

Laboratory measurements of H-D substitution rates in solid methanol- d_n ($n=0-2$) at 10 K

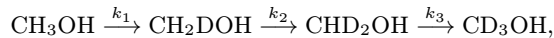
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Abstract. The deuterium fractionation of interstellar methanol is investigated experimentally using the ASURA (Apparatus for SURface Reactions in Astrophysics) system. Recent observations toward the low-mass protostars IRAS16293 found the very high D/H ratios in formaldehyde and methanol up to 0.2 and 0.4, respectively (Loinard et al. 2000; Parise et al. 2004; Aikawa et al. 2005). To date, several models have been proposed to explain D-fractionation mechanism. Pure gas-phase models are difficult to reproduce the D-fractionation, particularly, for multideuterated species, while the results of some gas-grain models can achieve the observed fractionation levels fairly well (Stantcheva & Herbst 2003). However, the gas-grain models require many assumptions regarding the grain surface reactions. Then, the experiments on the surface reaction have been highly desirable. In this context, we performed the experiments on the formation of deuterated formaldehyde and methanol on cold (10 K) interstellar grain analogues and revealed that a key route for the D-fractionation is not successive addition of H and D to CO as previously considered (e.g., Charnley, Tielens, & Rodgers 1997) but H-D substitution in solid CH₃OH on icy grains (Nagaoka, Watanabe, & Kouchi 2005).

We report the results of further experiments on the deuteration of CH₃OH using a cold (30 K) atomic D beam. The relative rates of H-D substitution reactions; CH₃OH → CH₂DOH, CH₂DOH → CHD₂OH, CHD₂OH → CD₃OH, were measured. Experiments were performed using the ASURA system described previously (Watanabe et al. 2004; Nagaoka, Watanabe, & Kouchi 2005). The experimental procedure is as follows. An aluminum substrate was placed in the centre of an ultra-high vacuum chamber (10⁻¹⁰ Torr) and cooled to 10 K by a helium refrigerator. The solid samples of normal and deuterated methanol (CH₃OH, CH₂DOH, CHD₂OH) were vapor-deposited on the substrate. The D atoms produced by dissociation of D₂ molecules by microwave discharge were irradiated to samples. D atoms were cooled to 30 K in the atomic source chamber before irradiation. During the irradiation with D atoms, we measured the variations of chemical composition of the samples, in-situ, with FT-IR.

From the attenuation curves of parent molecules upon the irradiation with cold D atoms, we determined the relative rates of H-D substitution reactions (k_1 , k_2 , k_3) of solid methanol;



to be approximately $k_2=0.5$, $k_3=0.2$ when $k_1=1$.

Keywords. astrochemistry - atomic processes - ISM: dust, extinction - molecular processes

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