for diffusion, while long-distance diffusion would be limited by thermal hopping beyond the boundaries between the crystalline pieces. To support this scenario, we performed an atom-coverage controlled experiment in which the isotope effect on the diffusion rate for each coverage was investigated. At higher atomic coverages, several atoms can exist within a single crystalline piece, and then these atoms can encounter each other to recombine within the piece. In such a case, the H₂ recombination rate would be dominated by tunnelling diffusion. In contrast, to meet the reaction partners at lower coverages, atoms may be required to overcome thermally the potential barriers of boundaries between crystalline pieces. Consequently, we expect the appearance of a significant isotope effect on the recombination rate at higher atomic coverages and a small effect at lower coverages. Because we could not experimentally determine the coverage of H (D) atoms on ice, we indirectly controlled them by changing the flux of atoms or, in other words, the deposition rate of atoms (Kuwahata *et al.* 2015). When atoms are continuously deposited on ice, the surface number densities of atoms come to equilibrium due to a balance between the atomic supply onto the surface and losses by recombination, as expressed by $pf_H = k_{H-H}[H]^2$ for H atoms, where p , f , k_{H-H} are the sticking coefficient, atomic flux, and H₂ recombination rate constant, respectively, and k_{H-H} is diffusion limited. In our experiments, the atomic fluxes of H and D atoms are the same. Assuming the sticking coefficients of H and D atoms are equivalent at approximately 10 K, the ratio of diffusion coefficients for H and D atoms, $k_{diff}[H]/k_{diff}[D]$, is simply expressed by $[D]^2/[H]^2$. We monitored [H] and [D] experimentally on both polycrystalline ice and amorphous solid water by the PSD-REMPI method as a function of the atomic flux, as plotted in Figure 3. It is clearly shown that the diffusion at the higher fluxes on polycrystalline ice demonstrates a significant isotope effect, indicating tunnelling diffusion. At lower fluxes for polycrystalline ice, the diffusion can be explained by thermal hopping. For amorphous solid water, the diffusion is always dominated by thermal hopping regardless of the flux.

4. Behaviour of H (D) atoms on pure solid CO

To clarify the diffusion of H (D) atoms on pure solid CO, the same methodology as that shown in section 3.1 was adopted. The H atoms were deposited with a coverage below 10⁻⁴ on pure solid CO at approximately 10 K. The attenuation of H atoms on the surface was monitored by the PSD-REMPI method. Although a fraction of H atoms should be consumed by the hydrogenation of CO, neither HCO, H₂CO, nor CH₃OH were detected by the FTIR probably due to very small yields below the detection limit. From the attenuation curves of H and D atoms on solid CO, the diffusion at 8, 12, and 15 K was found to be governed by thermal hopping over the barriers of 22, 30, and 37 meV, respectively (Kimura *et al.* 2018). Because the atoms tend to be trapped

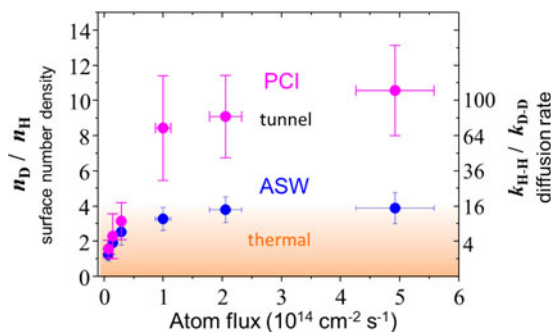


Figure 3. D and H signal intensity ratio as a function of the flux of H (D) atoms, obtained from the PCI (pink circles) and ASW (blue circles) surfaces. The right Y axis is the ratio of surface diffusion rates. The shaded area represents the thermal-diffusion dominated region.

in deeper adsorption sites as the surface temperature increases, the diffusion at higher temperatures is dominated by the higher barriers.

5. Behaviour of H (D) atoms on diamond-like carbon

Because diamond-like carbon (DLC) is a good analogue for potential C-dominated ISM dust, we investigated the behaviour of H atoms on DLC (Tsuge *et al.* 2019). The DLC surface was prepared on the aluminium substrate by the laser ablation of a graphite disk *in situ* within the experimental chamber to avoid contamination in air. The structure of the carbon material produced by this method was found to be sp^3 -dominated amorphous DLC by a transmission electron micrograph. For the DLC surface, the diffusion cannot be followed by the procedure described in section 3.1 probably due to the low efficiency of PSD. Instead, we monitored the recombined H_2 (D_2) on the surface during H (D) deposition. Figure 4 shows the temporal variation of H_2 (D_2) (sum of $J=1$ and 0) on the surface as monitored by the PSD-REMPI method during both H_2 molecular and H atomic deposition. In this experiment, the dissociation fraction in the atomic beam was approximately 70%, and the gas flow rates were the same for both cases. The most striking feature is that the H_2 intensities for H atom deposition are equivalent to those for H_2 deposition (Fig. 4 (c)), indicating that most H atoms recombine and remain on the surface even at 20 K when the adsorption of H and H_2 on ice is significantly suppressed. At lower temperatures, the H_2 intensities for H atom deposition are 70-80% of those for H_2 deposition. Considering the dissociation fraction in the atomic beam, this result indicates that some fraction of H adatoms cannot diffuse and thus remain unreacted on the surface at these temperatures. At 22 K, the difference in the H_2 intensities between H atom and H_2 deposition may result from the lower sticking coefficient of H atoms. For deuterium, the D_2 intensities for D atom deposition are always below those for D_2 deposition, indicating that the diffusion of D atoms is sufficiently slower than that of H atoms. A more detailed analysis has been presented elsewhere (Tsuge *et al.* 2019).

6. Monitoring OH radical on ice

The OH radical is considered to be one of the most abundant radicals on ice dust because it is easily produced by the photolysis of water ice and the reaction of H and O atoms. Therefore, the reactions of OH radicals with the other radicals would contribute significantly to the production of various complex molecules and precursors such as HCOOH, HNOH, CH_3OOH and H_2O_2 . Although radicals that are heavier than H atoms hardly migrate on ice at temperatures as low as 10 K, reactions are enhanced during the warming of dust. To evaluate the OH radical reactions in chemical models, quantitative

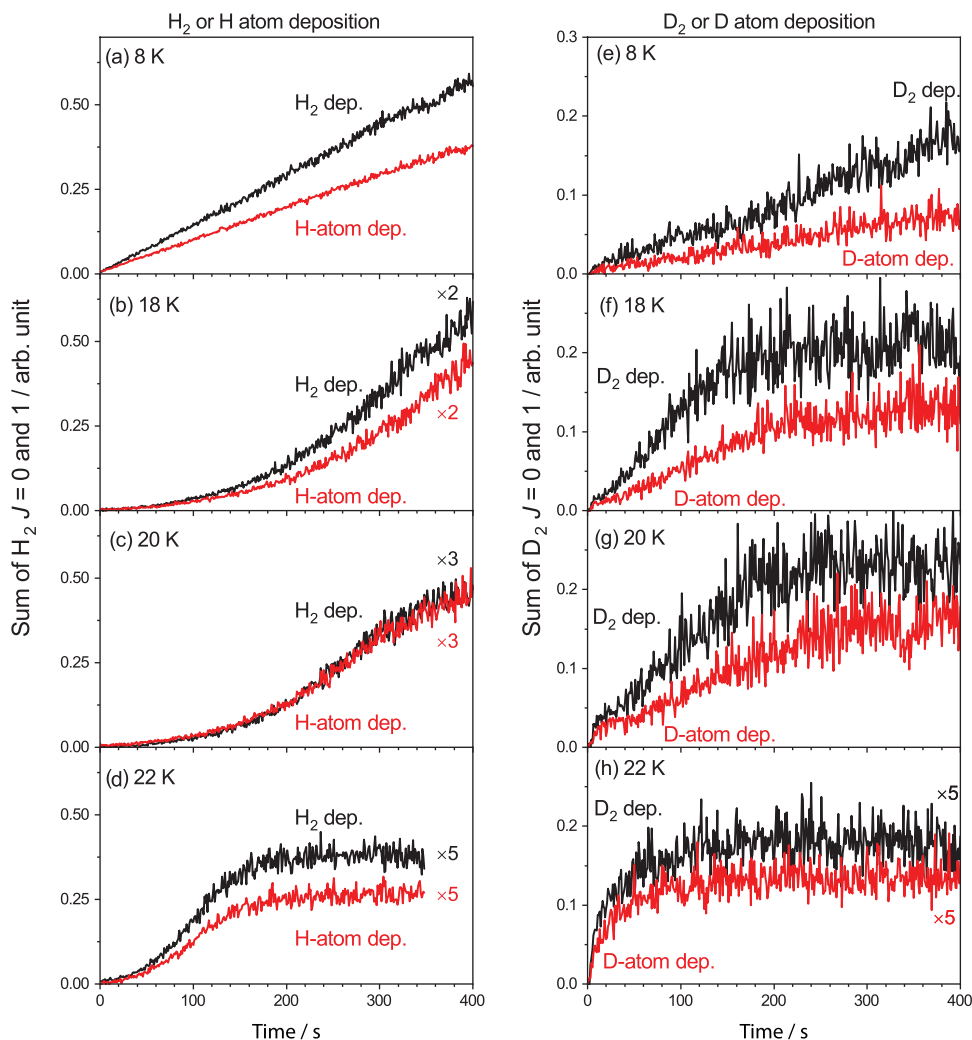


Figure 4. Time variation of the PSD-REMPI signals measured during (left) H_2 or H-atom deposition and (right) D_2 or D-atom deposition at various temperatures shown in panels. The signals following molecular deposition are shown in black lines, and those following atomic deposition are in red lines. The sum of $J''=0$ and 1 are presented, and each trace was obtained as an average of three measurements. For scaled traces, the multiplication factors are shown..

information on the adsorption sites and diffusion is desirable. However, as described in section 1, conventional experimental methods cannot feasibly detect the OH radical on ice. Therefore, we applied the PSD-REMPI method to monitor OH on ice.

Ice samples (about 40 ML) were produced by the vapour deposition of H_2O on an aluminium substrate at 10–100 K. OH radicals were obtained by the UV photolysis of ice at given temperatures. The OH radicals on ice were photodesorbed by unfocused weak laser radiation at 532 nm and subsequently ionized by (2+1) REMPI via $\text{D}^2 \Sigma (v'=0) \leftarrow \text{X}^2\Pi (v''=0)$ at approximately 1 mm above the ice surface. The obtained REMPI spectrum was well reproduced by calculations for the REMPI transition of OH, indicating that OH radicals on ice was successfully monitored. The REMPI intensities were measured as a function of the delay between the PSD and the REMPI laser shot. Because the delay time is equivalent to the time of flight for the distance between the surface and the focal point of

the REMPI laser, the variation of OH intensity is directly correlated to the translational energy distribution of OH. We found that the translational energy distribution can be well fitted by the sum of two Boltzmann distributions. We deduced that higher and lower temperature components originate from desorption by a photochemical process on the surface and by a phonon-mediated process, respectively. We will perform additional experiments and quantum chemical calculations to support our idea.

7. Conclusion

The PSD-REMPI method which was applied to monitored radicals on the surfaces of dust analogues has a great advantage to approach the surface diffusion of radicals without modifying the surface morphology, composition, and temperature. However, the mechanism of photostimulated desorption by photon at 532 nm is not always clear although the PSD has been ensured to efficiently pick up radicals on the surfaces so far. Therefore, we still need to examine the PSD-REMPI method whether it is applicable for more species and surface materials.

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