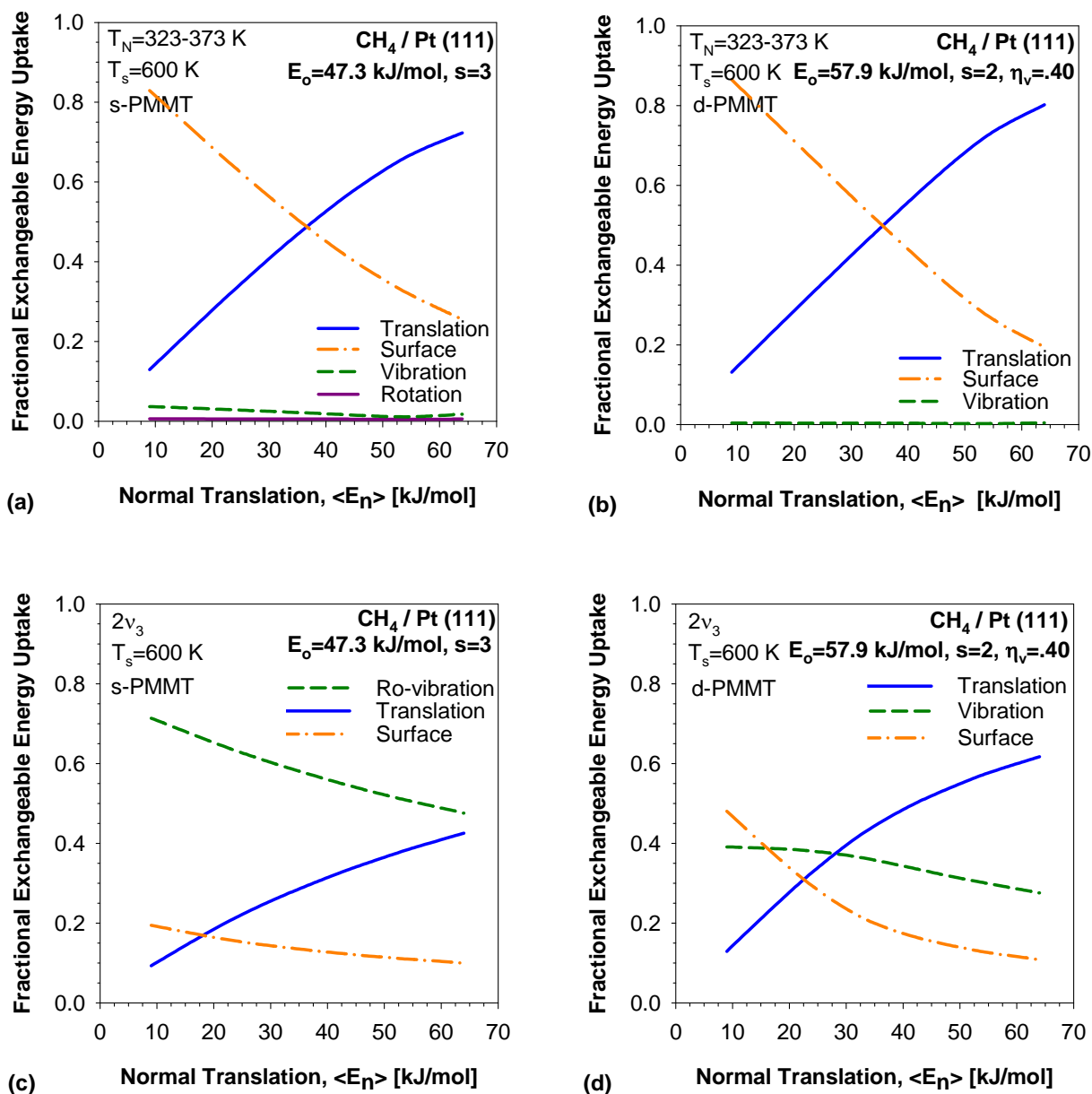


Electronic Supplementary Information



Supplemental Figure 1 Fractional exchangeable energy uptakes for Beck's thermal and ($2\nu_3, J=2$) state-resolved supersonic molecular beam experiments¹⁹ 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, η_v . Compare to Fig. 8.

	$\nu(\text{TS})$	Normal Mode Description	$\nu(\text{CH}_4(\text{g}))$
E_b [kJ/mol]	89.5		--
f1 [cm^{-1}]	3126	ν_3 : Asymmetric C-H Stretch	3099
f2 [cm^{-1}]	3064	ν_3 : Asymmetric C-H Stretch	3099
f3 [cm^{-1}]	2970	ν_3 : Asymmetric C-H Stretch	3097
f4 [cm^{-1}]	1633	ν_1 : Symmetric C-H Stretch	2980
f5 [cm^{-1}]	1389	ν_2 : Scissor Deformation	1513
f6 [cm^{-1}]	1352	ν_2 : Scissor Deformation	1512
f7 [cm^{-1}]	1161	ν_4 : Umbrella Deformation	1288
f8 [cm^{-1}]	832	ν_4 : Umbrella Deformation	1288
f9 [cm^{-1}]	813	ν_4 : Umbrella Deformation	1287
f10 [cm^{-1}]	418	Perpendicular Translation	--
f11 [cm^{-1}]	315	Rotation	--
f12 [cm^{-1}]	130	Parallel Translation	--
f13 [cm^{-1}]	128	Rotation	--
f14 [cm^{-1}]	119	Rotation	--
f15 [cm^{-1}]	953 <i>i</i>	Reaction Coordinate	--

Supplemental Table 1: Identification of the normal modes⁶⁰ associated with the GGA-DFT calculated vibrational frequencies reported for the $\text{CH}_4/\text{Pt}(111)$ “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 $\text{CH}_4/\text{Pt}(111)$ 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 $\nu_1 - \nu_4$ 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.