EFFECTS OF REACTANT ROTATIONAL EXCITATION ON Cl + CH₄ / CHD₃ REACTIONS

HUILIN PAN, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; FENGYAN WANG, Fudan University, Department of Chemistry, Shanghai, China; YUAN CHENG, JUI-SAN LIN, KOPIN LIU, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

Effects of reactant rotation, which can disentangle the stereodynamical properties of chemical reactivity, are of great importance in understanding and controlling the steric effects in chemical reactions. Here, we report the rotational quantum-state control of a late-barrier reaction of chlorine atom with CH₄ and CHD₃ in a crossed molecular beam experiment. Experimental results demonstrate that, in both reactions, the more detailed product translational and angular distributions are essentially the same for different rotational states of the vibrationally excited CH₄ and CHD₃ reactants. Yet, the integral cross sections show strong dependence on the reactant rotational excitation, suggesting that the reactivity diversity arises from the anisotropic interactions enroute to the reaction barrier. More detailed analysis indicates that the effects of reactant rotation do not derive from the rotational-energy effects or long-range forces, rather are the result of short-range forces in the transition state region. Exactly how the transition-state properties, e.g., the barrier location and the tightness of barrier, influence the rotational reactivity diversity, however, remains unclear. Further investigations are on-going to gain deeper insights.