Methanol formation via transient-diffusion-driven sequential reactions by methane deposition onto OH adsorbed amorphous solid water at low temperatures

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Recently, sequential reactions have been experimentally observed at 10 K as a result of transient surface diffusion of radicals driven by the heat of reactions [1,2]. We propose that such transient diffusion of radicals may play an important role in various reactions. In this context, we investigated the association reaction between CH_3 and OH as a formation pathway for CH_3OH at 10 K. Under the preset experimental condition, this reaction is expected to proceed via the transient diffusion of CH_3 radicals, facilitated by the heat of preceding reaction of $CH_4 + OH \rightarrow CH_3$. In addition, the temperature dependence of CH_3OH yield were measured at surface temperatures up to 60 K.

The experiments employed the highly sensitive Cs^+ pickup method, a powerful technique for mass-analyzing trace amounts of adsorbates on amorphous solid water (ASW) [1]. In this method, surface species (X) on ASW are identified as ionic complexes (Cs^+-X) by mass spectrometry following low-energy Cs^+ beam irradiation. Figure 1 shows the pickup mass spectra of (a) photolyzed ASW and (b) photolyzed ASW with CH_4 deposition at 10 K. Signals corresponding to CH_3 (148u) and CH_3OH (165u) were observed only after CH_4 deposition onto photolyzed ASW. This indicates that CH_3OH is formed via the $CH_3 + OH$ reaction, since the direct reaction of $CH_4 + OH \rightarrow CH_3OH + H$ is highly endothermic (+58.8 kJ/mol) [3]. Furthermore, CH_3OH yields measured at various initial OH coverages exhibited a square dependence on OH concentration, providing further evidence that CH_3OH produced through the association of OH and CH_3. This is consistent with the fact that CH_3 is the product of preceding hydrogen abstraction of CH_4 by OH.

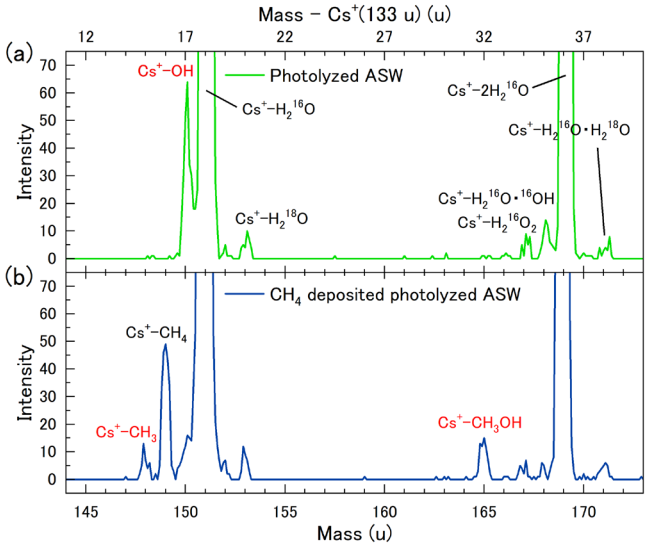

Figure 1: The pickup mass spectra for (a) photolyzed ASW and (b) CH_4 deposited on photolyzed ASW. The deposition time of CH_4 was 15 minutes (coverage 0.17).

References

[1] A. Ishibashi, H. Hiroshi, Y. Oba, A. Kouchi, & N. Watanabe, 2021, ApJL 921, L13.
[2] A. Ishibashi, G. Molpeceres, H. Hidaka, Y. Oba, T. Lamberts, & N. Watanabe, 2024, ApJ 976, 162.
[3] C. Tao & J. Li, 2022, Comput. Theor. Chem. 1217, 113906.