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RRKM Theory at the Gas-Surface Interface: Hydrogen Dissociation Dynamics on Cu(111) HEATHER ABBOTT, IAN HARRISON, Chemistry Department, University of Virginia — A simple picture of the hydrogen dissociation/associative desorption dynamics on Cu(111) emerges from a two-parameter, full dimensionality microcanonical unimolecular rate theory (MURT) model of the gas-surface reactivity. Vibrational frequencies for the reactive transition state were taken from 6D density functional theory calculations [Hammer, *et al. Phys. Rev. Lett.* **73**, 1400 (1994)]. The MURT's parameters were fixed by simulation of experiment as: a H_2 dissociation threshold energy of $E_0 = 79$ kJ/mol and $s = 1$ surface atoms that actively exchange energy within the reactive transition state. Remarkably, MURT quantitatively predicts much of the dynamical behavior observed. The divergence of the statistical theoretical predictions from the experimental results at low rotational quantum numbers, $J \leq 5$, points towards the importance of dynamical steering at low J. The surface degrees of freedom are calculated to provide $\sim$30% of the energy required to surmount E_0 under thermal equilibrium conditions. Explicit treatment of the surface (i.e., $T_s > 0\ K$) is a novel aspect of the MURT theoretical approach.

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