Direct determination of the activation energy for diffusion of OH radicals on water ice[†]

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Physicochemical processes such as surface reactions of radicals, photolysis by ultraviolet (UV) irradiation, and ion bombardment on interstellar icy grains are indispensable for chemical evolution during star formation. The chemical evolution begins in molecular clouds where the temperature is as low as 10 K. In molecular clouds, the hydrogenation of primordial atomic and molecular species is crucial because hydrogen atoms can migrate and encounter reaction partners on the grain surface even at ∼10 K.[1–7] During temperature elevation in star-forming regions, heavier species can diffuse on the ice and many types of complex organic molecules (COMs) are considered to be produced through reactions among heavier species, particularly radicals. Thus, the behavior of radicals on the ice surface should be investigated to understand the formation pathways of COMs. OH radical would be one of the most abundant radicals on ice surface as they can be produced through photolysis of H_2O and hydrogenation of O atoms on the ice surface. Therefore, OH radicals are expected to participate in various physicochemical processes on ice surface. However, conventional methods for detecting OH radicals, such as Raman, infrared, and electron spin resonance spectroscopies, are not applicable because of their low detection efficiencies and non-surface selectivity. In this study, we applied a combination of photostimulated desorption (PSD) and resonance-enhanced multiphoton ionization (REMPI) to facilitate direct detection of OH radicals on the ice surface.[8] Using this PSD-REMPI method, we determined the activation energy for diffusion (E_{diff}) of OH radicals on compact amorphous solid water (c-ASW), because the surface diffusion of radicals often becomes a rate-limiting process in reactions involving radicals.

The c-ASW samples were deposited on a sapphire disk at 100 K by introducing the water vapor into an ultrahigh vacuum chamber ($\sim 10^{-8}$ Pa). After the preparation of ASW sample, OH radicals were produced via photolysis of water molecules using a deuterium lamp in the temperature range of 54–80 K. In this photolysis, H_2O is dissociated mainly into H + OH with minor channels, H_2 + O and 2H + O, and as secondary products, H_2 and O_2 are also produced on the surface. To avoid the undesired effect of these species other than OH, the experiments were performed at temperatures above 54 K where hydrogen and oxygen cannot stay on the surface. The OH radicals on the sample surface were detected with the PSD-REMPI method.[8] The OH radicals were photodesorbed by weak-pulsed laser radiation at 532 nm from an Nd:YAG laser. The photon energy at 532 nm is below the dissociation energy of H_2O. Photodesorbed OH radicals were selectively ionized by the (2 + 1) REMPI process above the c-ASW surface and detected with a time-of-flight mass spectrometer. We performed two types of measurements. In the first measurement, the OH intensities were monitored during UV exposure. We monitored the OH intensities in the steady state during UV irradiation. In the other measurement, the OH intensities were measured following a particular period of UV exposure. Note that we can selectively monitor OH radicals based on one-photon chemical process.[8]

When monitoring OH during UV exposure, we found that the OH intensities in steady state gradually decreased with the temperature of c-ASW in the range of approximately 60–80 K. We experimentally confirmed that OH radicals were lost through OH–OH recombination rather than thermal desorption of OH. The recombination rate should be limited by the diffusion of OH radicals on the c-ASW surface because the radical-radical reaction itself is barrierless. By analyzing the recombination rate with the Arrhenius type formula, the activation barrier of surface diffusion, E_{diff}, was evaluated to be 0.14 ± 0.01 eV (1650 ± 60 K). Furthermore, in the other measurement of OH monitoring after UV exposure, the OH intensities decreased with time after UV termination. Again, considering that this decrease is dominated by OH–OH recombination, we derived E_{diff} to be 0.13 ± 0.01 eV (1540 ± 80 K). This value is consistent with the previously obtained value.

Under a simple assumption that the activation energy of diffusion has the single value of 1650 K, the OH radicals can migrate over 100 nm on the icy dust within 105 years at temperatures above 36 ± 1 K. The present results suggest that OH reactions start at approximately 36 K and become important in the warming-up of star-forming regions. Note that we do not exclude the possibility that the OH radicals drift to a certain extent through shallower sites even at temperatures below 36 K.

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