Semi-Classical TST Calculations of Thermal Rates and KIEs for $H + H_2$, $H + CH_4$ and $CN + H_2$ Reactions

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Semi-classical transition state theory (SCTST) was developed by W. H. Miller[1] and recently implemented by us using a new algorithm for polyatomic reactions.[2] SCTST in combination with second-order vibrational perturbation theory (VPT2)[3] intrinsically includes fully coupled-anharmonic vibration modes as well as multi-dimensional quantum mechanical tunneling. It has been used to calculate, from first principles, highly accurate thermal rate constants and kinetic isotopic effects (KIE).[4] However, tests on additional reactions are needed to explore its capabilities.

In this work, the microcanonical version of SCTST as implemented in MULTIWELL[5] is used to compute thermal rate constants and KIEs for three reactions, including $H + H_2$, $H + CH_4$, and $CN + H_2$. Potential energy surfaces for these reactions are constructed using the highly accurate HEAT[6] protocol, while rovibrational parameters and anharmonic constants are obtained at CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ levels of theory. The *ab initio* calculated results obtained with no adjustments are in excellent agreement with experimental data and with fully quantum dynamic calculations.

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