

Supplementary information for

**Observation of HOCO generation in $[\text{CO}-(\text{H}_2\text{O})_n]^+$ ($n = 2$ and 3) clusters
by infrared photodissociation spectroscopy**

Ryonosuke Okimoto, Tatsuki Hosoda, Mizuhiro Kominato, and Asuka Fujii*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

* To whom correspondence addressed Email: asuka.fujii.c5@tohoku.ac.jp

Contents

- 1. Optimized structures of $[\text{CO}-(\text{H}_2\text{O})_n]^+$ ($n = 2$ and 3) calculated at the MP2/aug-cc-pVTZ level**
- 2. Tables of calculated frequencies and intensities of each optimized structure of $[\text{CO}-(\text{H}_2\text{O})_n]^+$ ($n = 2$ and 3) across the full frequency range**

1. Optimized structures of $[\text{CO}-(\text{H}_2\text{O})_n]^+$ ($n = 2$ and 3) calculated at the MP2/aug-cc-pVTZ level

A. $n = 2$

W2-HOCO

O	-0.68978400	-1.12696400	0.35586600
H	-0.36031700	-2.00871500	0.10830700
H	-2.26466600	3.02803000	0.41996000
C	-0.08323500	-0.20374500	-0.32567900
O	-0.24699400	0.98867100	-0.26933400
O	-1.68255200	2.51755400	1.00922300
H	-1.15147500	3.13104800	1.54613200
H	-1.07327300	1.82593000	0.47027300

W2-HCOOH

O	-0.68978400	-1.12696400	0.35586600
H	-0.36031700	-2.00871500	0.10830700
H	-2.26466600	3.02803000	0.41996000
C	-0.08323500	-0.20374500	-0.32567900
O	-0.24699400	0.98867100	-0.26933400
O	-1.68255200	2.51755400	1.00922300
H	-1.15147500	3.13104800	1.54613200
H	-1.07327300	1.82593000	0.47027300

W2-PT-1

H	1.38720000	-1.34643600	-0.08659500
O	1.61519200	-0.40620200	-0.00462200
H	0.80477800	0.17971700	-0.16736500
C	-0.57131300	1.24174200	-0.55348500
O	-1.43570400	1.92103300	-0.81905000
O	2.73992700	0.30695300	2.17892400
H	3.58666100	-0.02379400	2.53358700
H	2.08800100	-0.19979300	0.88071600

W2-PT-2

H	2.63825300	1.00243200	-0.01849800
O	1.90798400	-0.04473800	-0.25523900
H	0.91242600	0.02430400	-0.14078200
C	-0.96067100	-0.02404900	0.05319600

O	-2.08452900	-0.10517900	0.16335900
O	3.34510300	1.84469200	0.24556200
H	4.27455000	1.56919400	0.30555800
H	3.28568200	2.62817200	-0.32411400

B. $n = 3$

W3-HOCO

O	-0.72807200	-0.04549900	-2.08031100
H	0.13298800	-0.32704100	-2.43058000
H	-1.91145400	0.78532300	2.88445000
C	-0.61078200	0.29766700	-0.82898700
O	-1.49295900	0.68969900	-0.11081300
O	-1.54952900	1.47633000	2.31066000
H	-2.08085500	2.37322500	2.39958800
H	-1.49212100	1.14604600	1.35173200
O	-2.69949800	3.66090100	2.46769400
H	-2.32392400	4.37777900	2.99277000
H	-3.64921000	3.81749500	2.40832900

W3-HCOOH

O	0.43708400	-0.85654900	-0.50249100
H	0.24833400	0.85025500	0.48294800
C	-0.33543300	0.02197100	0.06166300
O	-1.55629100	-0.05872300	0.11903900
O	-3.20652800	-1.75911500	-0.71348400
H	-3.76709200	-2.16719100	0.06078600
H	-3.77548100	-1.36247700	-1.38903400
H	-2.49845700	-1.08139200	-0.38923000
O	-4.43925800	-2.81113100	1.17236800
H	-4.57245500	-3.76617000	1.19984200
H	-5.14838400	-2.41276700	1.69038900

W3-PT-1

H	1.49718100	0.82046000	-0.26639400
O	1.05106800	-0.05136100	-0.60535900
H	0.08457400	-0.08450500	-0.38685500
O	2.50532500	-2.09942500	0.21510500
H	2.47852400	-3.02394200	-0.09000900

H	1.53032900	-0.87339600	-0.30250600
O	2.05552100	2.10969400	0.12743900
H	2.50384800	2.27464400	0.96518700
H	2.45645100	2.69819500	-0.52346600
C	-1.79536900	-0.09921900	-0.09574300
O	-2.91845900	-0.09631200	0.04948100

W3-PT-2

H	2.72424000	1.26007700	0.03866400
O	1.81620500	0.17235300	-0.52479300
H	0.85063000	0.09954200	-0.32537400
C	-1.10694800	-0.18551100	0.00446200
O	-2.20894300	-0.39382700	0.16918900
O	3.41659300	1.91185100	0.42243700
H	4.40046600	1.56984400	0.33084200
H	3.30763800	2.80030400	0.05435400
O	5.71781900	1.01083600	0.30800300
H	6.28446600	0.96028000	-0.47060200
H	6.29461700	1.03052100	1.08098400

2. Tables of calculated frequencies and intensities of each optimized structure of [CO-(H₂O)_n]⁺ (*n* = 2 and 3) across the full frequency range

All frequencies are scaled by 0.9529

A. *n* = 2

W2-HOCO

Mode	Frequency (cm ⁻¹)	Intensity (km/mol)
1	39.67	45.9264
2	64.19	18.8677
3	177.53	65.9508
4	372.11	264.1011
5	452.05	11.3257
6	521.29	125.5673
7	582.96	86.3176
8	627.45	25.7027
9	1096.53	232.3823
10	1133.44	75.3837
11	1226.02	363.4778
12	1559.54	192.3262
13	1608.66	61.4301
14	1745.24	1285.4840
15	2057.02	2970.3242
16	3515.57	215.6547
17	3545.63	263.6303
18	3600.59	335.7013

W2-HCOOH

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	85.49	35.8618
2	102.90	30.5869
3	210.84	49.1663
4	408.05	396.3326
5	490.02	171.6327
6	518.82	0.1903
7	557.98	150.3370
8	886.54	3473.6133
9	983.97	0.1046
10	1129.84	66.6661
11	1287.32	180.6365
12	1392.77	206.9475
13	1484.94	79.3392
14	1583.72	260.2915
15	1643.40	579.8084
16	2961.73	31.5683
17	3561.05	120.6877
18	3655.17	261.0154

W2-PT-1

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	50.53	0.8105
2	104.99	146.4899
3	159.95	3.9064
4	180.68	4.9135
5	223.42	57.3416
6	305.69	65.4333
7	367.68	66.7545
8	426.73	140.0339
9	551.78	47.2987
10	775.86	44.6516
11	1004.01	220.7500
12	1594.89	6.0526
13	1649.71	24.9545
14	2070.89	1.0030
15	2616.24	2685.9533
16	2806.61	1537.0491
17	3544.81	110.4418
18	3583.51	275.8431

W2-PT-2

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	44.59	10.8916
2	64.00	51.6775
3	144.07	8.1401
4	150.45	44.7621
5	187.29	41.5787
6	447.73	80.8098
7	497.79	51.3017
8	522.94	252.4521
9	571.07	158.1622
10	828.60	25.3928
11	1057.09	626.7589
12	1225.64	2479.4588
13	1581.60	170.2683
14	1665.02	1030.5794
15	2061.28	4.8511
16	3031.55	1135.8900
17	3537.83	141.9825
18	3627.46	310.7668

B. $n = 3$

W3-HOCO

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	30.93	34.3000
2	44.58	6.0806
3	71.02	15.9274
4	91.16	2.6498
5	110.67	18.3029
6	228.53	227.6836
7	261.02	152.2265
8	353.79	84.1707
9	385.48	170.0077
10	432.40	16.1731
11	558.27	38.5719
12	569.72	66.8183
13	638.68	5.5249
14	884.18	89.3224
15	1138.15	83.9454
16	1205.75	160.0529
17	1228.07	325.0325
18	1532.33	4.2416
19	1616.85	39.7916
20	1633.51	15.7601
21	1746.19	788.7061
22	2294.72	3291.1338
23	2767.36	2180.9195
24	3570.99	263.0872
25	3608.73	97.6093
26	3616.66	207.5085
27	3712.08	210.6094

W3-HCOOH

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	16.24	0.4228
2	60.64	1.1867
3	68.64	13.1879
4	116.58	21.2121
5	165.30	27.6227
6	242.27	231.0513
7	318.06	157.1208
8	347.76	83.0622
9	383.09	157.2634
10	435.75	36.4276
11	508.94	34.4187
12	589.35	5.6634
13	954.47	67.6539
14	984.96	2.0262
15	1091.11	55.8623
16	1201.14	194.4289
17	1313.82	7.9946
18	1534.84	21.7395
19	1590.40	595.0011
20	1626.00	84.8873
21	1638.96	22.2469
22	2353.76	4096.4096
23	2537.54	1428.2833
24	2936.14	10.8482
25	3609.50	92.3976
26	3618.03	206.5953
27	3712.70	203.7386

W3-PT-1

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	38.49	2.4801
2	51.51	5.6727
3	64.91	3.1100
4	108.32	64.9267
5	114.17	77.6131
6	156.72	14.2835
7	168.03	1.2741
8	181.72	13.0793
9	255.07	35.5331
10	271.12	201.5718
11	357.65	144.8203
12	365.88	102.6662
13	414.34	85.8631
14	621.49	48.5078
15	696.20	13.3655
16	829.14	97.5793
17	1157.17	179.6419
18	1552.00	31.1918
19	1613.33	6.2969
20	1650.40	17.3909
21	2059.14	5.6782
22	2434.54	2797.0036
23	3041.66	1459.0848
24	3160.07	1340.7570
25	3566.75	86.2064
26	3609.69	70.1820
27	3711.78	199.7946

W3-PT-2

Mode	Frequency (cm⁻¹)	Intensity (km/mol)
1	11.37	1.2215
2	33.62	2.4428
3	66.52	6.1375
4	107.91	22.0458
5	124.39	6.5380
6	131.50	11.9239
7	166.88	21.8139
8	216.67	239.6140
9	334.88	36.3286
10	353.22	121.7980
11	384.31	162.9229
12	422.60	36.0833
13	474.16	95.9188
14	570.08	17.9992
15	674.34	60.6087
16	925.09	73.7757
17	1184.24	194.0691
18	1526.25	4.2709
19	1596.96	33.5337
20	1632.22	21.1552
21	2050.63	12.6234
22	2293.83	3626.8650
23	2610.57	1891.2750
24	3289.64	660.3870
25	3609.65	90.3071
26	3622.29	208.6555
27	3712.63	212.1518