

Negative catalytic effect of amorphous solid water on the hydrogen abstraction from dimethyl ether with deuterium atoms at low temperatures

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Amorphous solid water (ASW) plays crucial roles in interstellar chemistry as a cold catalytic surface for various chemical and physical processes. Previous studies reported that the surface of ASW lowers an activation barrier of some reactions such as tunneling hydrogen addition to formaldehyde [1]. In addition, some reactions of H and D atoms with molecules such as CO were found to be enhanced on ASW at higher temperatures due to the longer residence time of the atoms on ASW [2]. So, does ASW always act as a “positive” catalyst for chemical reactions on interstellar grains? In the present poster, we will show experimental results on the “negative” catalytic effect of ASW on the quantum-tunneling hydrogen abstraction from dimethyl ether (DME: CH₃OCH₃) by deuterium (D) atoms at low temperatures. By forming a complex with water via a hydrogen bond, the C-H stretching band of DME shows a blue-shift as a result of the C-H bond contraction [3], which may suppress the reaction compared to that of pure solid DME with D atoms.

The experiments were performed in an apparatus named ASURA, which is mainly composed of an ultra-high vacuum chamber, an atomic source, and a FTIR. The base pressure of the reaction chamber is about 10⁻⁸ Pa. DME-H₂O complex with the thickness of ~25 monolayers (1 monolayer = 10¹⁵ molecules cm⁻²) was produced by the vapor-deposition of the mixed gas (DME:H₂O = 1:4) onto an Al substrate at 15 K. D atoms were produced by the dissociation of D₂ molecules in microwave-induced plasma and cooled to 100 K. The sample solid was exposed to D atoms for up to 240 min at 15 K. Progress in reaction was monitored in-situ by the FTIR. The reaction of pure solid DME (~10 monolayers) with D atoms was also investigated under the same experimental conditions for comparison.

When pure solid DME was exposed to D atoms at 15 K, the formation of deuterated DME was observed on the FTIR spectrum of the reaction product, which indicates the occurrence of hydrogen (H)-D substitution of DME. We propose the successive H-abstraction and D-addition occurred as follows: (1) CH₃OCH₃ + D → CH₂OCH₃ + HD, (2) CH₂OCH₃ + D → CH₂DOCH₃. Since reaction (1) has a large activation barrier of ~3600 K in the gas phase [4], quantum-tunneling is required for the reaction to occur at 15 K.

When solid DME in the complex reacted with D atoms, the H-D substitution reactions also occurred under the same experimental conditions. However, the reaction was more than 20 times slower than pure solid DME + D. This would be due to the strengthening of the C-H bond, which is attributable to the formation of a complex with H₂O via hydrogen bond.

References

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