

Supporting Materials for

Molecular-Level Electrocatalytic CO₂ Reduction Reaction Mediated by Single Platinum Atoms

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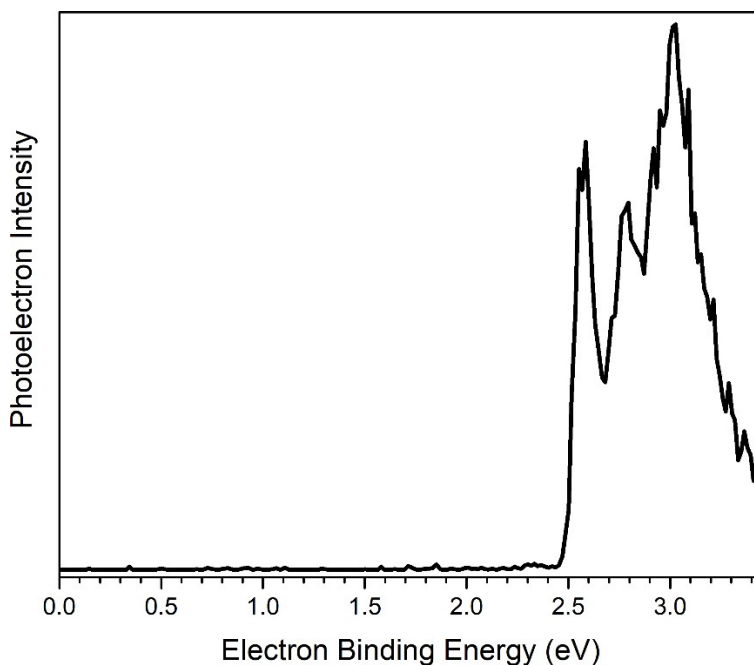


Figure S1. Photoelectron spectrum of H-Pt-OH.

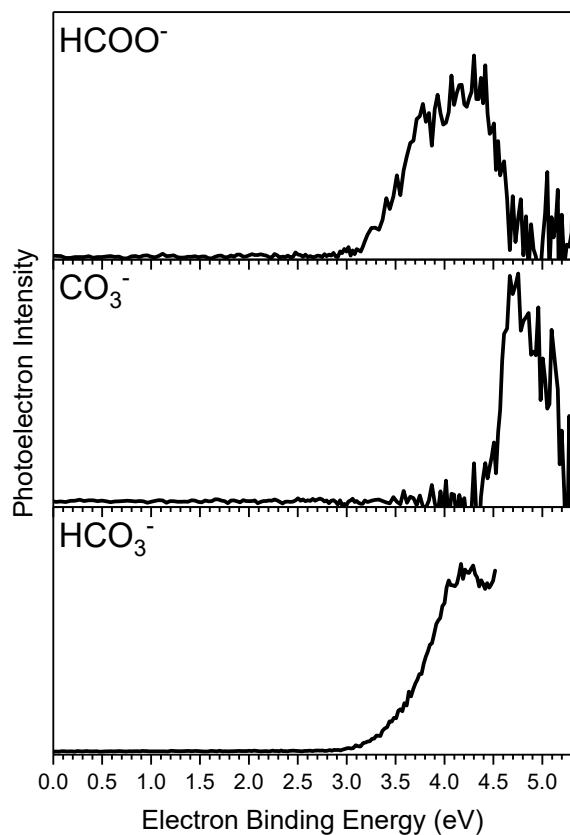


Figure S2. Photoelectron spectra of HCOO^- (formate), CO_3^- , and HCO_3^- .

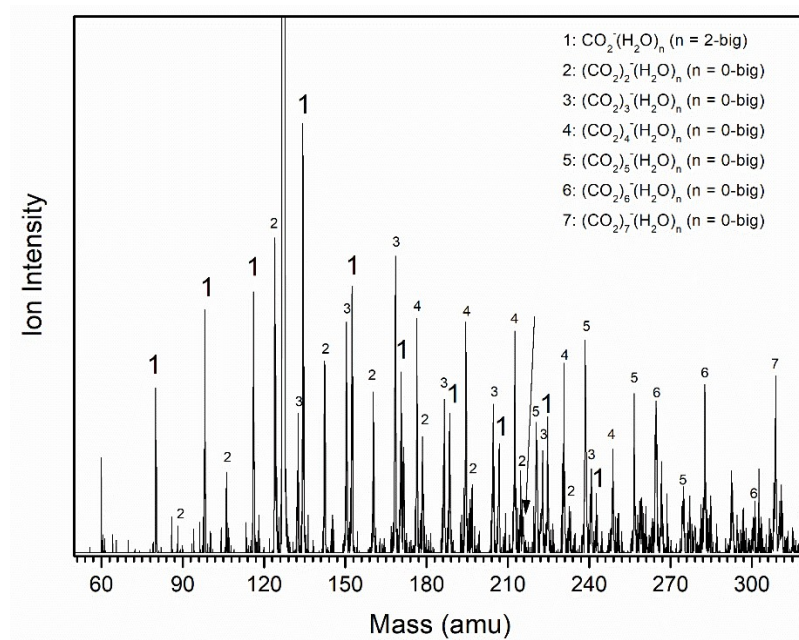


Figure S3. Mass spectrum of the reaction with H_2O and CO_2 with the presence of electrons but not Pt atoms.

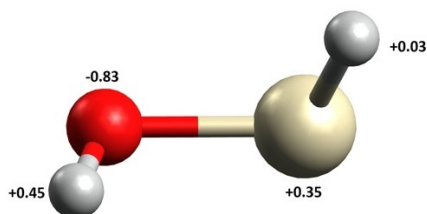


Figure S4. The NBO charge of neutral H-Pt-OH.

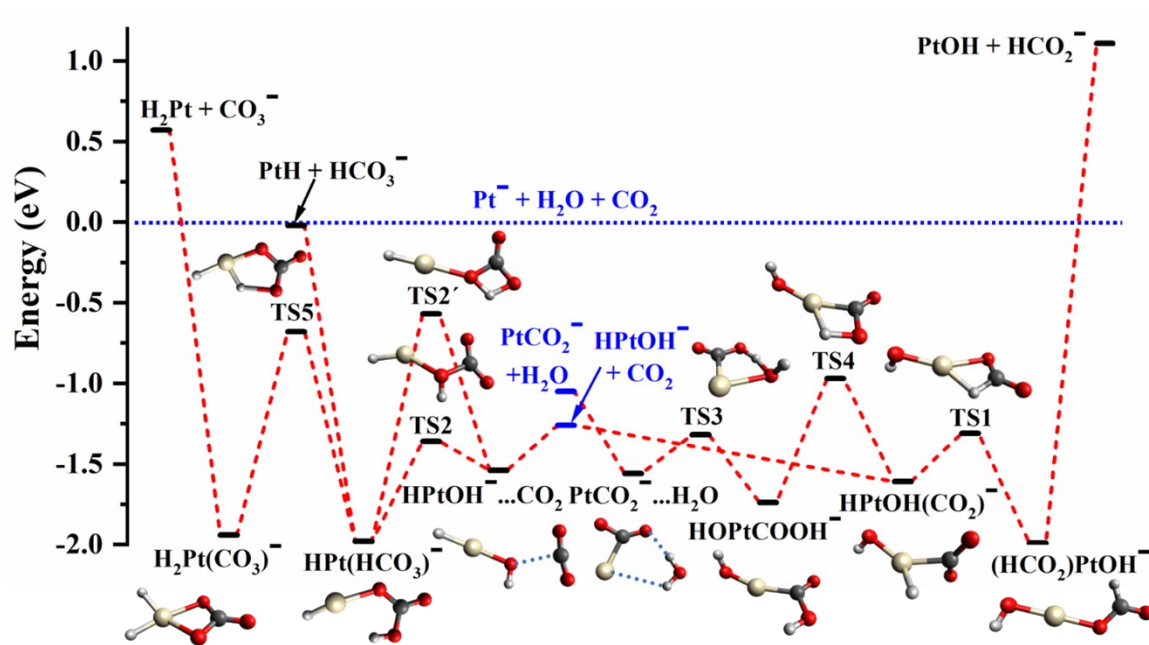


Figure S5. A more complete reaction profile for the reactions among Pt⁻, H₂O, and CO₂, showing the route where Pt⁻ reacts first with CO₂ then with H₂O.

Cartesian coordinates (Å) and harmonic vibrational frequencies (cm⁻¹) for the B3LYP/aug-cc-pVTZ(C,H,O),aug-cc-pVTZ-PP(Pt) optimal structures of all intermediates.

HPtOH(CO₂)⁻

Pt	0.328028	-0.087693	-0.127006
H	-0.375541	-0.398881	-1.489010
H	2.693420	-0.085919	0.672692
O	-1.951783	-0.997008	0.577109

O	-2.287724	1.190271	-0.026784
C	-1.708200	0.142760	0.153585
O	2.032646	0.615274	0.674836

36.6558
88.6876
221.7544
280.1340
285.5807
496.4301
543.7175
613.6168
655.4146
669.2542
739.1893
1207.2675
1811.8834
2203.6300
3788.4606

TS1

Pt	0.381787	-0.023357	0.012219
H	-1.132234	-0.856499	0.402221
H	2.692364	0.023453	0.689246
O	-1.639115	1.127305	-0.024510
O	-3.083684	-0.635810	-0.084080
C	-2.014916	-0.066116	0.055247
O	2.316550	-0.110051	-0.188419

128.9783 i
65.2992
137.7860
207.2410
288.3067
400.3065
569.1082
732.5334
852.5105
857.6339
1246.2840
1624.7104

1761.5238
1800.6433
3770.3542

(HCO₂)PtOH⁻

Pt	0.462571	-0.038755	-0.000000
H	2.823939	-0.425876	0.000093
O	-3.628844	0.099236	-0.000099
O	-1.477837	-0.520593	0.000058
H	-2.096818	1.413829	0.000273
C	-2.435729	0.360633	0.000063
O	2.332521	0.405248	-0.000050

81.1213
119.8144
128.2613
248.3714
278.4213
361.5135
611.1560
815.0375
875.6847
1054.8051
1266.0252
1387.4476
1691.2431
2896.9661
3738.7550

HPtOH⁻...CO₂

O	3.038371	1.305696	-0.036551
C	3.239987	0.162674	0.028954
O	3.660999	-0.923513	0.108319
O	0.913292	-0.546550	-0.155421
H	0.934169	-1.508116	-0.098898
H	-2.354280	0.432850	0.757918
Pt	-1.011809	0.018130	-0.002096

26.1298
47.1661

95.4493
165.8615
222.3338
404.6783
479.9023
556.0099
600.7484
680.4730
803.7136
1348.2456
2076.7419
2350.8166
3780.4926

TS2

O	2.027626	1.310112	0.127327
C	2.346286	0.142060	0.019413
O	3.317948	-0.528921	-0.288810
O	1.131945	-0.783534	0.401023
H	1.329102	-1.641106	0.011125
H	-2.311916	-0.497942	0.013458
Pt	-0.832244	0.016736	-0.026377

139.4999 i
69.8138
140.5831
258.5191
296.2755
392.8941
514.7363
598.8210
713.2081
774.3419
1086.7150
1277.5810
1884.6734
2155.0015
3814.8475

HPt(HCO₃)⁻

H	2.055972	0.705775	0.641355
Pt	0.811623	-0.018342	-0.015625
O	-2.007269	1.284115	-0.003200
H	-1.039403	1.434073	0.003683
O	-3.310278	-0.527374	-0.021428
O	-1.086874	-0.787756	0.084152
C	-2.181303	-0.076838	0.016255

95.1234

148.6680

306.3841

328.0046

439.6829

605.0932

662.5970

698.2270

812.7066

981.2606

1189.0141

1366.0926

1745.1803

2133.8174

3466.7665

PtCO₂⁻...H₂O

H	-2.793301	-0.159058	-0.000062
O	-3.179454	-1.058870	0.000517
H	-2.387928	-1.607869	0.000726
O	-1.770679	1.392769	-0.000952
Pt	0.572771	-0.319855	-0.000053
O	0.428788	2.050685	0.000952
C	-0.554025	1.273163	-0.000104

27.7285

39.8080

175.0438

223.8021

227.5081

326.2730

387.4249

592.7848
699.5048
754.8146
1213.8447
1686.3021
1735.9962
3517.4206
3815.4180

TS3

H	-0.862775	1.727224	-0.047232
O	0.359730	2.052381	-0.075185
H	0.610282	2.297067	0.821614
O	-1.860962	1.119084	-0.033290
Pt	0.495622	-0.253030	-0.003061
O	-2.193682	-1.109086	0.037077
C	-1.474455	-0.131168	0.005924

854.7255 i
98.0139
283.7398
292.8681
313.1826
563.6594
582.8444
600.2224
621.6390
883.2396
1257.1140
1457.4565
1619.3782
1734.4423
3805.7697

HOPtCOOH⁻

Pt	-0.350920	-0.082470	-0.005487
O	-2.278175	0.354459	-0.078791
O	2.372339	-0.921679	0.025205
H	1.737861	-1.652438	0.030648
H	-2.571326	0.534769	0.822139
O	2.233929	1.302678	-0.001965

C	1.596741	0.277771	0.003267
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70.3171

96.3350

240.7706

310.1398

343.1185

463.5900

536.2744

611.4812

666.1786

764.3639

859.4897

1233.8316

1734.5685

3705.3240

3770.8295

TS4

H	0.683258	-1.416419	0.122741
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Pt	-0.319935	-0.072491	-0.015437
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O	-2.241046	0.453404	-0.039188
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O	1.999078	-1.041587	0.045685
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H	-2.519986	0.577948	0.874691
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O	2.370296	1.207704	0.008439
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C	1.627507	0.256095	0.014531
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1381.9569 i

103.2376

113.4419

331.8549

356.7774

429.5066

463.8905

520.7286

581.5357

725.6203

777.8244

1047.4032

1694.4445

1781.5688

3783.1647

TS5

H	0.062639	1.264609	-0.094221
H	-2.153771	0.710931	0.255057
Pt	-0.769132	-0.025312	-0.023463
O	1.924419	1.293073	0.081479
O	3.184492	-0.551267	-0.202961
O	1.054884	-0.780563	0.297824
C	2.128844	0.051469	0.043096

471.2550 i

112.8909

263.6227

318.7538

399.3498

490.8932

603.7800

647.0971

648.7645

774.0271

830.1510

1252.2342

1565.8938

2126.0741

2202.2640

H₂Pt(CO₃)⁻

O	3.112883	-0.082388	-0.025024
H	-1.863537	-0.993553	-0.082625
Pt	-0.652193	0.002479	-0.016176
O	1.079878	-1.064997	0.085538
O	1.189298	1.121361	-0.000984
C	1.899023	0.027120	0.018739
H	-1.716046	0.845699	0.755702

136.2691

308.0792

326.9868

425.2987

523.1408

607.5264

649.8193

729.1614
823.3402
840.2165
949.7501
1197.1508
1697.6088
2209.6779
2239.7115

H₂O

O	-0.000000	-0.000000	0.116933
H	0.000000	0.763545	-0.467731
H	-0.000000	-0.763545	-0.467731

1626.6809
3798.5724
3901.4499

CO₂

C	0.000000	0.000121	0.000079
O	1.073146	-0.240785	0.370166
O	-1.073146	0.240695	-0.370225

673.5954
1369.2949
2400.6521

HPtOH⁻

Pt	0.190942	-0.002083	0.012709
H	1.677165	0.167044	-0.562822
H	-2.126870	0.800611	0.058763
O	-1.805469	-0.100643	-0.060902

398.4240
510.6835
556.6839
752.5437
2051.9129
3762.3056

PtCO₂⁻

Pt	-0.497553	-0.037089	0.000000
O	1.479956	1.260347	0.000004
O	2.273962	-0.900597	0.000005
C	1.462963	0.002496	-0.000015

228.4199

322.4901

596.7472

737.4369

1194.6430

1767.0122

PtH

H	-0.000000	0.000000	-1.514187
Pt	0.000000	-0.000000	0.019413

2319.0573

PtOH

Pt	0.010629	-0.196242	-0.000000
O	0.010629	1.668115	0.000000
H	-0.914074	1.961945	0.000000

644.9714

932.8863

3704.7142

HCO₂⁻

H	-0.000074	1.450772	0.000151
O	-1.135840	-0.209063	0.000020
O	1.135992	-0.208983	0.000020
C	-0.000191	0.315600	-0.000080

744.2030

1041.8569

1338.0562

1370.8070

1649.1797

2573.5730

HCO₃⁻

O	-1.047405	-0.735745	-0.000115
O	-0.056482	1.294847	-0.000020
O	1.201234	-0.598868	0.000079
C	0.160080	0.063922	-0.000083
H	-1.739257	-0.065399	0.000950

537.4675

546.0120

620.7137

819.7067

841.7805

1194.0776

1290.6578

1750.1819

3791.8956

H₂Pt

Pt	0.027648	0.000000	0.000000
H	-1.078251	-1.036534	-0.000012
H	-1.078289	1.036498	0.000011

772.6400

2406.2237

2447.3742

CO₃⁻

C	-0.000095	-0.000228	-0.001013
O	0.989427	-0.760114	0.000262
O	-1.153245	-0.476394	0.000283
O	0.163889	1.236679	0.000215

282.8799

284.0133

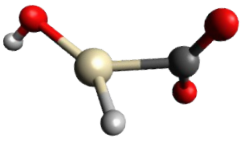
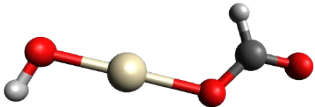
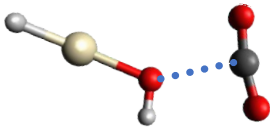
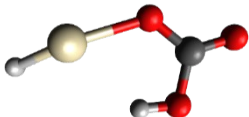
768.0089

1140.2120

1518.1417

1518.7866

Table S1. VDEs (eV), intensities (arbitrary units), and FWHMs of considered species.

Structure	VDE to singlet	Intensity singlet	VDE to triplet	Intensity triplet	EA (to singlet)	EA (to triplet)	FWHM (singlet)	FWHM (triplet)
	3.54	2.88	4.43	14.26	1.67	3.21	1.87	1.22
	4.15	12.57	3.92	10.11	3.61	3.63	0.54	0.29
	3.37	3.78	3.32	3.40	2.14	3.05	1.23	0.27
	4.36	11.83	4.35	13.74	3.08	4.13	1.28	0.22