

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 $\cdot\text{OOH}$ and HCOOH systems.

Molecule	Mode		B3LYP/6-311++G(2d,2p)		MP2/6-311++G(2d,2p)		M052X/6-311++G(2d,2p)		v(exp)
			v(har)	v(anhar)	v(har)	v(anhar)	v(har)	v(anhar)	
$\cdot\text{OOH}$	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 $\text{HCOOH}\cdots\text{OOH}$ (C1) complex.

<i>Mode</i>		B3LYP/6-311++G(2d,2p)		MP2/6-311++G(2d,2p)		M052X/6-311++G(2d,2p)	
		<i>v(har)</i>	<i>v(anhar)</i>	<i>v(har)</i>	<i>v(anhar)</i>	<i>v(har)</i>	<i>v(anhar)</i>
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 $\text{HCOOH}\cdots\text{OOH}$ (C1) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

<i>Mode</i>		<i>I(har)</i>	<i>v(har)</i>	<i>v(anhar)</i>
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 $\text{CH}_3\text{COOH}\cdots\text{OOH}$ (C2) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

<i>Mode</i>		<i>I(har)</i>	<i>v(har)</i>	<i>v(anhar)</i>
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	A''	171.3 (199.5)	869.9 (867.8)	798.8 (815.9)
H(O)-O out wag	A'	29.0 (31.8)	636.7 (632.7)	621.7 (630.7)
O=C-O bend	A''	0.7 (0.6)	603.3 (596.5)	595.2 (588.8)
HOC=O torsion	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 $\text{HNO}_3\cdots\text{HOO}$ (C3) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

<i>Mode</i>		<i>I(har)</i>	<i>ν(har)</i>	<i>ν(anhar)</i>
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 $\text{H}_2\text{SO}_4\cdots\text{HOO}$ (C4) complex. The values in parentheses are at B3LYP/6-31+G(d,p) level.

<i>Mode</i>		<i>I(har)</i>	<i>v(har)</i>	<i>v(anhar)</i>
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 ²A" 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 ²A" 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 ¹A' 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 ¹A' 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

CH₃COOH ¹A' 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
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CH₃COOH 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

HNO₃ 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

HNO₃ 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

H₂SO₄ 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

H₂SO₄ ¹A 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 ²A'' 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 ²A'' 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

CH₃COOH...OOH ²A'' 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

CH₃COOH...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

HNO₃...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

HNO₃...OOH ²A'' B3LYP/6-311+G(2d,2p)

N	-1.092346	-0.495412	0.000000
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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

H₂SO₄...OOH ²A 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

H₂SO₄...OOH ²A 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