Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The benzoic acid–water complex: A potential atmospheric nucleation precursor studied using microwave spectroscopy and *ab initio* calculations

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Supplementary data

Measured rotational transition frequencies

Table S1 Measured rotational transition frequencies and quantum number assignments of benzoic acid.

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency/MHz	Residual[a]/MHz	J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency/MHz	Residual[a]/MHz
2	1	1	1	1	0	4614.5070	-0.0017	5	2	4	4	2	3	10747.6694	-0.0008
5	1	4	5	0	5	5590.6400	-0.0005	5	3	3	4	3	2	10867.9973	-0.0012
3	1	3	2	1	2	6023.4968[b]	-0.0002	5	2	3	4	2	2	11174.7247	0.0009
3	0	3	2	0	2	6387.4470[b]	0.0000	5	1	4	4	1	3	11421.8220	0.0005
4	0	4	3	1	3	6405.3717	0.0007	6	1	6	5	1	5	11918.4576	0.0000
3	2	2	2	2	1	6479.6393[b]	0.0005	6	0	6	5	0	5	12267.4293	0.0007
2	1	2	1	0	1	6669.9763[b]	0.0011	2	2	1	1	1	0	12549.3924	-0.0003
3	1	2	2	1	1	6906.5863[b]	0.0000	6	2	5	5	2	4	12854.9309	0.0000
6	1	5	6	0	6	6947.3359	0.0004	2	2	0	1	1	1	12867.4268	0.0001
6	2	4	6	1	5	6964.3665	-0.0001	6	3	4	5	3	3	13057.4422	0.0002
5	2	3	5	1	4	7043.4289[b]	0.0006	6	3	3	5	3	2	13120.2329	-0.0001
7	2	5	7	1	6	7122.8844	-0.0006	7	0	7	6	1	6	13270.1318	0.0005
4	2	2	4	1	3	7290.5265[b]	0.0008	6	2	4	5	2	3	13545.0629	0.0004
6	1	5	5	2	4	7347.7732	-0.0004	6	1	5	5	1	4	13624.1238	-0.0004
8	2	6	8	1	7	7573.4758	-0.0009	7	1	7	6	1	6	13846.7162	0.0003
3	2	1	3	1	2	7623.4145[b]	0.0005	7	0	7	6	0	6	14122.5701	-0.0004
2	2	0	2	1	1	7958.1695	-0.0002	3	2	2	2	1	1	14414.5225	-0.0002
4	1	4	3	1	3	8006.7165[b]	-0.0004	7	1	7	6	0	6	14699.1551	0.0000
7	1	6	7	1	7	8020.5498	0.0008	7	2	6	6	2	5	14939.9433	0.0003
9	2	7	9	1	8	8357.4062	0.0012	7	3	5	6	3	4	15247.5478	-0.0004
3	1	3	2	0	2	8396.9981[b]	0.0006	7	3	4	6	3	3	15385.0137	-0.0001
4	0	4	3	0	3	8414.9210[b]	-0.0004	3	2	1	2	1	2	15414.2455	0.0007
7	1	6	7	0	7	8597.1333	-0.0004	8	1	8	7	1	7	15758.7571	0.0000
4	3	2	3	3	1	8682.8182[b]	0.0006	7	1	6	6	1	5	15772.3680	-0.0006
4	3	1	3	3	0	8689.7133[b]	-0.0006	7	2	5	6	2	4	15930.8871	0.0001
5	0	5	4	1	4	8770.6082	0.0000	8	0	8	7	0	7	15960.1065	0.0002
2	2	1	2	1	2	8819.1273	-0.0013	4	2	3	3	1	2	16129.3123	0.0000
4	1	3	3	1	2	9178.8098[b]	-0.0001	8	2	7	7	2	6	17000.1038	-0.0009
10	2	8	10	1	9	9499.8732	-0.0005	9	1	9	8	1	8	17657.3054	0.0003
4	2	3	4	1	4	9889.9290	-0.0003	8	3	5	7	3	4	17696.6274	0.0003
5	1	5	4	1	4	9972.0190	0.0000	5	2	4	4	1	3	17698.1728	0.0001
4	1	4	3	0	3	10016.2667	-0.0007	9	0	9	8	0	8	17795.5940	-0.0002
5	0	5	4	0	4	10371.9550	0.0007	8	1	7	7	1	6	17853.1554	0.0002

[a] (Measured transition frequency) – (Fit transition frequency). [b] Also measured by Onda *et al.* (1999).

Table S2 Measured transition frequencies and quantum number assignments of benzoic acid-H_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency/MHz	Residual[a]/MHz
4	1	4	3	1	3	4651.5951	0.0013
4	0	4	3	0	3	4823.2474	-0.0007
4	1	3	3	1	2	5027.6071	-0.0010
5	1	5	4	1	4	5810.8267	-0.0013
5	0	5	4	0	4	6013.8889	0.0007
5	1	4	4	1	3	6280.4666	-0.0007
6	1	6	5	1	5	6967.7672	-0.0011
6	0	6	5	0	5	7194.7980	0.0007
6	2	5	5	2	4	7256.3164	-0.0001
6	2	4	5	2	3	7327.0540	-0.0009
6	1	5	5	1	4	7530.4747	0.0003
4	1	4	3	0	3	7611.1471	-0.0008
7	1	7	6	1	6	8122.1002	0.0000
7	0	7	6	0	6	8364.6482	-0.0003
7	2	6	6	2	5	8460.5179	-0.0003
7	3	5	6	3	4	8491.7904	0.0012
7	3	4	6	3	3	8495.3000	-0.0003
7	2	5	6	2	4	8572.2956	0.0009
7	1	6	6	1	5	8776.9013	0.0005
8	1	8	7	1	7	9273.5807	-0.0001
8	0	8	7	0	7	9522.6825	-0.0004
8	2	7	7	2	6	9662.3389	-0.0002
8	3	6	7	3	5	9708.5702	-0.0007
8	3	5	7	3	4	9715.5724	0.0001
8	2	6	7	2	5	9826.9275	0.0006
8	1	7	7	1	6	10018.9317	0.0000
9	1	9	8	1	8	10422.0446	0.0001
7	1	7	6	0	6	10479.9117	0.0009
9	0	9	8	0	8	10668.8746	0.0002
9	2	8	8	2	7	10861.4534	-0.0001
9	2	7	8	2	6	11090.6124	0.0009
9	1	8	8	1	7	11255.6561	0.0013
10	1	10	9	1	9	11567.4056	0.0009
10	0	10	9	0	9	11803.9992	0.0000
10	2	9	9	2	8	12057.5450	-0.0012
10	2	8	9	2	7	12362.1918	0.0005
10	1	9	9	1	8	12486.0540	-0.0009
11	1	11	10	1	10	12709.6535	0.0006
11	0	11	10	0	10	12929.5543	-0.0013
11	2	10	10	2	9	13250.3179	0.0004
11	2	9	10	2	8	13639.7632	-0.0018
11	1	10	10	1	9	13709.0189	0.0014

[a] (Measured transition frequency) – (Fit transition frequency).

Table S3 Measured transition frequencies and quantum number assignments of benzoic acid-D_2O.

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency/MHz	Residual[a]/MHz
6	1	6	5	1	5	6689.4949	0.0092
6	0	6	5	0	5	6902.2381	0.0131
6	1	5	5	1	4	7207.1625	0.0104
7	1	7	6	1	6	7798.4638	0.0024
7	0	7	6	0	6	8027.6124	0.0101
7	2	6	6	2	5	8109.0922	0.0000
7	1	6	6	1	5	8401.0980	0.0069
8	0	8	7	0	7	9142.6926	0.0053
8	1	7	7	1	6	9591.3666	-0.0029
9	1	9	8	1	8	10008.8668	-0.0155
9	0	9	8	0	8	10247.2503	-0.0062
9	1	8	8	1	7	10777.2247	-0.0172

[a] (Measured transition frequency) – (Fit transition frequency).

Table S4 Cartesian coordinates of the benzoic acid-water dimer in its principal axis system, optimized using the B3LYP, M06-2X, and MP2 methods and the 6-311++G(2df,2pd)

	B3LYP			M06-2X			MP2		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
C	1.1577	-1.2134	-0.0010	1.1543	-1.2119	0.0014	1.1489	-1.2159	-0.0015
C	0.4354	-0.0186	-0.0030	0.4372	-0.0198	-0.0012	0.4298	-0.0198	-0.0048
C	1.1134	1.2022	-0.0010	1.1046	1.2007	-0.0025	1.1000	1.2049	-0.0012
C	2.5014	1.2236	0.0024	2.4907	1.2252	-0.0020	2.4906	1.2269	0.0051
C	3.2173	0.0308	0.0040	3.2063	0.0353	0.0005	3.2111	0.0343	0.0078
C	2.5442	-1.1876	0.0025	2.5389	-1.1832	0.0025	2.5381	-1.1864	0.0048
C	-1.0482	-0.0879	-0.0068	-1.0484	-0.0919	-0.0028	-1.0509	-0.0928	-0.0118
O	-1.6693	-1.1378	-0.0071	-1.6591	-1.1392	-0.0064	-1.6685	-1.1474	-0.0121
O	-1.6459	1.1067	-0.0107	-1.6409	1.0963	-0.0009	-1.6397	1.1048	-0.0180
H	-2.6219	0.9664	-0.0115	-2.6138	0.9604	-0.0013	-2.6131	0.9534	-0.0196
H	0.6170	-2.1487	-0.0014	0.6099	-2.1457	0.0033	0.6057	-2.1501	-0.0031
H	3.1011	-2.1146	0.0043	3.0989	-2.1078	0.0051	3.0965	-2.1120	0.0076
H	4.2990	0.0504	0.0069	4.2876	0.0572	0.0014	4.2922	0.0560	0.0129
H	3.0249	2.1698	0.0043	3.0133	2.1714	-0.0031	3.0125	2.1736	0.0081
H	0.5511	2.1238	-0.0014	0.5354	2.1187	-0.0035	0.5327	2.1235	-0.0026
O	-4.1661	0.0508	0.0610	-4.1487	0.0575	0.0514	-4.1322	0.0607	0.0703
H	-3.5765	-0.7237	0.0121	-3.5995	-0.7400	-0.0006	-3.5535	-0.7177	0.0071
H	-4.7914	-0.0293	-0.6640	-4.7979	-0.0032	-0.6512	-4.7796	-0.0335	-0.6310

Table S5 Equilibrium constant of benzoic acid-water dimer, partial pressure of water, ambient pressure, and percent of benzoic acid hydrated, at different altitudes under subarctic summer, mid-latitude summer, and tropical conditions

Altitude	Subarctic summer				Mid-latitude summer				Tropical			
/ km	K_p [a]	p_{H_2O} [b] / bar	$p^{\ominus}$ [c] / bar	χ [d] / %	K_p	p_{H_2O} / bar	$p^{\ominus}$ / bar	χ / %	K_p	p_{H_2O} / bar	$p^{\ominus}$ / bar	χ / %
0	1.43E+00	1.20E-02	1.01E+00	1.70E+00	1.04E+00	1.85E-02	1.01E+00	1.91E+00	8.06E-01	2.52E-02	1.01E+00	2.00E+00
1	1.83E+00	7.94E-03	8.96E-01	1.63E+00	1.25E+00	1.23E-02	9.02E-01	1.70E+00	1.04E+00	1.72E-02	9.04E-01	1.98E+00
2	2.38E+00	5.56E-03	7.93E-01	1.67E+00	1.57E+00	7.75E-03	8.02E-01	1.51E+00	1.34E+00	1.23E-02	8.05E-01	2.05E+00
3	3.11E+00	3.56E-03	7.00E-01	1.58E+00	2.09E+00	4.54E-03	7.10E-01	1.34E+00	1.67E+00	6.22E-03	7.15E-01	1.46E+00
4	4.15E+00	2.18E-03	6.16E-01	1.47E+00	2.82E+00	2.50E-03	6.28E-01	1.12E+00	2.26E+00	3.52E-03	6.33E-01	1.26E+00
5	5.76E+00	1.29E-03	5.41E-01	1.37E+00	3.85E+00	1.32E-03	5.54E-01	9.19E-01	3.18E+00	2.03E-03	5.59E-01	1.15E+00
6	8.67E+00	7.19E-04	4.73E-01	1.32E+00	5.38E+00	8.06E-04	4.87E-01	8.91E-01	4.55E+00	1.14E-03	4.92E-01	1.05E+00
7	1.34E+01	3.84E-04	4.13E-01	1.24E+00	7.74E+00	4.91E-04	4.26E-01	8.93E-01	6.65E+00	6.24E-04	4.32E-01	9.59E-01
8	2.12E+01	1.72E-04	3.59E-01	1.02E+00	1.15E+01	2.78E-04	3.72E-01	8.60E-01	9.91E+00	3.31E-04	3.78E-01	8.68E-01
9	3.46E+01	5.53E-05	3.11E-01	6.17E-01	1.75E+01	1.56E-04	3.24E-01	8.43E-01	1.52E+01	1.60E-04	3.29E-01	7.41E-01
10	5.48E+01	2.32E-05	2.68E-01	4.75E-01	2.72E+01	8.51E-05	2.81E-01	8.24E-01	2.37E+01	6.49E-05	2.86E-01	5.37E-01
11	5.74E+01	1.13E-05	2.30E-01	2.83E-01	4.31E+01	2.90E-05	2.43E-01	5.14E-01	3.83E+01	2.37E-05	2.47E-01	3.68E-01
12	5.74E+01	5.56E-06	1.98E-01	1.62E-01	7.08E+01	8.55E-06	2.09E-01	2.90E-01	6.30E+01	8.05E-06	2.13E-01	2.38E-01
13	5.74E+01	2.73E-06	1.70E-01	9.21E-02	1.09E+02	2.20E-06	1.79E-01	1.34E-01	1.09E+02	2.37E-06	1.82E-01	1.41E-01
14	5.74E+01	1.35E-06	1.46E-01	5.31E-02	1.20E+02	1.32E-06	1.53E-01	1.03E-01	1.91E+02	1.31E-06	1.56E-01	1.60E-01
15	5.74E+01	1.03E-06	1.25E-01	4.73E-02	1.20E+02	1.11E-06	1.30E-01	1.03E-01	3.55E+02	1.00E-06	1.32E-01	2.69E-01
16	5.74E+01	8.86E-07	1.08E-01	4.71E-02	1.20E+02	9.40E-07	1.10E-01	1.03E-01	6.89E+02	8.43E-07	1.11E-01	5.23E-01
17	5.74E+01	7.61E-07	9.28E-02	4.71E-02	1.20E+02	8.13E-07	9.50E-02	1.03E-01	7.78E+02	7.18E-07	9.37E-02	5.96E-01
18	5.74E+01	6.54E-07	7.98E-02	4.71E-02	1.18E+02	6.94E-07	8.12E-02	1.01E-01	5.26E+02	5.93E-07	7.89E-02	3.96E-01
19	5.74E+01	5.63E-07	6.86E-02	4.71E-02	1.09E+02	5.91E-07	6.95E-02	9.23E-02	3.55E+02	4.90E-07	6.66E-02	2.61E-01
20	5.74E+01	4.83E-07	5.89E-02	4.71E-02	9.84E+01	5.03E-07	5.95E-02	8.32E-02	2.45E+02	4.08E-07	5.65E-02	1.77E-01

[a] Equilibrium constant of benzoic acid-water dimer. [b] Partial pressure of water. [c] Ambient pressure. [d] Percent of benzoic acid hydrated.