GAS-SURFACE DYNAMICS OF VIBRATIONALLY AND ROTATIONALLY EXCITED REAGENTS: METHANE (ν_3, J=0-3 AND $3\nu_4$, J=2) DISSOCIATION ON NICKEL SURFACES

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A high resolution infrared laser prepares a significant population of vibrationally excited methane molecules in a supersonic molecular beam. The prepared molecules impinge on a clean Ni(100) or Ni(111) surface housed in an ultrahigh vacuum chamber. Some of the methane dissociates and chemically binds to the surface upon impact. We quantify reaction probability as a function of incident translational energy, Ni surface temperature, and methane's vibrational and rotational state. The state-resolved reaction probabilities reveal how energy deposited into different energetic coordinates activates methane's dissociative chemisorption. We find that the more energetic $3\nu_4$ bending state is less reactive than ν_3 antisymmetric C-H stretch state on both Ni(100) and Ni(111). This result highlights the presence of vibrational mode specificity in a gas-surface reaction on a metal surface. We also find that vibrational energy in ν_3 is more effective than translational energy in its ability to promote reaction on Ni(111). Both of these results point to the importance of non-statistical energy flow in this reaction.