The Interaction of Methyl Formate with Proton-bound Solvent Clusters in the Gas Phase and the Unimolecular Chemistry of the Reaction Products

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Supporting Information

Table S1. Additional reactions observed in the ion-molecule reactions explored in this study. Energies calculated at the B3LYP/6-311+G(d,p) level of theory.

$(W)_3H^+$ (m/z 55) → $(W)_2H^+$ (m/z 37) + W	**ΔE= 0.95 eV**
$(MF)H^+$ (m/z 61) + MF (m/z 60) → $(MF)_2H^+$(m/z 121)	**ΔE=-1.34 eV**
$(MF)_2H^+$ (m/z 121) + E (m/z 46) → $(MF)_2(E)H^+$ (m/z 167)	**ΔE=-0.86 eV**
$(E)_3H^+$ (m/z 139) → $(E)_2H^+$ (m/z 93) + E	**ΔE= 0.83 eV**

Water = W, methanol = M, ethanol = E, and methyl formate = MF

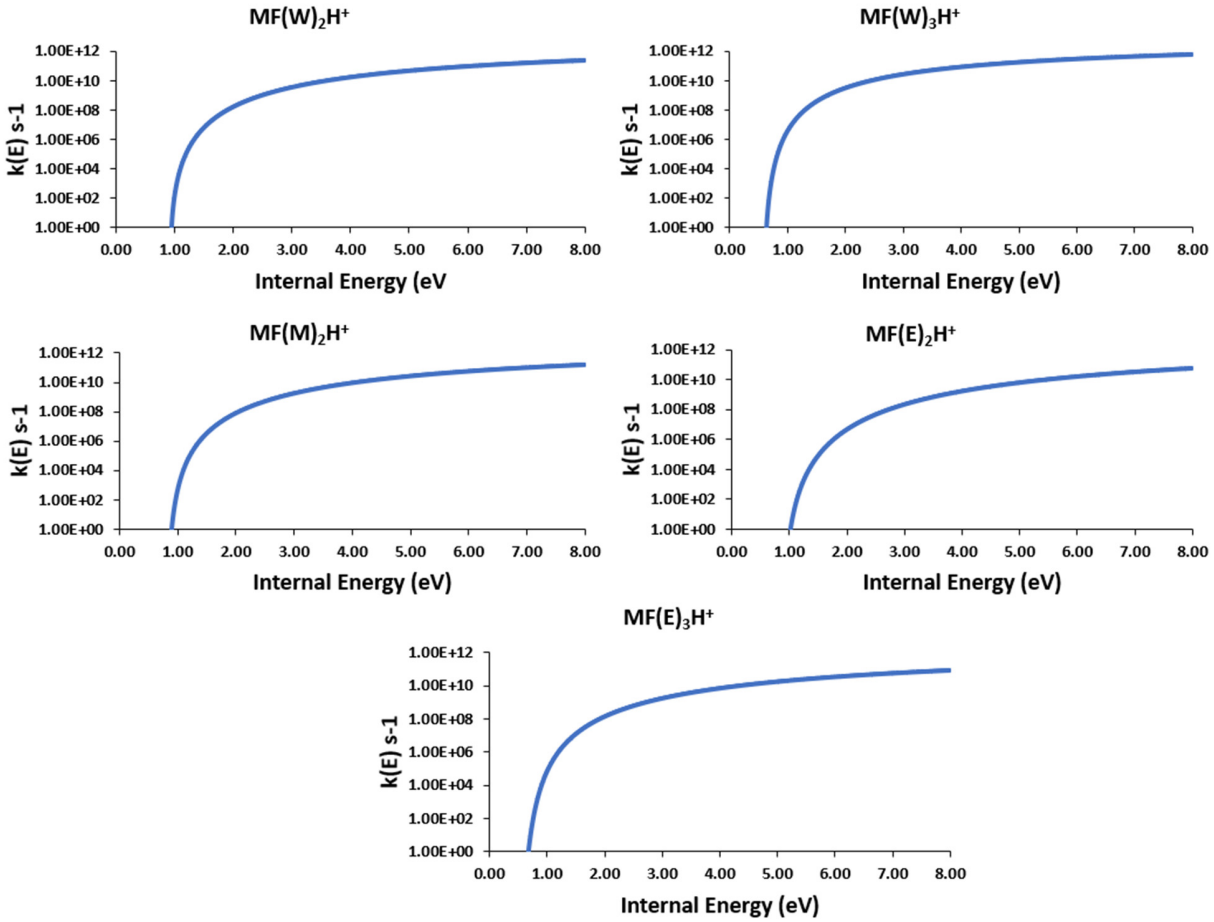


Figure S1. RRKM k(E) vs E curves for the dissociation of the ion-molecule encounter complexes

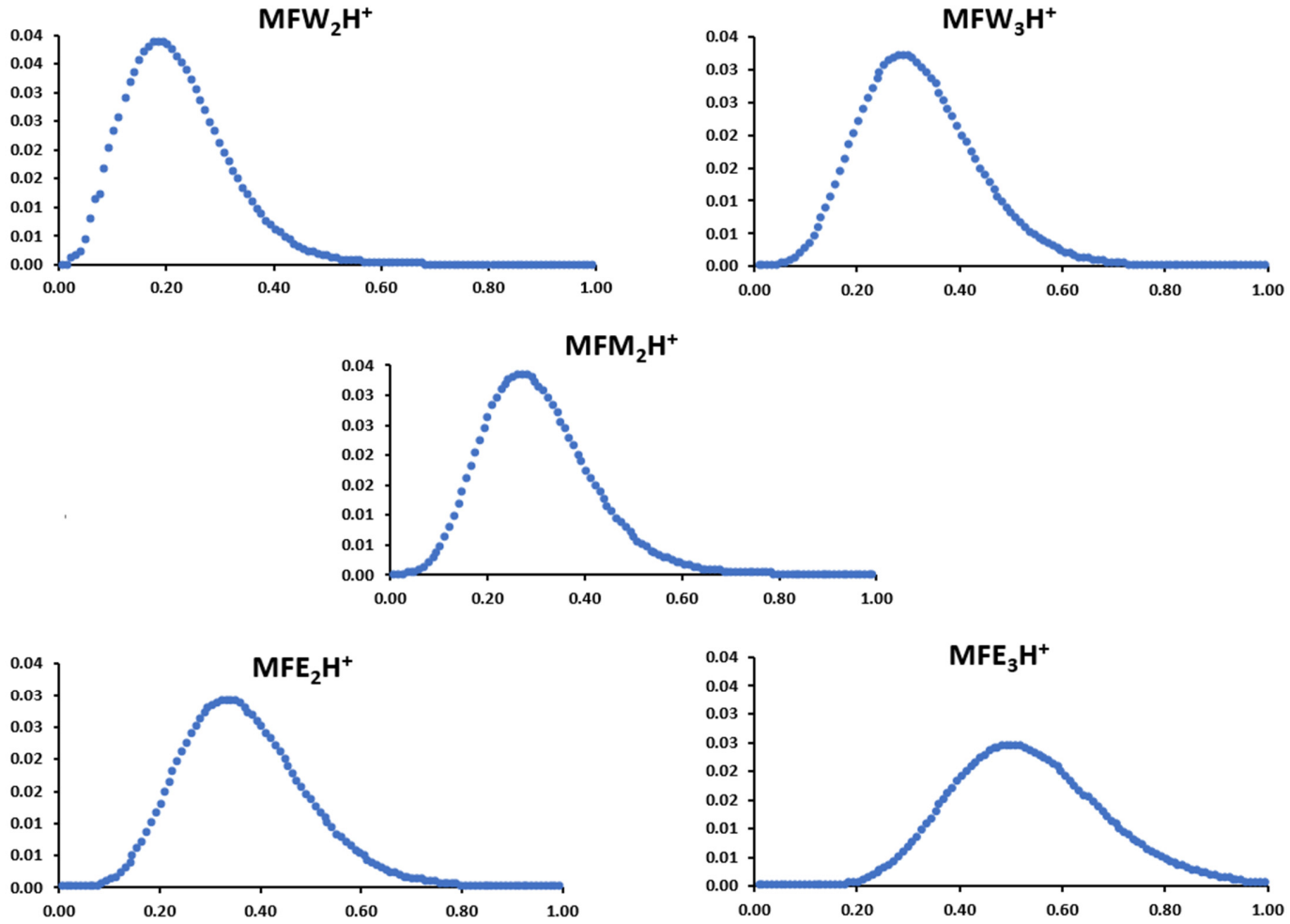
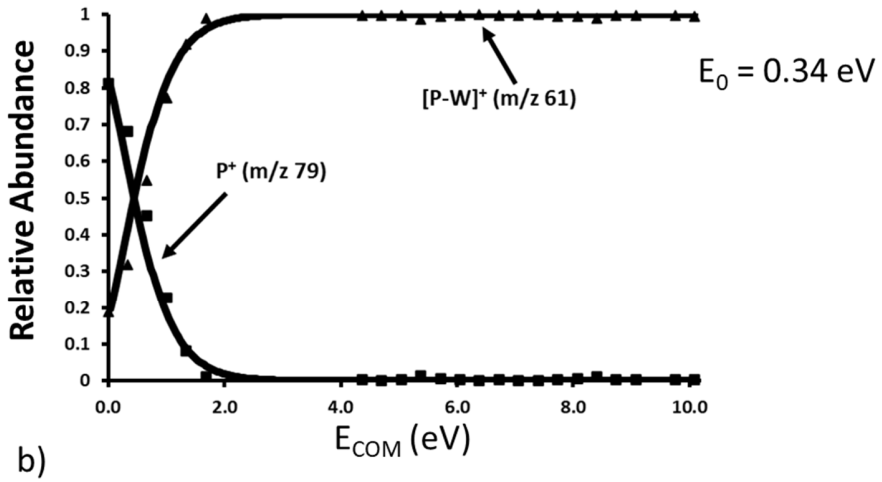
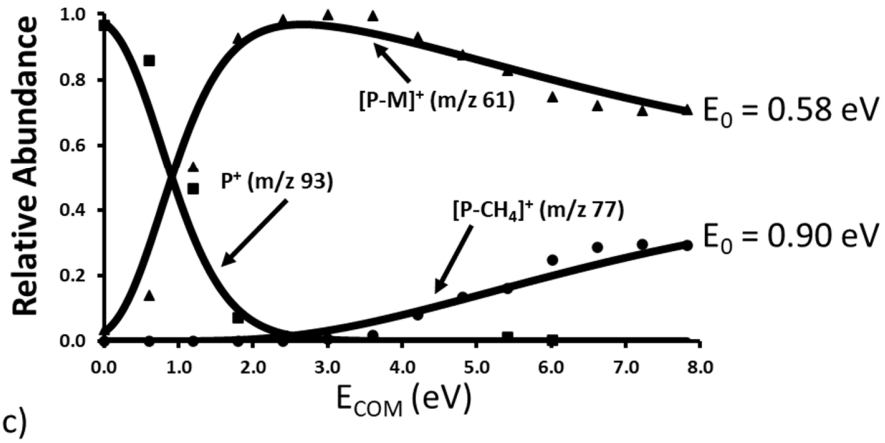


Figure S2. Vibrational internal energy distributions at 300 K for the encounter complexes in R1-R5.

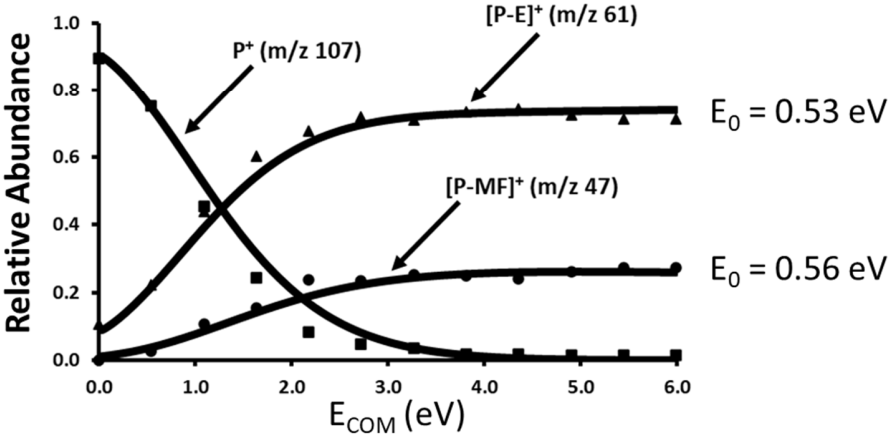
a)


Relative Abundance
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.0
2.0
4.0
6.0
8.0
10.0
E_COM (eV)
[P-W]+ (m/z 61)
P+ (m/z 79)
E0 = 0.34 eV

b)


Relative Abundance
1.0
0.8
0.6
0.4
0.2
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
E_COM (eV)
[P-M]+ (m/z 61)
P+ (m/z 93)
[P-CH4]+ (m/z 77)
E0 = 0.58 eV
E0 = 0.90 eV

c)


Relative Abundance
1.0
0.8
0.6
0.4
0.2
0.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
E_COM (eV)
[P-E]+ (m/z 61)
P+ (m/z 107)
[P-MF]+ (m/z 47)
E0 = 0.53 eV
E0 = 0.56 eV

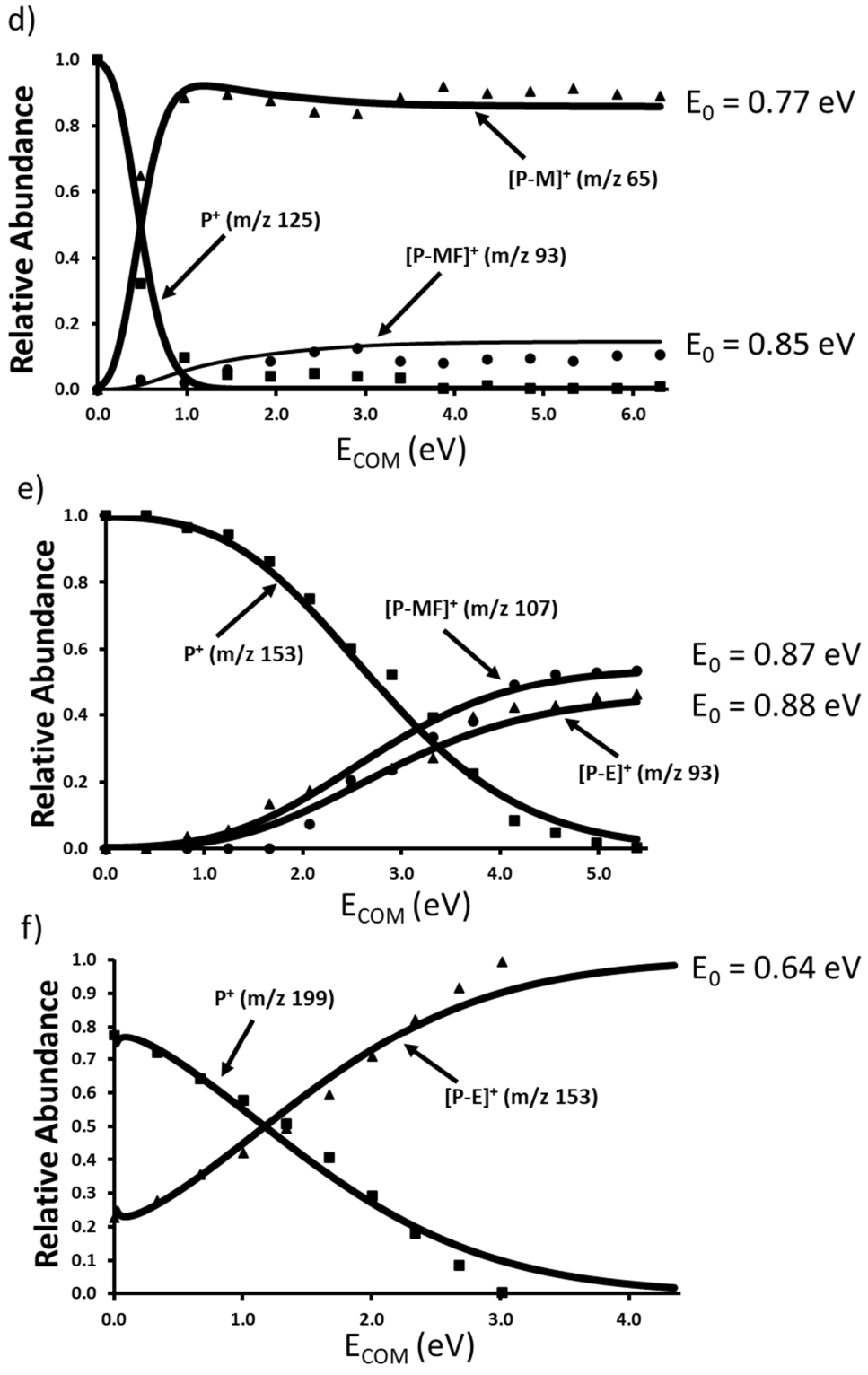


Figure S3. RRKM modeled breakdown curves for reactions in Figures 3 and 4. To accommodate the model, sequential reactions (such as loss of H_2O from m/z 33 in Figure 3a) were summed into the primary product ion abundance.