**Supplemental Figure 1** Fractional exchangeable energy uptakes for Beck’s thermal and \((2\nu_3, J = 2)\) state-resolved supersonic molecular beam experiments\(^{19}\) performed at \(T_s = 600\) K for two different MURT models whose parameters were optimized to the Luntz experiments\(^{26,35}\) of Figs. 3(a),(b). (a),(c) s-PMMT simulations with active rotations and no vibrational biasing. (b),(d) d-PMMT simulations with rotation as a spectator and vibrational efficacy parameter, \(\eta_v\). Compare to Fig. 8.
Supplemental Table 1: Identification of the normal modes associated with the GGA-DFT calculated vibrational frequencies reported for the CH$_4$/Pt(111) “D1” transition state (TS) of Table IV of J. Chem. Phys. 132 054705 (2010). These D1 transition state vibrational frequencies were used in our MURT models. The electronic energy barrier, $E_b = 89.5$ kJ/mol, for the D1 transition state along with the GGA-DFT calculated frequencies for methane in the gas-phase are also listed.

The 3 rotations and 3 translations of methane in the gas phase become frustrated motions at the CH$_4$/Pt(111) transition state for chemisorption with different vibrational frequencies. Of these frustrated modes, the one corresponding to translation perpendicular to the surface plane stays relatively pure, whereas the five remaining modes (3 rotations and 2 parallel translations) can be described as having composite modal properties. The table above associates vibrational normal mode frequencies with descriptors calling out the predominant motion of each mode. The f1-f9 modes evolve primarily from the normal modes of gas-phase methane. The f15 reaction coordinate mode has an imaginary frequency and is an admixture of one of the parallel translational modes, some rotation, and a separation of the CH$_3$ and H product fragments parallel to the surface plane. Because parallel translations were treated as spectator degrees of freedom in the PMMT models, the f12 mode was always removed from the chemisorption transition state. Removal of the second parallel translation mode was always accounted for because it is primarily associated with the separation of products along the reaction coordinate. The modes predominantly associated with rotations (f11, f13, f14) were included or removed from the chemisorption transition state in the accordance with whether the rotations were being treated as active or spectator degrees of freedom. The mean phonon frequency for bulk Pt was used for the surface oscillators. Experimentally determined vibrational frequencies and rotational constants for gas-phase CH$_4$ were used in the desorption transition state calculations as appropriate.