Supplemental Material for "Activation of Methane by FeO^+: Determining Reaction Pathways Through Temperature Dependent Kinetics and Statistical Modeling"

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Molecular parameters used in modeling:

Vibrational frequencies (in cm^{-1}, obtained from DFT calculations).

FeO^+(6): 819.1; FeO^+(4): 676.9; $FeOH^+$(5): 241.9, 812.6, 3840.0; $FeOD^+$(5): 183.2,792.7,2801.0; TS1(H,4): 33.4, 272.8, 463.5, 556.9, 712.0, 898.8, 1125.8, 1237.0, 1397.2, 1409.3, 1677.8, 2997.2, 3086.8, 3156.7; TS1(D,4): 25.5, 259.4, 337.0, 508.5, 563.3, 825.0, 864.9, 914.8, 1023.1, 1032.6, 1193.8, 2151.7, 2274.1, 2274.1, 2346.8. Data for CH_4, CD_4, CH_3, CD_3 , CH_3OH, and CD_3OD taken from the literature.

Rotational constants (in cm^{-1}, obtained from DFT calculations).

FeO^+(6): 0.503; FeO^+(4): 0.471; $FeOH^+$(5): 95.530, 0.410, 0.408; $FeOD^+$ (5): 53.960, 0.368, 0.368; TS1(H,4): 0.463, 0.263, 0.174; TS1(D,4):0.416, 0.213, 0.149. Data for CH_4,CD_4, CH_3, CD_3, CD_3OH, and CH_3OH taken from the literature.

Numbers of rotational states used in statistical modeling (high *J*-expressions, *E* the same units as *A* and *B*)

Atom + symmetric top (*A*, *B*): $W(E)=(4/3)(E^3/A\,B^2)^{1/2}$

Rotor (B_r) + symmetric top (A_t , B_t): $N(E)=(8/15)(E^2/B_r\,B_t)(E/A_t)^{1/2}$

Very prolate symmetric top (A_{pt} , B_{pt}) + symmetric top (A_t , B_t):

$N(E)=(8/15\,B_{pt}\,B_t)(1/A_t)^{1/2}[\,E^{5/2}+2S(E)]$ with $S(E)=\sum_{i=1}^{k_0}\left(E-A_{pt}i^2\right)^{5/2}$ and

k_0 = integer $(E/A_{pt})^{1/2}$; at large energies $N(E)$ approaches $N(E)=(\pi\,E^3/6\,B_t\,B_{pt})(1/A_t\,A_{pt})^{1/2}$.