"Dissociation-Induced Depletion of High-Energy Reactant Molecules as a Mechanism for Pressure-Dependent Rate Constants for Bimolecular Reactions"

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Electronic Supplementary Information

Fig. S1 compares our semi-microcanonical rate constants for CH_4 with energy E reacting with H with the trajectory calculations of Jasper et al.[33] There are a few noteworthy differences between the present semi-microcanonical calculations and the trajectory calculations of Jasper et al.[33] First, the present calculations are for the energy in the rotational and vibrational modes of CH_4 whereas the calculations of Jasper are for the energy in only the vibrational modes CH_4 (with the remaining modes treated as thermal with given temperature). Second, the present calculations employ quantum densities of states and quantum, tunneling-corrected numbers of states whereas the trajectory calculations assume classical mechanics. Third, the present calculations make statistical estimates based on assumptions for how each mode couples to the reaction coordinate whereas the trajectory calculations, which capture the quasi-classical dynamics, require no such assumptions. All three of these differences are expected to be largest at lower energies and low temperatures, where the largest differences between our semi-microcanonical estimates and the trajectory results are observed. At higher energies and higher temperatures, our statistical estimates using the semi-microcanonical approach and the trajectory results agree within a factor of 2-3 – consistent with a similar finding in Jasper et al.[33] regarding the performance of their statistical model (the effective temperature model).

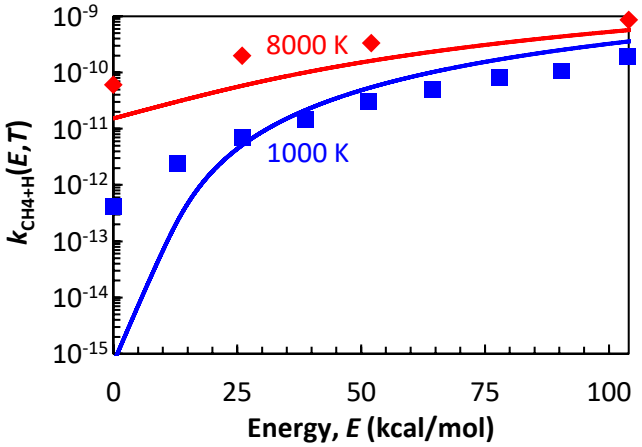

Figure S1. Rate constant for CH_4 with energy E reacting with H at 1000 K and 8000 K as a function of E. Solid lines correspond to the results of our semi-microcanonical calculations for CH_4* + H and symbols correspond to the results of the classical trajectory calculations of Jasper et al.[33]