Electronic Supplementary Material for PCCP

Role of vibrational anharmonicity in atmospheric radical hydrogen-bonded complexes

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(Supporting Information)

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Table S1: Experimental and calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and M052X/6-311++G(2d,2p) levels for the ·OOH and HCOOH systems.

			B3LYP/6-311++G(2d,2p		MP2/6-311++G(2d,2p)		M052X/6-311++G(2d,2p)		
Molecule	**Mode**		**ν(har)**	**ν(anhar)**	**ν(har)**	**ν(anhar)**	**ν(har)**	**ν(anhar)**	**ν(exp)**
·OOH	O-H st	A'	3617.3	3411.0	3704.3	3498.9	3729.8	3422.9	3436.2
	O-O-H ben	A'	1441.3	1399.7	1466.6	1425.0	1478.4	1407.5	1391.8
	O-O st	A'	1166.4	1142.8	1218.8	1215.6	1251.2	1217.6	1097.6
Δ_{mean}			99.8	26.1	154.7	71.3	177.9	49.7	
Δ_{max}			181.1	45.2	268.1	118.0	293.6	120.0	
HCOOH	O-H st	A'	3739.6	3547.2	3777.6	3583.2	3810.4	3616.0	3570.0
	C-H st	A'	3057.1	2902.4	3126.9	2996.7	3165.9	3147.1	2942.8
	C=O st	A'	1809.3	1776.4	1784.1	1751.2	1858.6	1823.3	1770.0
	H-C-O bend	A'	1403.2	1386.4	1424.2	1397.3	1428.3	1406.5	1387.0
	H-O-C bend	A'	1305.9	1256.2	1314.2	1244.9	1322.9	1269.3	1229.0
	C-O st	A'	1120.5	1088.3	1119.9	1087.4	1159.8	1134.2	1105.3
	H(C) out wag	A"	1050.1	1030.6	1060.8	1039.1	1088.5	1063.5	1033.0
	H(O) out wag	A"	675.0	615.4	630.0	595.6	678.9	615.2	638.0
	O-C=O bend	A'	628.6	622.2	674.6	623.4	645.4	640.5	625.0
Δ_{mean}			54.3	15.8	69.8	20.0	95.4	51.2	
Δ_{max}			169.6	40.4	207.6	53.9	240.4	204.3	

Table S2: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) at B3LYP/6-311++G(2d,2p), MP2/6-311++G(2d,2p), and M052X/6-311++G(2d,2p) levels for the HCOOH···OOH (**C1**) complex.

		B3LYP/6-311++G(2d,2p)		MP2/6-311++G(2d,2p)		M052X/6-311++G(2d,2p)	
Mode		***v(har)***	***v(anhar)***	***v(har)***	***v(anhar)***	***v(har)***	***v(anhar)***
CO-H st	A'	3201.8	2872.4	3294.2	2998.5	3258.9	3184.3
C-H st	A'	3093.2	2933.3	3159.6	2993.1	3189.7	2699.5
OO-H st	A'	2976.0	2608.8	3061.1	2641.5	2999.4	2364.0
C=O st	A'	1730.6	1696.7	1729.9	1698.1	1779.8	1719.6
O-O-H bend	A'	1625.8	1522.4	1634.5	1577.9	1631.8	1544.2
H-O-C bend	A'	1474.2	1455.6	1487.9	1441.0	1470.2	1441.2
H-C-O bend	A'	1396.2	1363.0	1417.4	1381.5	1426.7	1394.4
C-O st	A'	1248.1	1220.1	1385.8	1360.1	1319.0	1295.8
O-O st	A'	1222.9	1200.2	1248.4	1217.6	1285.3	1261.8
H(C) out wag	A"	1078.2	1054.4	1095.8	1068.8	1112.8	1122.2
H(O)-C out wag	A"	963.4	925.9	976.7	932.2	954.8	942.5
unique mode H(O)-O out wag	A"	844.1	742.4	855.9	749.4	840.1	798.4
O-C=O bend	A'	709.2	701.9	708.0	698.0	717.0	721.3
unique mode	A'	329.4	315.4	334.3	318.9	309.6	335.4
unique mode	A'	245.7	234.0	242.3	228.8	229.6	244.4
unique mode	A"	232.3	223.8	230.0	229.5	222.4	258.0
unique mode	A'	194.6	181.0	189.4	171.3	153.3	138.9
unique mode	A"	110.6	108.3	108.3	111.5	102.7	106.4

Table S3: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the HCOOH···OOH (**C1**) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Mode		***I(har)***	***ν(har)***	***ν(anhar)***
CO-H st	A'	1490.2 (1346.7)	3201.9 (3197.9)	2873.5 (2810.3)
C-H st	A'	122.2 (179.9)	3093.3 (3124.9)	2933.6 (2949.9)
OO-H st	A'	356.9 (431.4)	2975.1 (2941.9)	2608.7 (2537.1)
C=O st	A'	292.7 (323.9)	1730.7 (1741.4)	1698.9 (1701.7)
O-O-H bend	A'	156.6 (153.3)	1626.2 (1605.3)	1530.4 (1497.6)
H-O-C bend	A'	2.5 (3.6)	1474.0 (1457.0)	1456.1 (1432.7)
H-C-O bend	A'	17.3 (21.0)	1395.9 (1393.7)	1363.0 (1359.1)
C-O st	A'	181.1 (179.4)	1248.3 (1259.4)	1220.5 (1231.7)
O-O st	A'	12.1 (12.4)	1223.0 (1222.1)	1200.3 (1200.1)
H(C) out wag	A"	13.6 (16.6)	1079.3 (1075.8)	1054.1 (1049.2)
H(O)-C out wag	A"	51.9 (63.0)	966.3 (958.8)	922.7 (922.1)
unique mode H(O)-O out wag	A"	163.4 (187.1)	849.5 (839.7)	753.7 (764.6)
O-C=O bend	A'	22.5 (24.4)	709.3 (702.6)	702.0 (696.2)
unique mode	A'	76.9 (24.4)	329.8 (328.3)	315.6 (319.5)
unique mode	A'	4.8 (6.0)	246.0 (243.8)	234.2 (237.7)
unique mode	A"	1.0 (0.7)	232.8 (232.8)	223.1 (226.1)
unique mode	A'	3.7 (3.3)	194.6 (188.4)	180.9 (177.3)
unique mode	A"	1.2 (1.2)	110.6 (112.0)	108.0 (110.8)

Table S4: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the $CH_3COOH\cdots OOH$ (**C2**) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Mode		*I(har)*	*ν(har)*	*ν(anhar)*
CO-H st	A'	1540.2 (1468.2)	3235.0 (3226.7)	2920.5 (2897.0)
C-H st	A'	10.9 (15.3)	3168.9 (3183.4)	3018.1 (3040.0)
C-H st	A"	1.8 (1.7)	3116.9 (3131.2)	2970.6 (2998.3)
C-H st	A'	0.2 (0.2)	3061.6 (3065.9)	2951.3 (2951.7)
OO-H st	A'	702.9 (780.2)	2917.0 (2867.2)	2468.0 (2400.0)
C=O st	A'	253.2 (289.6)	1732.4 (1741.1)	1685.4 (1690.9)
OOH bend	A'	217.4 (207.1)	1633.6 (1616.8)	1576.1 (1496.6)
H-C-H bend	A"	24.3 (11.8)	1486.1 (1481.7)	1430.2 (1435.2)
H-C-H bend	A'	9.1 (41.1)	1482.2 (1478.7)	1439.6 (1429.1)
H-O-C bend	A'	34.1 (48.3)	1466.5 (1463.7)	1417.8 (1415.3)
H-C-H bend	A'	36.1 (29.7)	1407.1 (1403.5)	1370.9 (1369.0)
C-O st	A'	203.0 (191.1)	1326.8 (1334.6)	1293.1 (1302.9)
O-O st	A'	10.5 (11.6)	1222.7 (1221.7)	1200.4 (1199.3)
CH_3 torsion	A"	8.4 (8.2)	1077.4 (1072.6)	1051.5 (1046.0)
CH_3 torsion	A'	21.6 (18.3)	1033.1 (1031.1)	1018.5 (1019.5)
H(O)-C out wag	A"	30.6 (36.9)	949.1 (945.0)	905.6 (909.9)
C-C st	A'	2.0 (1.2)	904.8 (908.6)	889.3 (894.3)
unique mode H(O)-O out wag	A"	171.3 (199.5)	869.9 (867.8)	798.8 (815.9)
O=C-O bend	A'	29.0 (31.8)	636.7 (632.7)	621.7 (630.7)
HOC=O torsion	A"	0.7 (0.6)	603.3 (596.5)	595.2 (588.8)
O=C-C bend	A'	29.9 (31.3)	466.3 (462.8)	465.8 (466.0)
unique mode	A'	54.1 (56.0)	312.1 (313.5)	304.9 (307.3)
unique mode	A'	3.9 (4.9)	222.7 (220.4)	212.1 (214.5)
unique mode	A'	6.0 (5.5)	176.2 (172.6)	168.6 (166.1)
unique mode	A"	0.3 (0.4)	114.1 (115.3)	112.0 (112.5)
unique mode	A"	0.4 (0.2)	95.1 (95.8)	90.4 (93.2)
CH_3 twist	A"	0.7 (0.9)	55.0 (46.5)	46.7 (23.7)

Table S5: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the HNO_3···HOO (**C3**) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Mode		***I(har)***	***v(har)***	***v(anhar)***
OO-H st	A'	954.5 (912.5)	3352.7 (3337.0)	3100.8 (3077.4)
NO-H st	A'	796.6 (837.2)	3104.7 (3077.3)	2828.6 (2789.1)
$N=O_2$ st asy	A'	265.3 (312.2)	1741.3 (1757.6)	1697.8 (1713.4)
H-O-O bend	A'	149.0 (183.7)	1547.1 (1526.7)	1550.3 (1512.5)
N-O-H bend	A'	260.6 (172.3)	1497.3 (1493.7)	1513.7 (1544.7)
$N=O_2$ st sy	A'	226.6 (230.6)	1299.8 (1317.2)	1267.2 (1300.7)
O-O st	A'	14.8 (16.0)	1218.3 (1217.9)	1192.3 (1192.4)
O-N st	A'	120.8 (122.1)	968.8 (971.5)	942.2 (943.4)
H(O)-N out wag	A''	50.8 (56.3)	859.4 (848.1)	819.8 (814.8)
N out wag	A''	16.8 (17.2)	787.4 (767.6)	777.0 (759.9)
NO_2 scissors	A'	5.7 (5.4)	696.0 (690.5)	683.4 (678.4)
unique mode H(O)-O out wag	A'	160.3 (190.7)	646.6 (636.8)	593.4 (609.5)
NO_2 rock	A''	2.0 (2.3)	644.2 (636.9)	631.0 (625.2)
unique mode	A'	66.5 (68.2)	280.6 (281.2)	269.8 (273.4)
unique mode	A'	10.9 (12.0)	205.9 (204.6)	194.9 (195.2)
unique mode	A'	0.7 (0.7)	175.7 (171.4)	160.6 (158.5)
unique mode	A''	3.2 (3.4)	96.1 (95.7)	94.2 (94.0)
unique mode	A''	0.0 (0.0)	73.1 (73.4)	72.7 (71.7)

Table S6: Calculated harmonic and anharmonic vibrational frequencies (in cm^{-1}) and harmonic intensities (in km mol^{-1}) at B3LYP/6-311+G(2d,2p) level for the H_2SO_4···HOO (**C4**) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

Mode		***I(har)***	***v(har)***	***v(anhar)***
SO-H st	A	133.9 (134.5)	3769.9 (3751.1)	3600.9 (3576.7)
OO-H st	A	1292.4 (1312.9)	3281.9 (3259.7)	3021.2 (2964.4)
SO-H st	A	791.6 (708.3)	3067.2 (3067.0)	2698.9 (2664.8)
H-O-O bend	A	29.8 (31.2)	1580.9 (1561.4)	1609.1 (1565.8)
S-O-H bend asy	A	273.0 (314.7)	1446.4 (1417.6)	1442.0 (1388.8)
$S=O_2$ st asy	A	185.3 (163.5)	1343.6 (1316.5)	1311.9 (1299.6)
O-O st	A	9.2 (10.2)	1222.3 (1221.3)	1198.5 (1197.9)
S-O-H bend sy	A	41.7 (49.3)	1185.4 (1154.8)	1159.4 (1124.0)
$S=O_2$ st sy	A	210.3 (214.5)	1140.9 (1118.9)	1117.8 (1093.1)
$S-O_2$ st asy	A	294.2 (316.8)	890.1 (877.7)	871.9 (862.6)
H(O)-S out asy	A	43.8 (82.2)	821.1 (800.3)	761.6 (757.7)
$S-O_2$ st sy	A	111.9 (77.5)	796.7 (784.7)	777.7 (762.9)
unique mode H(O)-O out wag	A	141.3 (168.4)	667.3 (652.1)	616.6 (634.8)
$S=O_2$ wagg	A	46.5 (50.8)	547.8 (531.0)	541.4 (525.2)
$S=O_2$ bend	A	18.1 (18.0)	527.5 (511.5)	523.6 (505.8)
O-S=O rock	A	4.3 (7.1)	502.9 (484.0)	497.6 (478.4)
O-S=O bend	A	29.0 (34.7)	419.6 (404.2)	397.8 (379.9)
O-S=O twist	A	3.2 (5.5)	360.9 (353.9)	343.5 (334.8)
unique mode	A	75.1 (75.1)	292.9 (292.0)	283.5 (285.5)
H(O)-S out sy	A	74.2 (80.6)	255.2 (252.3)	232.6 (216.9)
unique mode	A	6.2 (5.8)	189.9 (187.5)	181.6 (181.4)
unique mode	A	9.8 (10.2)	169.6 (164.1)	161.0 (154.5)
unique mode	A	1.8 (1.7)	88.7 (91.0)	89.8 (91.8)
unique mode	A	1.3 (1.1)	45.1 (45.3)	47.6 (44.4)

Cartesian coordinates in Ångstroms for all structures studied in this work

OOH ^{2}A" B3LYP/6-31+G(d,p)

O	0.067131	-0.635641	0.000000
H	-0.860012	-0.953613	0.000000
O	-0.012942	0.695727	0.000000

OOH ^{2}A" B3LYP/6-311+G(2d,2p)

O	0.055316	-0.610372	0.000000
H	-0.885050	-0.867848	0.000000
O	0.055316	0.718853	0.000000

HCOOH ^{1}A' B3LYP/6-31+G(d,p)

C	0.098490	0.415066	0.000000
H	0.029147	1.511261	0.000000
O	-1.137414	-0.121797	0.000000
H	-1.041431	-1.091143	0.000000
O	1.127306	-0.216072	0.000000

HCOOH ^{1}A' B3LYP/6-311+G(2d,2p)

C	0.101450	0.412172	0.000000
H	0.033876	1.505369	0.000000
O	-1.134388	-0.120088	0.000000
H	-1.039365	-1.084898	0.000000
O	1.121632	-0.215633	0.000000

CH_3COOH ^{1}A' B3LYP/6-31+G(d,p)

C	1.461454	-0.055543	0.000000
C	-0.036082	0.100150	0.000000
O	-0.667279	-1.103994	0.000000
O	-0.645299	1.148668	0.000000
H	-1.622945	-0.924508	0.000000
H	1.776517	-0.621791	0.881777
H	1.776517	-0.621791	-0.881777

H	1.929808	0.927960	0.000000

CH_3COOH $^1A'$ B3LYP/6-311+G(2d,2p)

C	1.068662	-0.901325	0.000000
C	0.000000	0.154705	0.000000
O	-1.243715	-0.390154	0.000000
O	0.180560	1.344938	0.000000
H	-1.871903	0.346121	0.000000
H	0.959967	-1.537525	0.878023
H	0.959967	-1.537525	-0.878023
H	2.045240	-0.429621	0.000000

HNO_3 $^1A'$ B3LYP/6-31+G(d,p)

N	0.020566	0.124942	0.000000
O	1.221142	0.330842	0.000000
O	-0.369211	-1.231050	0.000000
O	-0.900193	0.898677	0.000000
H	0.480187	-1.711704	0.000000

HNO_3 $^1A'$ B3LYP/6-311+G(2d,2p)

N	0.000000	0.154468	0.000000
O	1.170859	0.461672	0.000000
O	-0.268539	-1.232059	0.000000
O	-0.979553	0.838717	0.000000
H	0.617862	-1.627926	0.000000

H_2SO_4 ^1A B3LYP/6-31+G(d,p)

S	0.000000	0.000000	0.166739
O	0.000000	1.281713	0.839566
O	-1.261372	-0.051653	-0.862279
O	0.000000	-1.281713	0.839566
O	1.261372	0.051653	-0.862279
H	-1.466765	0.854976	-1.152203
H	1.466765	-0.854976	-1.152203

H_2SO_4 ^{1}A B3LYP/6-311+G(2d,2p)

S	0.000000	0.000000	0.163255
O	0.598714	-1.114699	0.827048
O	1.076426	0.632890	-0.850721
O	-0.598715	1.114703	0.827040
O	-1.076424	-0.632894	-0.850720
H	1.691723	-0.065609	-1.116636
H	-1.691728	0.065600	-1.116629

HCOOH···OOH ^{2}A" B3LYP/6-31+G(d,p)

C	-1.563634	-0.138256	0.000000
O	-1.130140	1.104253	0.000000
O	-0.854094	-1.140087	0.000000
O	1.717795	-0.588106	0.000000
O	1.566460	0.730549	0.000000
H	0.770006	-0.954916	0.000000
H	-2.657338	-0.197618	0.000000
H	-0.127033	1.106770	0.000000

HCOOH···OOH ^{2}A" B3LYP/6-311+G(2d,2p)

C	-1.542070	-0.001909	0.000000
O	-0.994676	1.190950	0.000000
O	-0.937228	-1.060313	0.000000
O	1.676490	-0.734381	0.000000
O	1.653171	0.588219	0.000000
H	0.703742	-1.006330	0.000000
H	-2.633369	0.044539	0.000000
H	0.000000	1.097441	0.000000

CH_3COOH···OOH ^{2}A" B3LYP/6-31+G(d,p)

C	0.000000	1.032993	0.000000
O	-1.053556	0.389282	0.000000
O	1.195482	0.459407	0.000000

H	1.088295	-0.534735	0.000000
O	0.557439	-2.194478	0.000000
O	-0.770524	-2.198641	0.000000
H	-1.024818	-1.209733	0.000000
C	0.047161	2.533188	0.000000
H	0.593543	2.882823	0.881215
H	0.593543	2.882823	-0.881215
H	-0.964257	2.937179	0.000000

$CH_3COOH\cdots OOH$ $^2A''$ B3LYP/6-311+G(2d,2p)

C	0.000000	1.031703	0.000000
O	-1.053081	0.403518	0.000000
O	1.187892	0.449778	0.000000
H	1.070499	-0.538881	0.000000
O	0.549970	-2.198781	0.000000
O	-0.773443	-2.191816	0.000000
H	-1.018131	-1.207804	0.000000
C	0.062536	2.528522	0.000000
H	0.610747	2.870676	0.877422
H	0.610747	2.870676	-0.877422
H	-0.939771	2.942390	0.000000

$HNO_3\cdots OOH$ $^2A''$ B3LYP/6-31+G(d,p)

N	-1.179287	-0.078552	0.000000
O	-0.420064	-1.059801	0.000000
O	-0.601724	1.160494	0.000000
O	-2.380582	-0.097329	0.000000
H	0.394418	1.009177	0.000000
O	2.054875	0.687569	0.000000
O	2.269654	-0.621424	0.000000
H	1.355875	-1.020900	0.000000

$HNO_3\cdots OOH$ $^2A''$ B3LYP/6-311+G(2d,2p)

N	-1.092346	-0.495412	0.000000

O	-0.043850	-1.146602	0.000000
O	-0.982049	0.867139	0.000000
O	-2.204976	-0.927534	0.000000
H	0.000000	1.066799	0.000000
O	1.669688	1.359706	0.000000
O	2.317256	0.206954	0.000000
H	1.597875	-0.476230	0.000000

H_2SO_4···OOH ^{2}A B3LYP/6-31+G(d,p)

S	0.893400	-0.062234	-0.105872
O	-0.053211	-1.135128	-0.428403
O	0.124660	1.330145	-0.169165
O	2.151837	0.084582	-0.801348
O	1.176270	-0.258931	1.481648
H	-0.859834	1.172151	-0.023558
H	1.967483	0.251488	1.731006
O	-2.474324	0.685925	0.122291
O	-2.670079	-0.609421	-0.085638
H	-1.757720	-0.991499	-0.243532

H_2SO_4···OOH ^{2}A B3LYP/6-311+G(2d,2p)

S	0	0.890193	-0.074383	-0.122962
O	0	-0.043037	-1.160198	-0.339755
O	0	0.118107	1.288743	-0.239906
O	0	2.103924	0.036931	-0.864697
O	0	1.238015	-0.169768	1.440672
H	0	-0.858866	1.135190	-0.072440
H	0	2.048512	0.332621	1.609099
O	0	-2.470134	0.696812	0.110157
O	0	-2.657580	-0.604230	-0.031477
H	0	-1.747092	-0.984003	-0.169215