Two State Reactivity (TSR) and Hydrogen Tunneling Reaction Kinetics Measured in the Co^+ Mediated Decomposition of CH_3CHO

Supplemental Information

I. SPIDRR results at several AL photon energies.

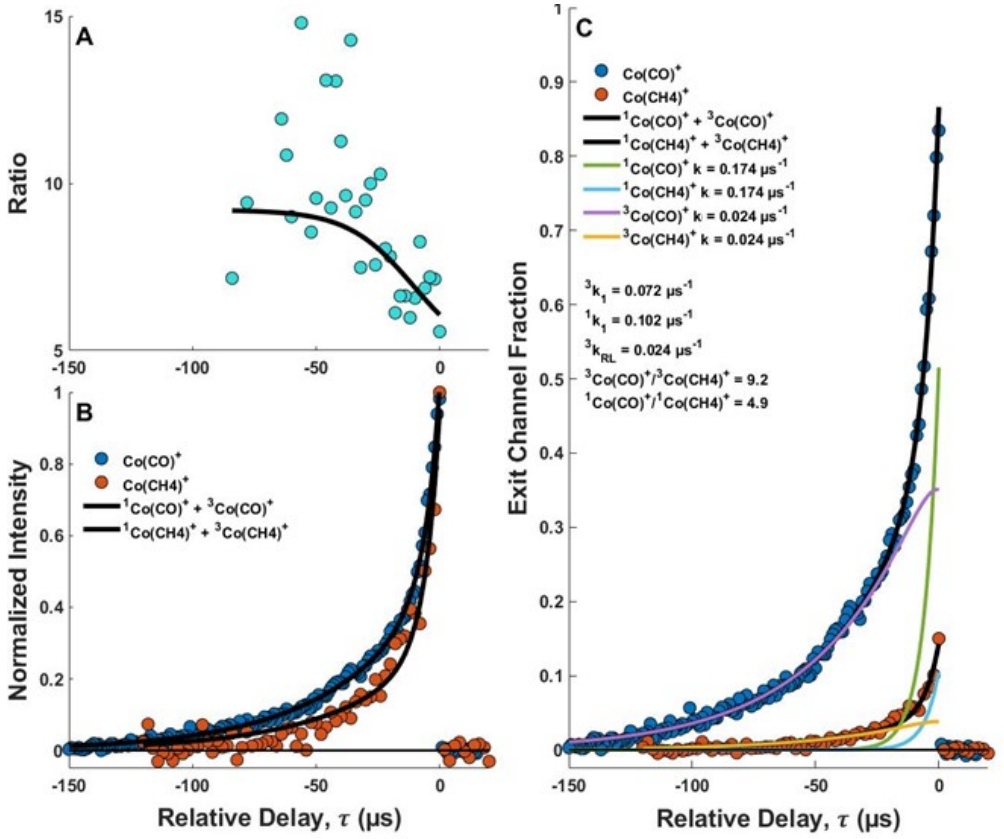

Figure SI-1. SPIDRR results measured in the Co^+ mediated decomposition of CH_3CHO into $CoCO^+$ and $CoCH_4^+$ measured at an AL energy = 14900 cm^{-1}. (A) The $CoCO^+$: $CoCH_4^+$ product ratio measured from product intensities recoded in panel C. (B) Each product channel's intensity is normalized to one at τ = 0 μs. Note that the SPIDRR results for each product are nonsuperimposable. (C) The product channel's summed intensity is normalized to one at τ = 0 μs. Solid curves in each panel are calculated from a deterministic treatment of a kinetic model.

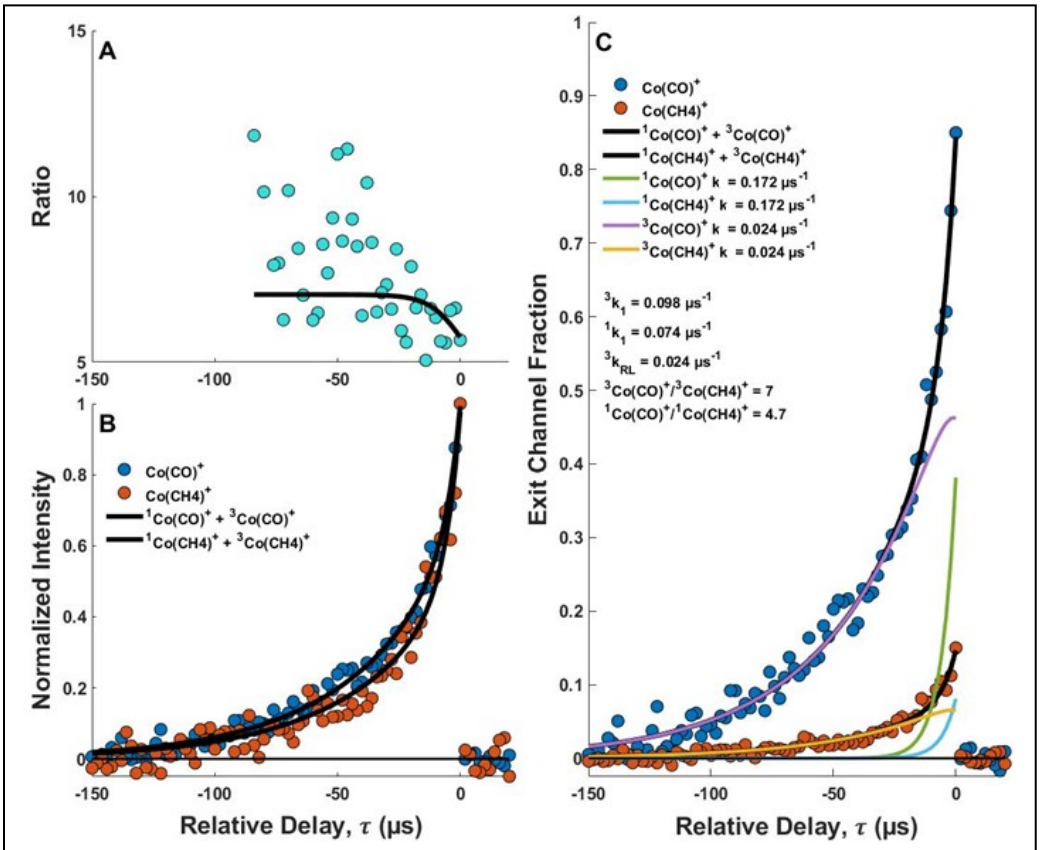

Figure SI-2. SPIDRR results measured in the Co^+ mediated decomposition of CH_3CHO into $CoCO^+$ and $CoCH_4^+$ measured at an AL energy = 14500 cm^{-1}. (A) The $CoCO^+$: $CoCH_4^+$ product ratio measured from product intensities recoded in panel C. (B) Each product channel's intensity is normalized to one at $\tau = 0$ μs. Note that the SPIDRR results for each product are nonsuperimposable. (C) The product channel's summed intensity is normalized to one at $\tau = 0$ μs. Solid curves in each panel are calculated from a deterministic treatment of a kinetic model.

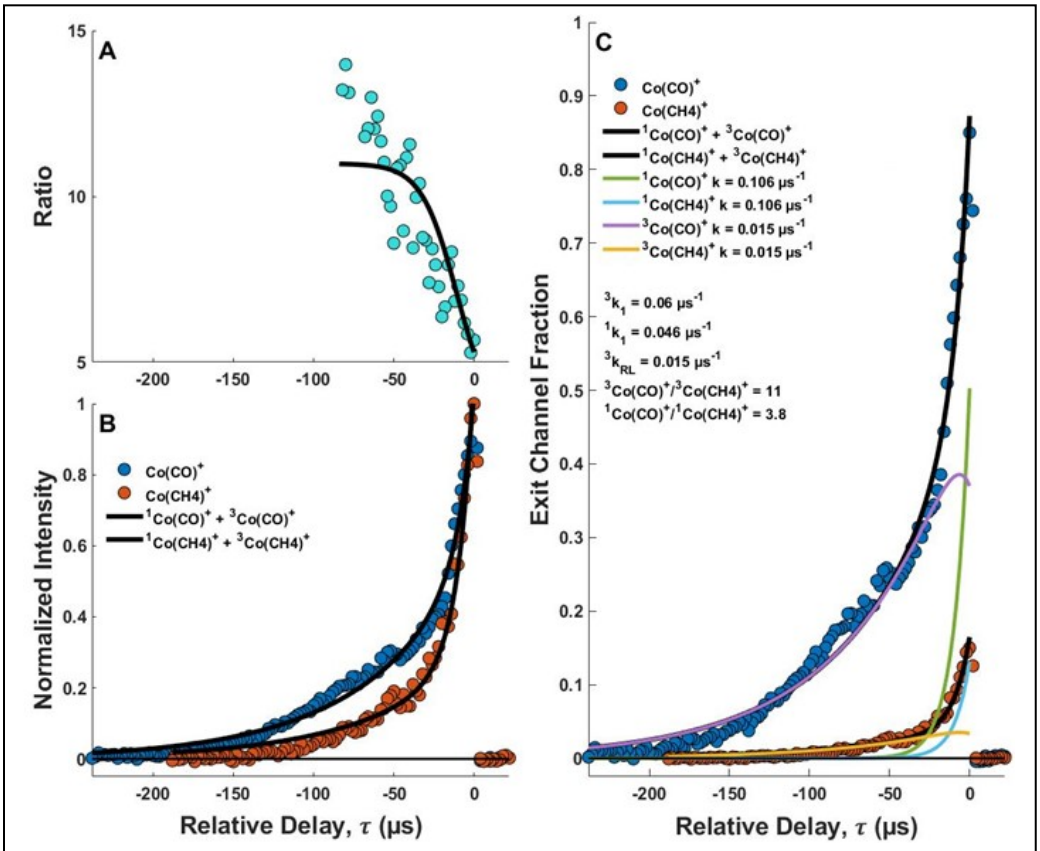

Figure SI-3. SPIDRR results measured in the Co^+ mediated decomposition of CH_3CHO into $CoCO^+$ and $CoCH_4^+$ measured at an AL energy = 13900 cm^{-1}. (A) The $CoCO^+$: $CoCH_4^+$ product ratio measured from product intensities recoded in panel C. (B) Each product channel's intensity is normalized to one at τ = 0 μs. Note that the SPIDRR results for each product are nonsuperimposable. (C) The product channel's summed intensity is normalized to one at τ = 0 μs. Solid curves in each panel are calculated from a deterministic treatment of a kinetic model.

II) Theory

Molecular Coordinates (Å)
Stationary points were calculated at the (u)PBE0/aug-cc-pVTZ level of theory

^{1}EC

C	2.109766	-0.733089	0.000014
H	1.374939	-1.538041	-0.000040
H	2.767155	-0.822293	0.872157
H	2.767545	-0.822464	-0.871804
C	1.506450	0.604054	-0.000212
H	2.170175	1.476140	-0.000309
O	0.299221	0.845246	-0.000066
Co	-1.228551	-0.158559	0.000063

^{1}TS1

C	-1.313465	0.749481	0.181624
H	-1.645715	0.350829	1.149259
H	-2.021716	0.607666	-0.637757
H	-1.182232	1.825656	0.347472
C	0.499477	0.936558	-0.418827
H	0.591676	1.797531	-1.082644
O	1.287121	0.504894	0.414534
Co	-0.042780	-0.693966	-0.061829

^{1}INT1

C	-1.533637	0.735808	0.128992
H	-2.043888	0.329355	1.014379
H	-2.085919	0.548133	-0.806421
H	-1.304508	1.791042	0.251442
C	1.158045	0.559120	-0.503994
H	1.722178	1.236952	-1.153765
O	1.369721	0.221111	0.638374
Co	-0.184892	-0.497924	-0.080097

^{1}TS2

C	1.231044	1.158464	0.033834
H	0.913978	1.699832	-0.862297
H	2.292892	0.868343	-0.014068
H	1.016975	1.723900	0.939461
C	-1.157387	0.009689	0.352730
H	-1.123537	-0.217564	1.468838
O	-2.036475	0.438378	-0.275714
Co	0.472206	-0.540387	-0.060948

^{1}INT2

C	-1.194519	1.182233	-0.006214
H	-0.765923	1.937851	-0.658905
H	-2.191052	0.859605	-0.362843
H	-0.251217	-0.515875	-1.353623

C	1.172003	0.000271	0.050417
H	-1.204112	1.495478	1.046432
O	2.227062	0.375530	-0.011772
Co	-0.491448	-0.513938	0.042885

^{1}TS3

C	1.357440	1.098373	-0.040134
H	1.185535	1.961365	0.599239
H	2.372751	0.696438	0.118345
H	0.535723	0.225980	1.179449
C	-1.222813	0.030549	-0.028906
H	1.173531	1.360730	-1.090794
O	-2.267561	0.437196	0.002442
Co	0.446859	-0.537615	-0.015242

^{1}PC

C	2.372638	0.286167	0.002176
H	3.435273	0.051899	-0.065686
H	2.207315	0.823651	0.939777
H	2.112894	0.867815	-0.889042
C	-1.568642	0.068805	0.000427
H	1.967215	-0.767583	0.007590
O	-2.679757	0.210968	0.000429
Co	0.255236	-0.177532	-0.000433

^{1}Co(CO)$^{+}$

C	0.001110	0.984616	0.000000
O	-0.000833	2.102734	0.000000
Co	0.000000	-0.841836	0.000000

^{1}Co(CH$_4$)$^{+}$

C	1.537649	-0.020507	0.011119
H	1.738377	-0.227203	1.061057
H	2.431927	0.392378	-0.459291
H	1.280603	-0.920216	-0.568033
H	0.876323	0.904851	-0.110563
Co	-0.576042	-0.000991	0.000375

^{3}EC

C	2.274453	-0.692350	0.000111
H	1.598281	-1.545558	0.000201
H	2.938063	-0.729745	0.871328
H	2.938133	-0.729994	-0.871041
C	1.572509	0.596297	-0.000124
H	2.180354	1.510709	-0.000056
O	0.354619	0.748727	-0.000112
Co	-1.317539	-0.145145	0.000020

^{3}TS1

C	1.238965	1.051512	0.146999
H	2.078541	0.521439	0.629704
H	0.895169	1.817049	0.845080
H	1.551600	1.499575	-0.793192
C	-0.835025	0.811139	-0.280659
H	-0.960400	1.735201	-0.857650
O	-1.665797	0.165897	0.285346
Co	0.271772	-0.669494	-0.048324

^{3}INT1

C	-1.700307	0.668026	-0.000112
H	-2.445079	-0.149387	0.000567
H	-1.795460	1.265636	-0.904033
H	-1.794911	1.266224	0.903509
C	0.999768	0.888521	0.000098
H	1.083495	1.983373	0.000305
O	1.836755	0.043135	-0.000133
Co	-0.205143	-0.520378	0.000030

^{3}TS2

C	-0.83297	1.4265	-0.02452
H	-1.74519	1.75679	-0.54209
H	0.03394	2.02585	-0.29019
H	-0.98312	1.34364	1.05122
C	1.26936	-0.37168	0.08195
H	1.42759	-1.49069	0.75869
O	2.05239	0.28545	-0.51009
Co	-0.67121	-0.49658	-0.02431

^{3}INT2

C	-0.687549	1.450628	0.000569
H	-1.789245	1.525386	-0.012041
H	-0.257250	1.890525	-0.895897
H	-0.277802	1.884960	0.909466
C	1.124909	-0.294341	0.000925
H	0.967236	-1.464801	0.005520
O	2.135565	0.257710	-0.000865
Co	-0.679690	-0.475388	-0.000337

^{3}TS3

C	-1.901028	0.785246	-0.044245
H	-2.758901	0.124393	0.124268
H	-1.895794	1.175097	-1.067325
H	-1.871832	1.589425	0.686445
C	1.374689	0.157543	0.076278
H	0.592426	0.755368	0.824948
O	2.478289	0.393712	-0.100865
Co	-0.397562	-0.461137	0.001718

^{3}PC

C	-2.389345	0.306548	0.012369
H	-2.472644	0.686786	1.029779
H	-3.386222	0.193408	-0.414147
H	-1.874497	1.016599	-0.658238
C	1.593581	0.070209	0.001458
H	-2.037922	-0.760959	-0.005495
O	2.701708	0.233773	0.002239
Co	-0.261770	-0.195058	-0.001954

^{3}Co(CO)$^+$

C	0.001864	1.017042	0.000000
O	-0.001398	2.135427	0.000000
Co	0.000000	-0.858729	0.000000

^{3}Co(CH$_4$)$^+$

C	1.540463	0.000000	0.007546
H	2.018282	-0.000072	0.984393
H	2.278806	0.000062	-0.793311
H	1.000946	-0.980369	-0.122092
H	1.000936	0.980381	-0.121968
Co	-0.575620	0.000000	0.000285

CP1

C	-0.1097268510	2.4778854281	0.3326993763
H	-0.6229767308	2.5294318065	-0.6396883618
H	0.7027802118	3.1935248366	0.3964571295
H	-0.7875204412	2.5568085570	1.1975898180
C	1.7387772589	0.8401305125	0.5650114008
H	0.8823823726	-0.1860350099	-0.6195655310
O	2.8462757027	1.0089291968	0.6782544524
CO	0.0475231771	0.5863823725	0.3549540156

CP2

C	1.2489631289	1.1468338963	0.0689587164
H	0.8372991795	1.9107176089	0.7221969780
H	2.2612448362	0.8516417198	0.3818310601
H	0.3719578842	-0.2714647465	1.2863483069
C	-1.3040428669	-0.0501389700	-0.1032849347
H	1.2058366374	1.4471525349	-0.9902770814
O	-2.3608325306	0.3033815242	0.0057343048
CO	0.4387814313	-0.5169670675	-0.1178842500

Energies and Vibrational Frequencies

Energies and Vibrational Frequencies at the PBE0/aug-cc-pVTZ level of theory.

Structure	Energies (Hartrees)	Energies Relative to ^{3}EC (cm^{-1})	Vibrational Frequencies (cm^{-1})
^{1}EC	-1535.9541411600	17502	101.9291, 147.7549, 274.3041, 444.6386, 542.1604, 785.6500, 919.5916, 1121.9061, 1159.2797, 1369.552, 1422.8861, 1430.4910, 1451.5852, 1723.6867, 3033.1932, 3089.6727, 3094.7215, 3148.8983
^{1}TS1	-1535.9245665700	23993	-294.1634, 179.3545, 319.9773, 494.1351, 528.6882, 671.2699, 709.7947, 827.2147, 944.2556, 1167.0556, 1257.8179, 1403.6637, 1410.8102, 1611.2356, 3001.4534, 3078.5464, 3142.5104, 3152.3156
^{1}INT1	-1535.9360507400	21473	111.6447, 165.2726, 195.8172, 477.1204, 544.7191, 618.8389, 655.6874, 741.4042, 882.0553, 1121.5563, 1223.2771, 1369.3393, 1423.1411, 1699.9798, 2961.5638, 3065.9593, 3113.5932, 3183.0161
^{1}TS2	-1535.9065182900	27954	-347.6419, 89.1499, 114.9202, 242.0872, 424.5730, 562.4308, 593.1125, 701.8139, 745.1575, 1079.7291, 1232.4850, 1386.0733, 1421.4846, 1967.6172, 2638.1673, 2977.2151, 3100.1260, 3164.1427
^{1}INT2	-1535.9524374800	17876	126.0074, 160.8536, 375.8911, 429.1318, 468.7643, 502.7044, 582.2521, 660.1961, 762.0903, 774.2813, 1223.0426, 1363.1921, 1420.9635, 2183.1912, 2261.3719, 2937.3813, 3064.0266, 3187.7515
^{1}TS3	-1535.9461589600	19254	-750.7294, 105.5598, 150.2576, 345.0090, 415.5412, 454.0665, 559.5683, 677.7785, 850.8165, 869.0435, 1249.9371, 1374.7213, 1435.8505, 1435.8505, 2256.8956, 2959.8330, 3066.9799, 3170.4574
^{1}PC	-1535.9691391200	14211	28.7822, 83.8175, 151.1613, 284.5637, 399.1108, 408.5796, 431.2466, 560.2803, 1264.9431, 1293.8641, 1361.4814, 1489.7192, 1610.2077, 2271.8068, 2733.2425, 3040.4535, 3125.7796,

			3153.7156,
$^{1}Co^{+}$	-1382.1452040000		
$^{1}Co(CO)^{+}$	-1495.4552953700		340.0250, 434.0331, 2290.1538
$^{1}Co(CH_4)^{+}$	-1422.6665373400		82.1146, 294.0038, 608.6766, 1191.0935, 1313.0136, 1384.1104, 1462.9370, 1662.2236, 2563.0186, 3003.5334, 3116.8922, 3171.9712
^{3}EC	-1536.0338882700	0	84.1940, 133.2817, 234.5009, 375.4638, 518.8055, 774.5738, 920.4549, 1129.3788, 1156.9436, 1369.8271, 1424.2054, 1435.6957, 1450.2291, 1742.0418, 3035.2157, 3065.0130, 3094.0062, 3162.4206
$^{3}TS1$	-1535.9639330000	15353	-217.9619, 111.6464, 192.1105, 296.5244, 471.0379, 612.7154, 649.0971, 804.5694, 934.3298, 1207.6647, 1248.9559, 1405.9214, 1437.6851, 1765.7262, 2965.4341, 3080.7635, 3106.4681, 3181.0035
$^{3}INT1$	-1535.9703097800	13954	63.0580, 126.1407, 153.1500, 277.6969, 490.3481, 643.1579, 675.7213, 706.5371, 833.4113, 1131.9825, 1206.6380, 1376.9425, 1435.7707, 1802.9417, 2958.2850, 3073.1152, 3131.4638, 3194.9867
$^{3}TS2$	-1535.9342341700	21872	-197.7871, 137.1046, 279.4303, 331.1384, 391.0396, 477.2086, 593.8843, 708.9005, 952.1047, 1133.7809, 1193.9424, 1365.3855, 1374.3045, 1422.4197, 1823.5625, 3008.9341, 3126.6430, 3200.4264
$^{3}INT2$	-1535.9557378600	17152	86.2242, 124.6264, 173.3359, 211.2425, 454.4832, 488.3171, 591.3794, 709.0368, 767.1572, 1135.1828, 1209.6392, 1379.8104, 1432.5477, 2048.4920, 2295.7884, 2968.8340, 3139.1428, 3201.3962,
$^{3}TS3$	-1535.9297831400	22848	-798.7111, 83.5926, 127.5958, 208.9956, 304.1409, 397.9465, 508.2441, 565.7994, 651.3237, 784.5493, 1094.8615, 1378.0068, 1414.7586, 1806.8107, 2081.4047, 3016.7645, 3114.3728, 3182.1036
^{3}PC	-1536.0521751600	-4014	67.6467, 74.7469, 155.7022, 287.4118, 355.1019, 362.4950, 414.1091, 502.3594, 1215.9899, 1323.9188, 1379.0574,

			1508.0608, 1579.5005, 2273.3709, 2768.6588, 2984.2072, 3119.2703, 3172.6472
$^3Co^+$	-1382.2455750800		
$^3Co(CO)^+$	-1495.4552953700		311.0820, 405.5742, 2290.6417
$^3Co(CH_4)^+$	-1422.6665373400		87.7208, 394.0553, 563.9285, 1159.4572, 1364.9362, 1407.0434, 1495.9002, 1581.9549, 2699.5163, 2808.5476, 3118.7453, 3191.2799
CP1	-1535.9343534000	21845	
CP2	-1535.9482612450	18793	
CH_3CHO	-153.7101966870		
CO	-113.2270298210		
CH_4	-40.4745863079		

Single Point Energy Corrections

CASPT2(2,2)/aug-cc-pVTZ single point energy corrections to DFT structures.

Structure	Energy (Hartrees)	Energy Relative to ^{3}EC (cm^{-1})
^{1}Co + CH_3CHO	-1535.2978038544	31485
^{1}EC	-1535.3788656997	13694
^{1}TS1	-1535.3334168995	23668
^{1}INT1	-1535.3221987673	26131
^{1}TS2	-1535.2893473634	33341
^{1}INT2	-1535.3854547814	12247
^{1}TS3	-1535.3784011596	13796
^{1}PC	-1535.4209070145	4467
$^1Co(CO)^+ + CH_4$	-1535.3760539878	14311
$^1Co(CH_4)^+ + CO$	-1535.3414729955	21900
^{3}Co + CH_3CHO	-1535.3625297546	17279
^{3}EC	-1535.4412581183	0
^{3}TS1	-1535.3850530305	12336
^{3}INT1	-1535.3940640200	10358
^{3}TS2	-1535.3560925510	18692
^{3}INT2	-1535.3809705814	13232
^{3}TS3	-1535.3433507107	21488
^{3}PC	-1535.4807452026	-8666
$^3Co(CO)^+ + CH_4$	-1535.4364275411	1060
$^3Co(CH_4)^+ + CO$	-1535.4061216955	7712
^{1}Co	-1381.7438170917	
$^1Co(CO)^+$	-1494.9616227574	
$^1Co(CH_4)^+$	-1422.1995042462	
^{3}Co	-1381.8085429919	
$^3Co(CO)^+$	-1495.0219963107	
$^3Co(CH_4)^+$	-1422.2641529462	

SA-CASPT2(2,2)/aug-cc-pVTZ single point energy corrections to DFT CP structures

Structure	Energy (Hartrees)	Energy (cm^{-1}; Relative to ^{3}EC)
CP1	-1535.3514175302	19718
CP2	-1535.3806441164	13303

MP2 Energies for neutral species with DFT structures

Structure	Energy (Hartrees)
CH_3CHO	-153.5539867627
CO	-113.1419687493
CH_4	-40.4144312304

RRKM Parameters

Rotational Constants, vibrational Frequencies, and zero-point energy corrections were computed at the uPBE0/aug-cc-pVTZ level of theory. Electronic energies were computed at the CASPT2(2,2)/aug-cc-pVTZ//PBE0/aug-cc-pVTZ level of theory.

Structure	Rotational Constants (cm^{-1})	Vibrational Frequencies (cm^{-1})	Electronic Energy Relative to ^{3}EC (cm^{-1})	Zero-Point Energy Corrections (cm^{-1})
^{3}INT2	0.317764609883825, 0.1321807578744717, 0.09507973201862346	80.095079 124.6264, 173.3359, 211.2425, 454.4832, 488.3171, 591.3794, 709.0368, 767.1572, 1135.1828, 1209.6392, 1379.8104, 1432.5477, 2048.4920, 2295.7884, 2968.8340, 3139.1428, 3201.3962,	13232	11208
^{3}TS3	0.5765829055463092, 0.08806069283568753, 0.07821087967411235	-798.7111, 83.5926, 127.5958, 208.9956, 304.1409, 397.9465, 508.2441, 565.7994, 651.3237, 784.5493, 1094.8615, 1378.0068, 1414.7586, 1806.8107, 2081.4047, 3016.7645, 3114.3728, 3182.1036	21488	10360
^{3}PC			-8666	11772

Landau-Zener Transition Parameters

Norm of the difference gradient and reduced mass along the spin crossing coordinate were determined from normal mode analysis at the (u)PBE0/aug-cc-pVTZ level of theory. Energies (and orbitals) were computed at the SA-CASPT2(2,2)/aug-cc-pVTZ/PBE0/aug-cc-pVTZ level of theory. Spin-orbit coupling constants were computed using the full Breit-Pauli Hamiltonian at the CASCI(2,2)/aug-cc-pVTZ//PBE0/aug-cc-pVTZ level of theory.

Structure	μ (amu)	|ΔG| (Hartree $Å^{-1}$)	H_{so}(cm^{-1})	Electronic Energy Relative to ^{3}EC (cm^{-1})
CP1	1.763937638487339	0.132991646134139	1108.74	19718
CP2	1.0372001090762852	0.18718519750480872	389.29	13303