EXPLORING DYNAMICAL EFFECTS OF BEND EXCITATION ON THE Cl + CH_4 REACTION

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Using a novel IR source, we have directly pumped the $CH_4(\nu_4{=}1)$ and $CH_3D(\nu_3{=}1)$ bending vibrations and detected the nascent CH_3 products from the Cl + CH_4 reaction with 2+1 REMPI in a time-of-flight mass spectrometer. Contrary to intuitive expectations, we find that these low-frequency bending vibrations enhance the cross section for reaction with Cl atoms by a factor of two or more. This enhancement is constant over the collision energy range 0.12 eV to 0.26 eV. Moreover, the nonlocalized motion in the methane reagent is transferred almost exclusively to translational motion of the escaping products, which is in sharp contrast to theoretical calculations that predict formation of methyl radicals predominantly excited into the umbrella bending mode. We also observe both H-atom and D-atom abstraction products from the Cl + $CH_3D(\nu_3{=}1)$ reaction, indicating that the reaction is not bond selective.

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