Electronic supplementary information for
Fractional molecular charge studied via molecular vibrational properties. Specific aspects in Jahn-Teller active molecular species

Ioan Bâldea * [a‡]

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Notes and references

1 M. Döscher, H. Köppel and P. G. Szalay, *J. Chem. Phys.*, 2002, **117**, 2645–2656.

[a] *Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany.*
‡ E-mail: ioan.baldea@pci.uni-heidelberg.de. Also at National Institute for Lasers, Plasmas, and Radiation Physics, Institute of Space Sciences, RO 077125, Bucharest-Măgurele, Romania

Table S1 Vibrational frequencies of the neutral (Bz^0) species.

No.	CCSD cc-pvtz	CCSD 6-311g(d,p)	PBE cc-pvtz	PBE TZVP	PBE 6-311g(d,p)	B3LYP cc-pvtz	B3LYP TZVP	B3LYP 6-311g(d,p)	MP2[1] DZ+P	MP2 cc-pvtz	SIESTA PBE TZP
1 (16b, 20, E_{2u})	412.1857	395.6880	395.5198	389.1520	395.3383	413.9434	408.6631	412.4557	396.018	405.5527	386.97
2 (16a, 20, E_{2u})	412.1855	395.6882	395.5198	389.1520	395.3383	413.9434	408.6631	412.4557	396.018	405.5531	386.98
3 (4, 8, B_{2g})	699.4880	507.9773	705.1625	670.4445	701.9542	726.5969	696.1751	722.9685	637.9842	687.8981	681.62
4 (6a, 18, E_{2g})	617.7783	615.9552	600.4418	603.3073	601.1282	624.1762	625.9846	623.3137	610.5614	607.2618	581.70
5 (6b, 18, E_{2g})	617.8070	615.9719	600.4418	603.3073	601.1282	624.1762	625.9846	623.3137	610.5614	607.2614	583.17
6 (11, 4, A_{2u})	701.0032	685.5588	661.5993	658.8126	661.0742	689.5617	686.4564	687.1813		690.6512	648.82
7 (10b, 11, E_{1g})	877.6747	854.4539	833.0414	825.8086	829.0142	866.4923	860.3810	861.2322	825.9113	863.2169	810.48
8 (10a, 11, E_{1g})	877.6746	854.4541	833.0414	825.8086	829.0142	866.4923	860.3810	861.2322	825.9113	863.2172	810.74
9 (5, 7, B_{2g})	999.9178	918.7245	978.5521	956.2770	974.3743	1021.0407	1001.3669	1015.4998	900.1143	977.4570	952.23
10 (17b, 19, E_{2u})	989.8913	936.9685	944.3005	912.0457	938.7719	987.7429	964.7420	980.4033	879.9504	963.8101	924.05
11 (17a, 19, E_{2u})	989.8915	936.9688	944.3005	912.0457	938.7719	987.7429	964.7420	980.4033	879.9504	963.8099	924.21
12 (12, 6, B_{1u})	1025.4467	1009.9714	995.0622	993.7757	988.4817	1030.6751	1029.8557	1023.4488	1013.032	1013.8275	961.04
13 (1, 2, A_{1g})	1024.7180	1018.3798	996.2977	995.6419	994.1938	1015.3088	1014.6867	1013.0754	1013.838	1018.1347	997.70
14 (18b, 13, E_{1u})	1071.8549	1066.5850	1036.2025	1036.5046	1035.4488	1062.2363	1061.9368	1060.3854	1065.458	1062.0638	1019.04
15 (18a, 13, E_{1u})	1071.8766	1066.5901	1036.2025	1036.5046	1035.4488	1062.2363	1061.9368	1060.3854	1065.458	1062.0657	1023.10
16 (15, 9, B_{2u})	1164.2851	1162.8990	1140.2867	1147.3001	1140.9701	1176.7027	1181.5266	1174.6971	1181.602	1169.7946	1100.03
17 (9b, 17, E_{2g})	1207.3550	1203.4528	1163.4302	1167.4629	1162.7098	1200.5918	1202.8812	1197.6063	1207.411	1196.7401	1128.05
18 (9a, 17, E_{2g})	1207.3578	1203.4603	1163.4302	1167.4629	1162.7098	1200.5918	1202.8812	1197.6063	1207.411	1196.7407	1128.61
19 (14, 10, B_{2u})	1309.4178	1297.8993	1343.3267	1342.8917	1345.6636	1334.9374	1334.1393	1334.7604	1468.735	1370.8513	1393.89
20 (3, 3, A_{2g})	1391.4505	1380.8671	1334.9147	1335.4185	1329.5745	1390.1526	1389.3416	1381.9552		1458.6168	1286.39
21 (19a, 12, E_{1u})	1532.4984	1525.2721	1468.7102	1468.6397	1465.0587	1518.9023	1517.8007	1513.0533	1514.708	1507.5504	1450.11
22 (19b, 12, E_{1u})	1532.5897	1525.3053	1468.7102	1468.6397	1465.0587	1518.9023	1517.8007	1513.0533	1514.708	1507.5514	1451.04
23 (8a, 16, E_{2g})	1672.3341	1665.1035	1593.8774	1592.6436	1595.2508	1637.4546	1635.6441	1637.2568	1657.468	1640.6142	1617.22
24 (8b, 16, E_{2g})	1672.3459	1665.1263	1593.8774	1592.6436	1595.2508	1637.4546	1635.6441	1637.2568	1657.468	1640.6147	1617.43
25 (13, 5, B_{1u})	3194.4378	3186.8707	3089.6220	3095.8371	3092.4024	3157.8203	3163.6118	3155.5022	3254.445	3201.3334	3077.44
26 (7a, 15, E_{2g})	3205.8234	3197.2667	3099.5183	3105.2204	3102.1411	3167.6010	3172.7767	3165.1310	3264.931	3212.9068	3083.54
27 (7b, 15, E_{2g})	3205.8295	3197.2937	3099.5183	3105.2204	3102.1411	3167.6010	3172.7767	3165.1310	3264.931	3212.9071	3085.46
28 (20a, 14, E_{1u})	3223.5112	3214.1043	3115.0775	3120.1477	3117.7087	3183.3070	3187.7441	3180.9207	3281.062	3229.5061	3094.01
29 (20b, 14, E_{1u})	3223.5172	3214.1117	3115.0775	3120.1477	3117.7087	3183.3070	3187.7441	3180.9207	3281.062	3229.5063	3094.94
30 (2, 1, A_{1g})	3234.4978	3224.8488	3125.0728	3130.1556	3128.0661	3193.3965	3197.8163	3191.5305	3291.547	3239.3788	3101.52

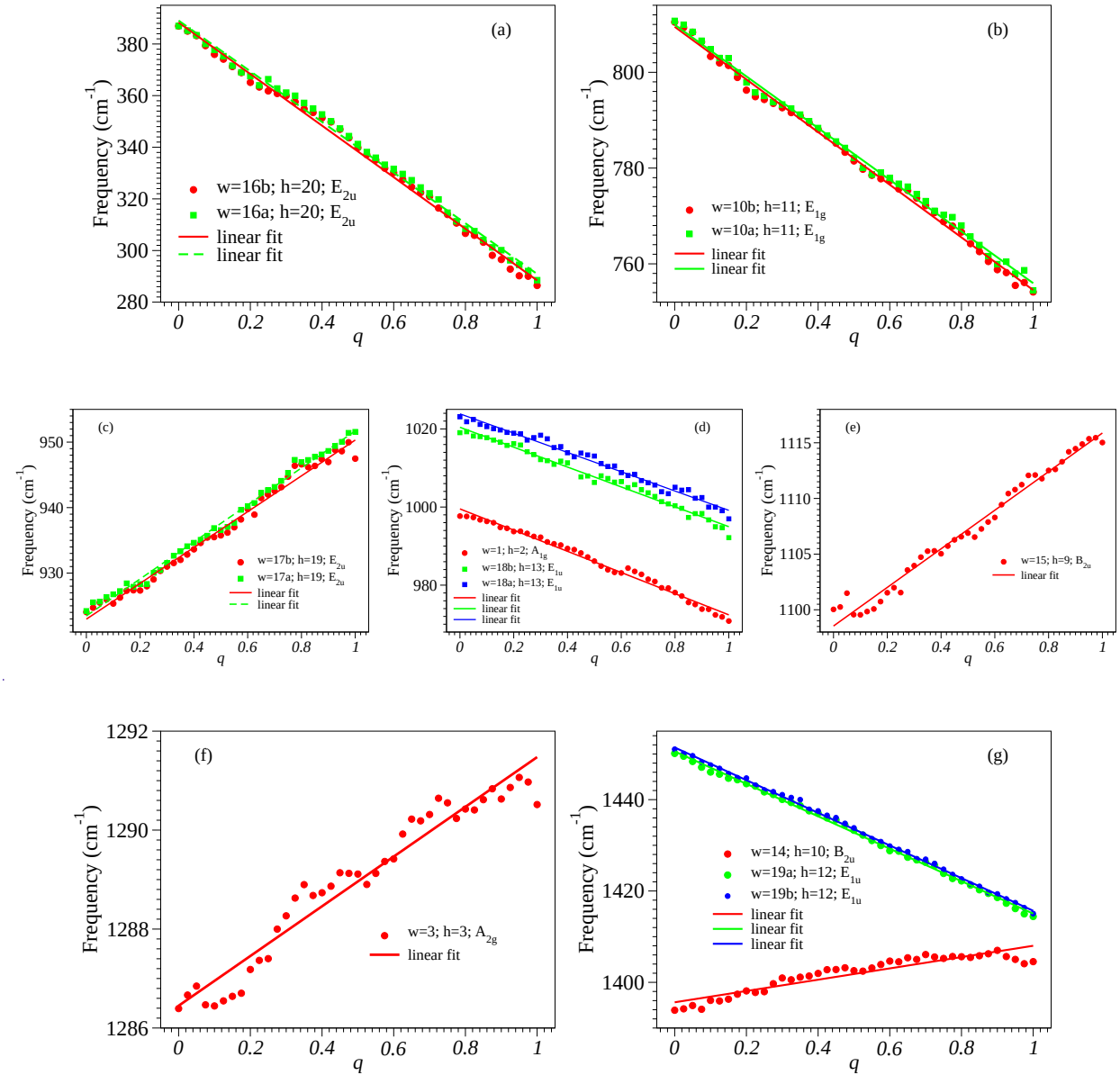

Fig. S1 Typically, the frequencies of non-JT active modes (Wilson (labelled $w = \ldots$) and Herzberg (labelled $h = \ldots$) labels are indicated in the legend) linearly depend on the charge deficit q. This supports the picture that charge removal acts on the vibrational frequencies as a first order perturbation.

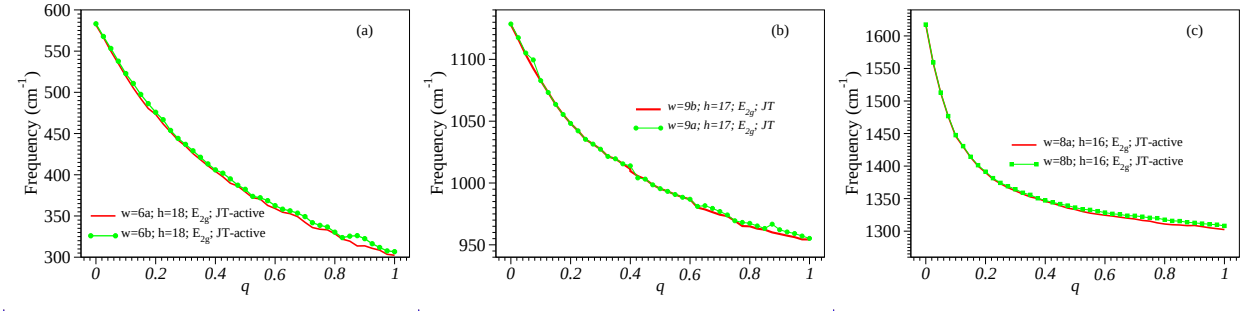

Fig. S2 The frequencies of the JT-active modes of benzene (Wilson ($w = \ldots$) and Herzberg ($h = \ldots$) labels are indicated in the legend) exhibit a strong nonlinear dependence on the electron removal q. This agrees with the idea that the JT interaction does not merely represent a first order perturbation.

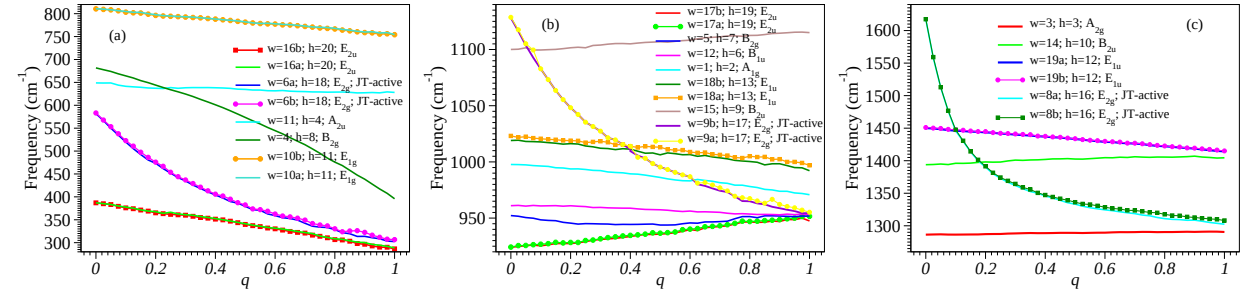

Fig. S3 In addition to the Wilson labelling ($w = ...$) of Fig. 4 in the main text, this figure indicates the Herzberg labelling ($h = \ldots$), the symmetry, and (where applicable) the JT-activity of the various modes.

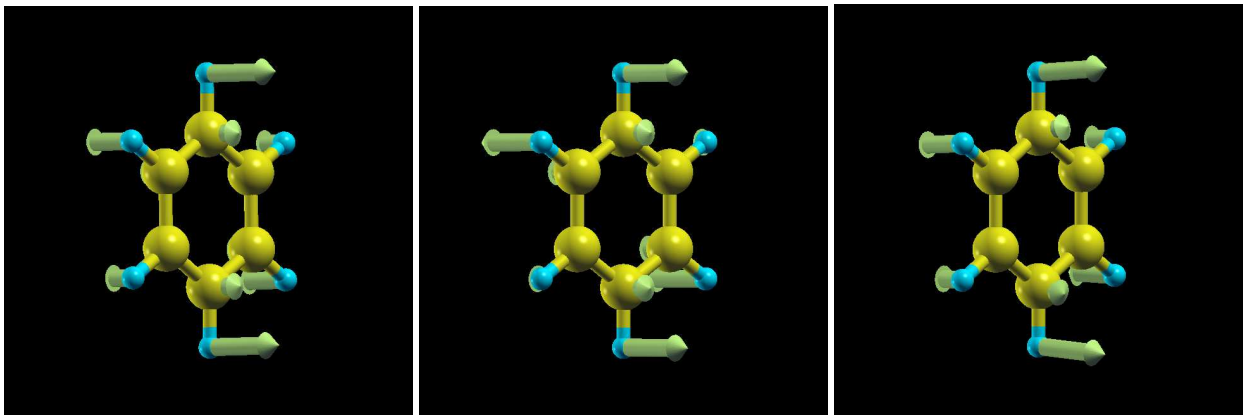

Fig. S4 Wilson mode 16*b* depicted for (from left to right) $q = 0; 0.5; 1.0$.

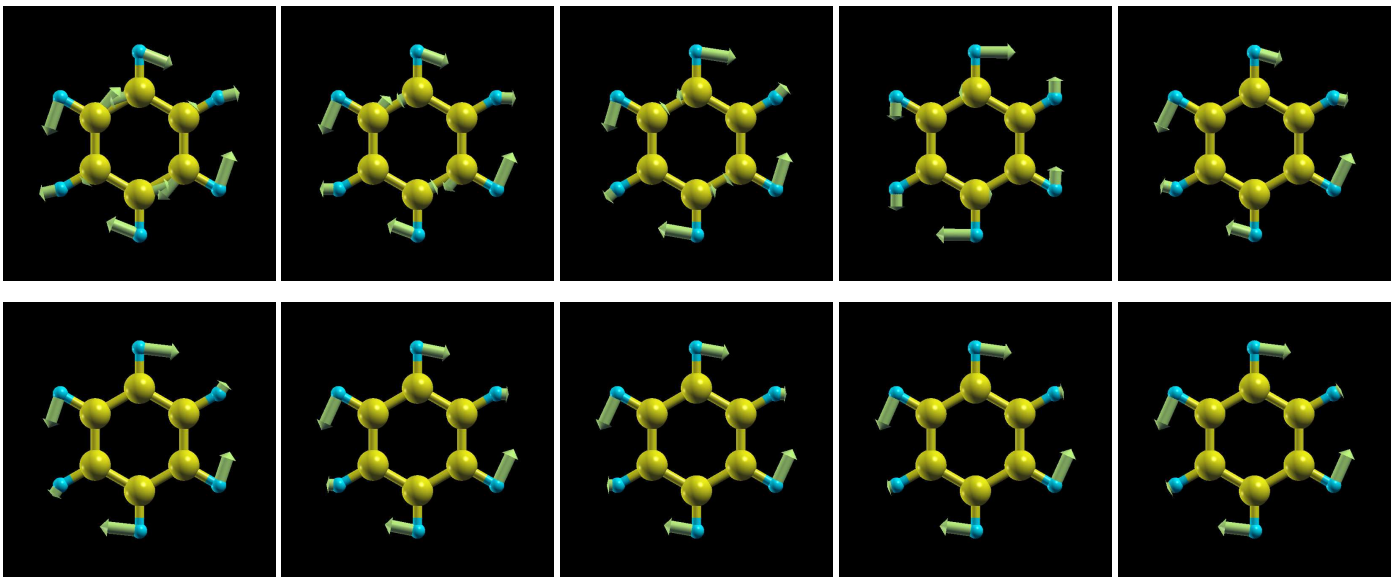

Fig. S5 Wilson mode 8*a*, Herzberg mode 16 depicted for (upper row from left to right) $q = 0; 0.05; 0.1; 0.15; 0.2$ and (lower row from left to right) $q = 0.25; 0.4; 0.6; 0.8; 1.0$.

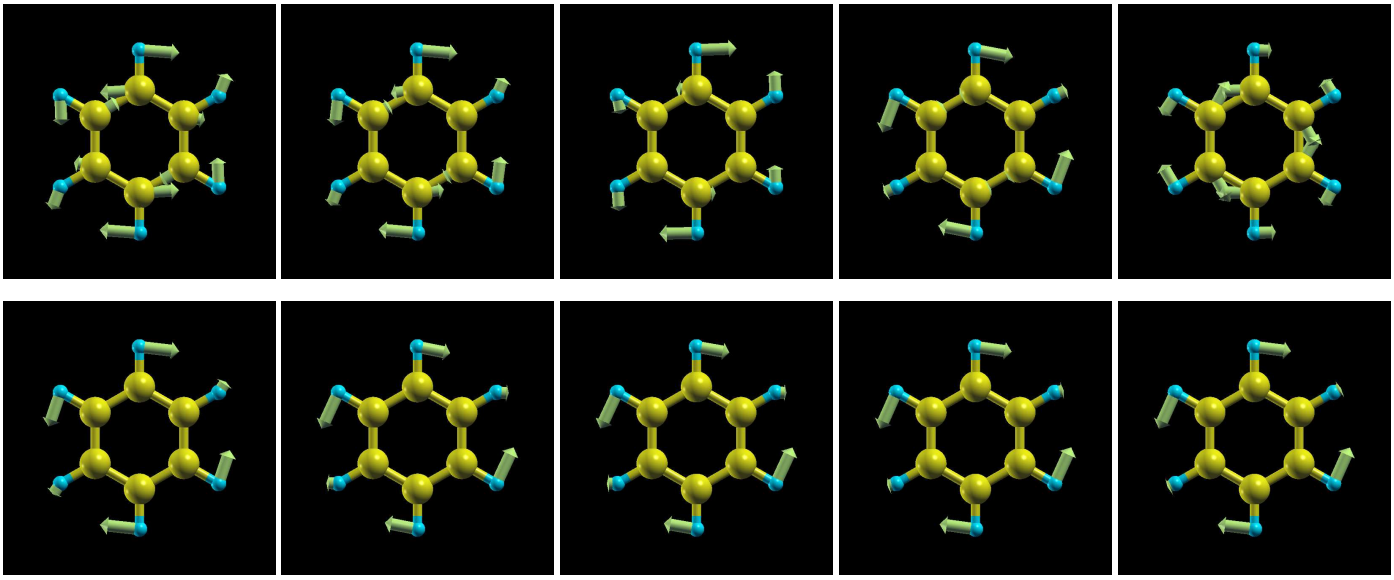

Fig. S6 Wilson mode 8*b*, Herzberg mode 16 depicted for (upper row from left to right) $q = 0; 0.05; 0.1; 0.15; 0.2$ and (lower row from left to right) $q = 0.25; 0.4; 0.6; 0.8; 1.0$.

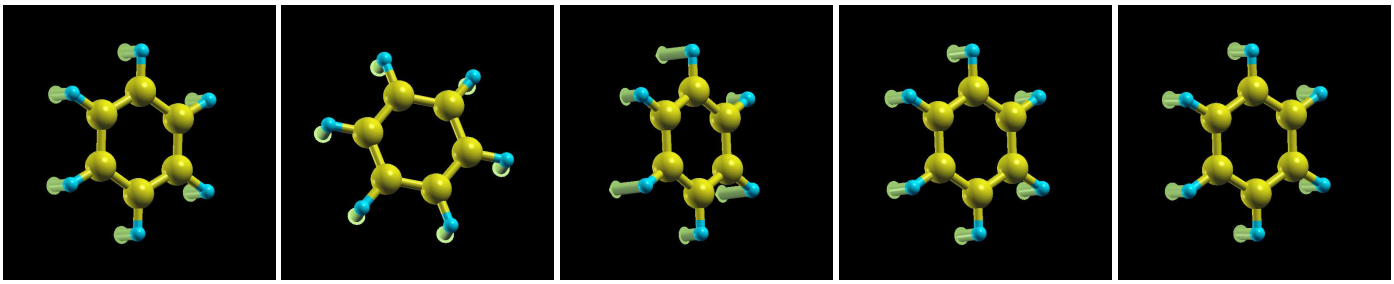

Fig. S7 Wilson mode 11 (Herzberg mode 4), an out-of-plane CH bending, depicted for (from left to right) $q = 0; 0.2; 0.25; 0.3; 1.0$.

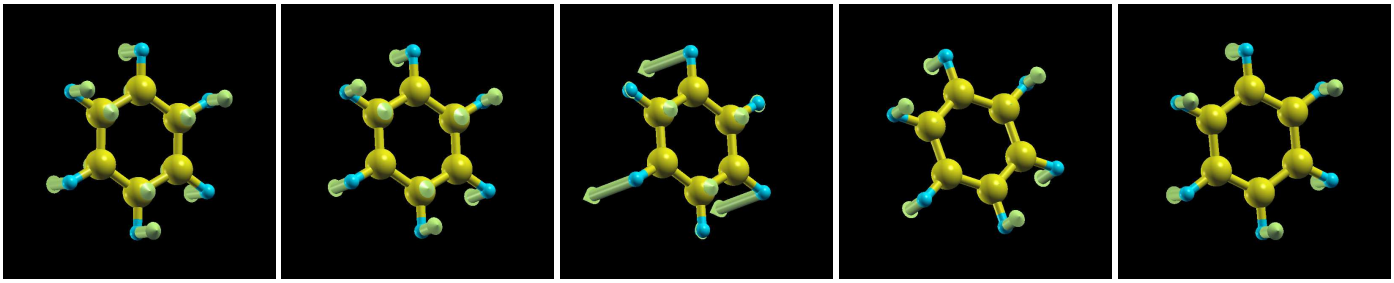

Fig. S8 Wilson mode 4 (Herzberg mode 8), an out-of-plane ring deformation, depicted for (from left to right) $q = 0; 0.2; 0.25; 0.3; 1.0$.