

## A novel assessment of the role of the methyl radical and water formation channel in the CH<sub>3</sub>OH + H reaction

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Abstract: A number of experimental and theoretical papers have accounted only for two H-abstraction channels in the reaction of methanol with atomic hydrogen (R1 and R2 channels) [1,2]. Recently, several astrochemical studies have claimed the importance of another channel for this reaction, which is crucial for kinetics simulations related to the abundance of molecular constituents in planetary atmospheres: methyl radical and water formation (R3 channel) [3,4]. Here, motivated by the lack of and uncertainties about the experimental and theoretical kinetic rate constant for the third channel, we developed a first-principle Car-Parrinello molecular dynamics thermalized at two significant temperatures – 300 and 2500 K. Furthermore, the kinetic rate constant of all three channels was calculated from a high-level *deformed*-Transition State Theory (d-TST) [5] at a benchmark electronic structure level. d-TST shows to be suitable to describe the overall rate constant for  $CH_3OH + H$  reaction (archetype of moderate tunnelling regime) with the precision required by pratical aplications. Considering experimental ratios at 1000 K,  $k_{R1}/k_{R2} = 0.84$  and  $k_{R1}/k_{R3} \approx 15 - 40$ , we provided a better estimate when compared with previous theoretical work: 7.47 and 637, respectively. The combination of these procedures explicitly demonstrates the role of the third channel in a significant range of temperatures and indicates its importance considering the thermodynamic control to estimate methyl radical and water formation. We expect that our results can help to shed new light on the fundamental kinetic rate equations for the  $CH_3OH + H$ reaction.

**Key-words**: CH<sub>3</sub>OH + H reaction, reaction rate constants, *d*-TST.

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