Dipole-bound states in the meta form of the green fluorescent protein chromophore observed by cryogenic action spectroscopy: Supplementary information

Anne P. Rasmussen, Nikolaj Klinkby, and Lars H. Andersen

Department of Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

In this supplementary information, you will find additional data and information about the results presented in the paper.

1 Detachment Energy

The detachment threshold was found by fitting 41 Gaussian functions corresponding to the number of peaks found in this part of the spectrum and adding a linear function to simulate the opening of the detachment channel. Figure S1 shows the final fit as a blue colored area underneath the experimental spectrum. The linear part simulating the non-detachment part is shown in red. The crossing point with the x-axis gives the vertical detachment energy 16400 cm^{-1}.

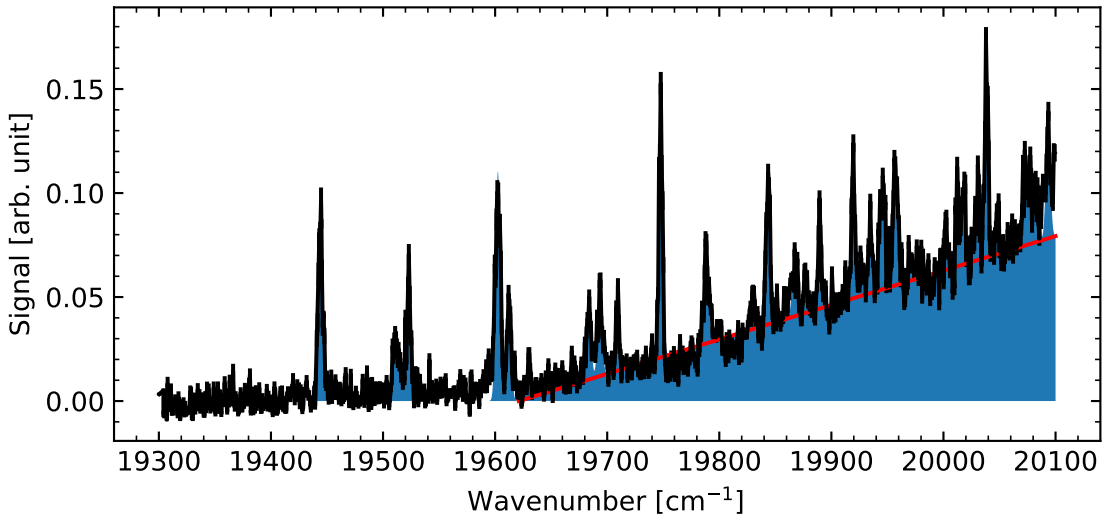

Figure S1: The measured action spectrum of mHBDI is shown in black. The blue area shows the fit to get the detachment energy, where the red line is the linear part of the fit.

2 Isomers

Figure S2 shows the structure of the four stable isomers of mHBDI.

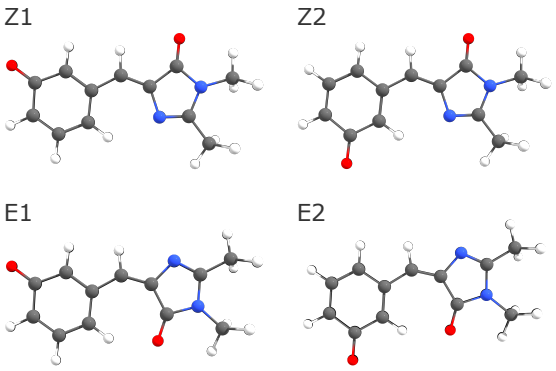

Figure S2: Molecular structure of the four stable isomers of mHBDI

3 Vibronic Spectra

Figure S4 shows the vibronic spectra of all four isomers of mHBDI calculated using the Gaussian16 program package [1] at the ωB97X-D/aug-cc-pVTZ [2, 3] level of theory as presented in the paper. Each spectrum is shifted such that the 0→0 transition matches the lowest measured peak and the frequencies are scaled by 0.9566. [4] A linear background starting from the DE is given to the calculated spectrum to account for the direct attachment signal.

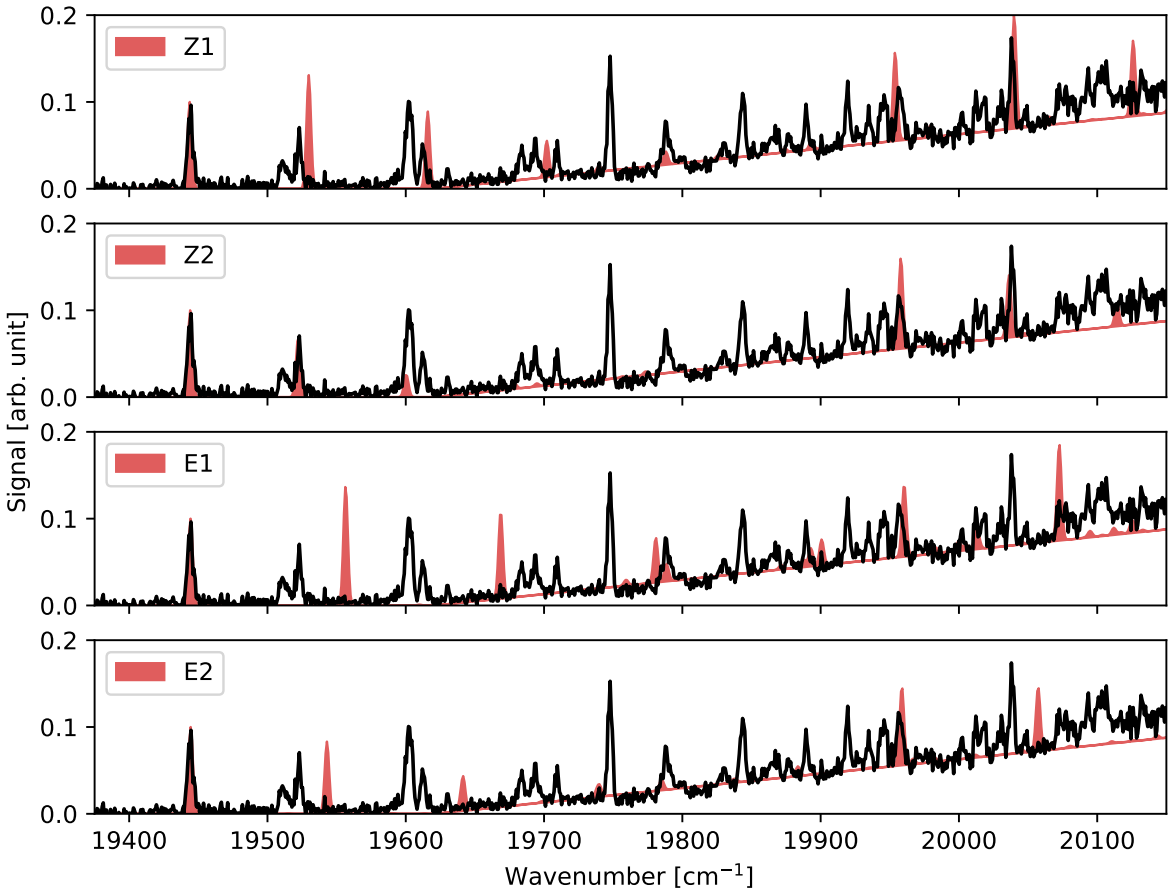

Figure S3: Vibronic spectra of all fours isomers of mHBDI overlaid on the the experimental spectrum.

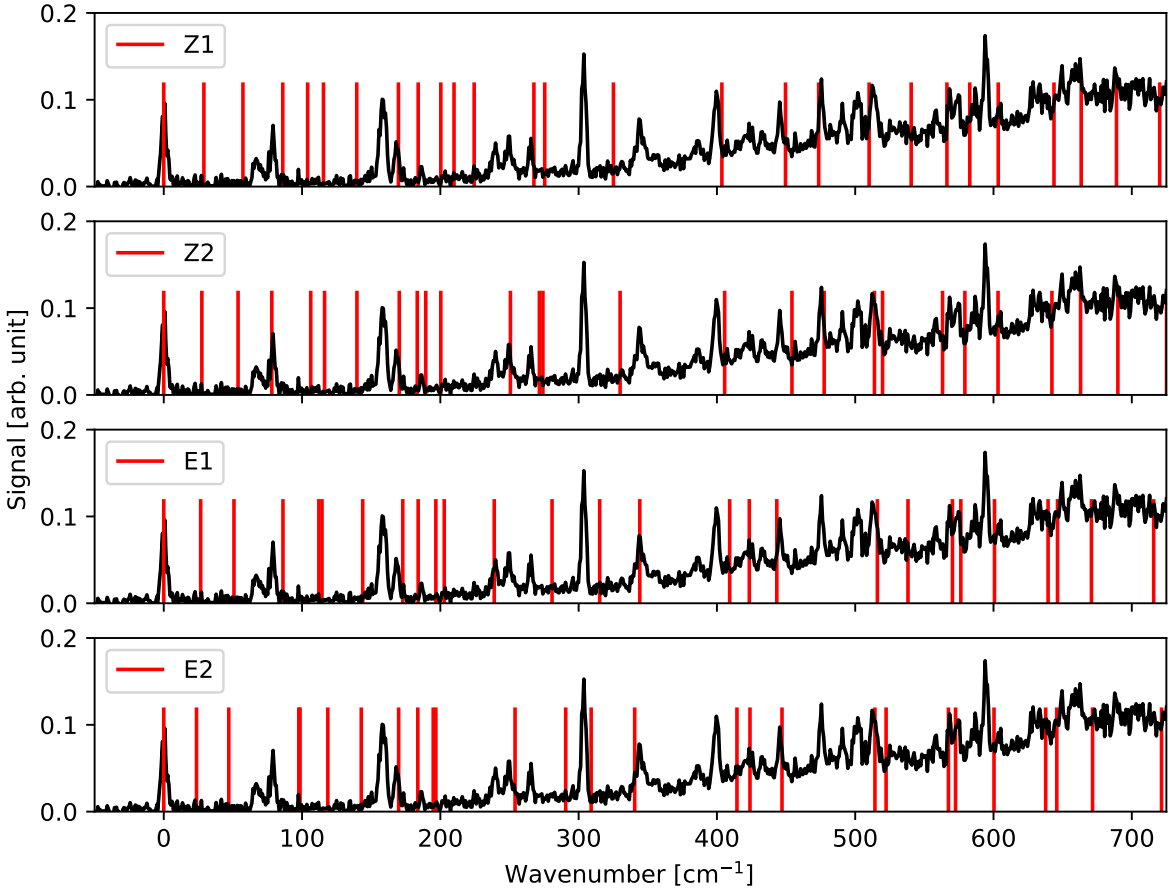

Figure S4: The vibrational frequencies scaled by 0.9566 plotted as equal height sticks alongside the experimental spectrum.

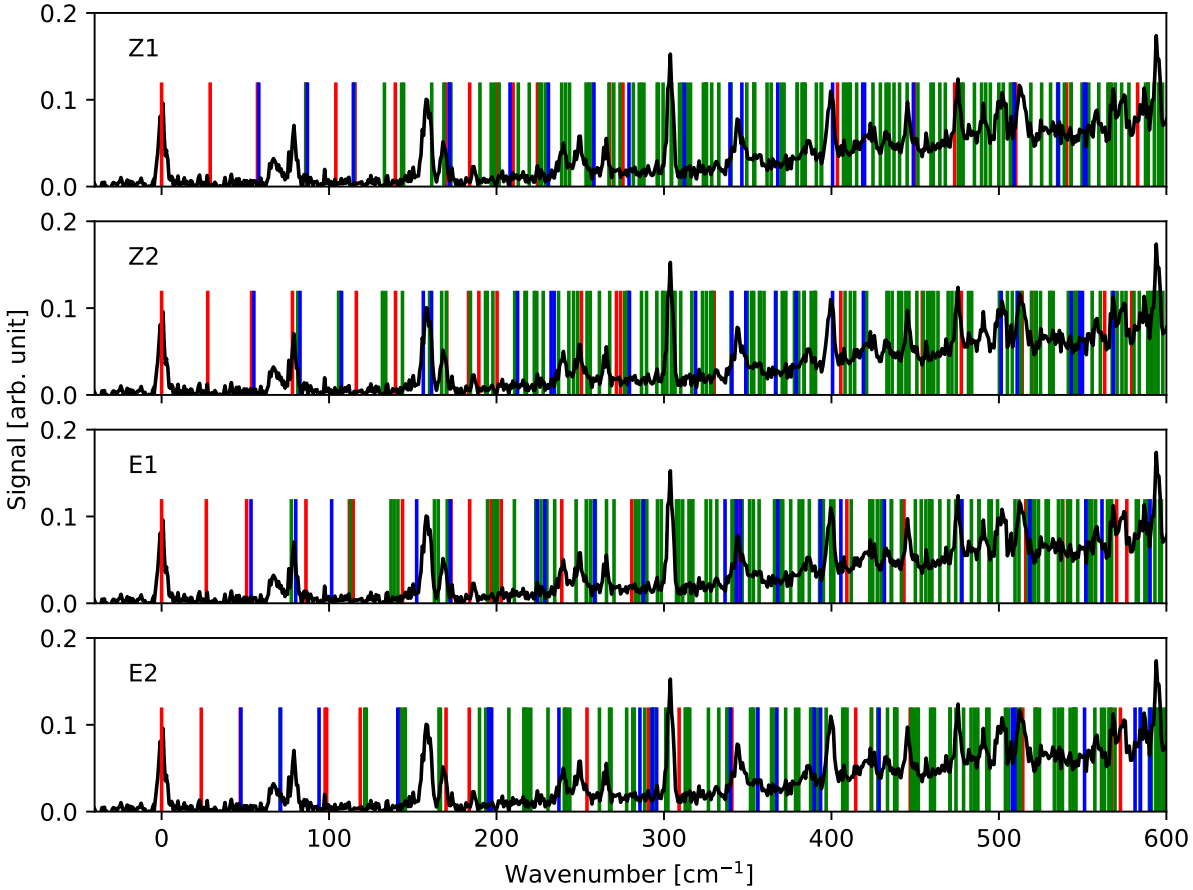

Figure S5: The vibrational harmonic frequencies ν_i (red), higher harmonics $\nu_i \times n$ (n=2 and 3) (blue) and combination bands $\nu_i + \nu_j$ (green) scaled by 0.9566 plotted as equal height sticks alongside the experimental spectrum.

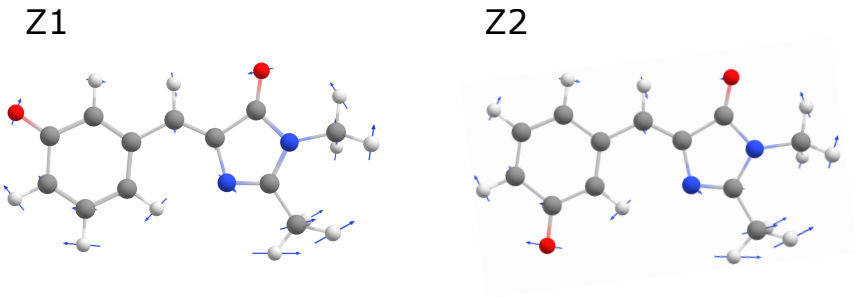

Figure S6: Visualization of the active mode (normal mode: 3).

4 Optimized Geometries

Here we provide the coordinates for the optimized geometries in Angstroms, calculated with the Gaussian16 [1] program package at the ωB97X-D/aug-cc-pVTZ [2, 3] level of theory as presented in the paper.

4.1 Z1 Anion

Atomic number	x	y	z
6	-2.731192	-0.951732	-0.000005
6	-1.605397	-0.125289	-0.000046
6	-1.748550	1.273663	-0.000193
6	-3.037419	1.787148	-0.000293
6	-4.158157	0.975884	-0.000254
6	-4.078962	-0.457979	-0.000104
1	-2.603833	-2.029087	0.000108
1	-0.881043	1.913299	-0.000225
1	-3.172016	2.864610	-0.000408
6	-0.321414	-0.785641	0.000068
1	-0.361400	-1.871288	0.000177
6	0.942011	-0.303732	0.000067
7	3.184581	-0.288625	0.000152
7	1.377238	1.033657	-0.000052
6	2.659585	0.993705	0.000000
6	3.550618	2.183679	-0.000089
1	4.196188	2.191598	0.880719
1	4.196232	2.191433	-0.880865
6	4.565511	-0.679618	0.000232
1	4.587356	-1.768123	0.000402
1	5.085761	-0.314854	0.888066
6	2.117473	-1.189343	0.000200
8	2.240728	-2.400611	0.000326
1	2.935625	3.078910	-0.000188
1	5.085790	-0.315133	-0.887701
1	-5.150259	1.413618	-0.000336
8	-5.087700	-1.211224	-0.000069

4.2 Z1 Neutral

Atomic number	x	y	z
6	-2.730277	-1.000371	-0.000028
6	-1.593765	-0.222421	-0.000049
6	-1.734796	1.185861	-0.000188
6	-2.998825	1.782517	-0.000302
6	-4.136662	1.022456	-0.000283
6	-4.053432	-0.420799	-0.000144
1	-2.671816	-2.081008	0.000077
1	-0.843855	1.795552	-0.000204
1	-3.067776	2.861881	-0.000407
6	-0.296704	-0.886760	0.000073
1	-0.318202	-1.971007	0.000176
6	0.930716	-0.351310	0.000078
7	3.179106	-0.251837	0.000165
7	1.309178	0.996265	-0.000032
6	2.598789	1.002009	0.000022
6	3.437284	2.225085	-0.000061

Atomic number	x	y	z
1	4.081992	2.249433	0.879769
1	4.082063	2.249265	-0.879843
6	4.584192	-0.575691	0.000251
1	4.663883	-1.660348	0.000375
1	5.078171	-0.183472	0.888892
6	2.159142	-1.197013	0.000217
8	2.301248	-2.394981	0.000332
1	2.794304	3.099403	-0.000170
1	5.078236	-0.183670	-0.888441
1	-5.124135	1.462397	-0.000369
8	-5.071852	-1.133868	-0.000122

4.3 Z2 Anion

Atomic number	x	y	z
6	3.395048	1.081963	-0.000005
6	2.614179	-1.694336	-0.000006
6	1.641528	-0.673866	-0.000005
6	2.020621	0.666219	-0.000002
6	4.338550	-0.006197	-0.000002
6	3.953830	-1.331972	-0.000003
1	2.313612	-2.734247	-0.000007
1	1.264868	1.437929	0.000000
6	0.264696	-1.113450	-0.000004
1	0.126864	-2.191478	-0.000005
6	-0.905829	-0.438325	0.000001
7	-3.117744	-0.073283	-0.000002
7	-1.124517	0.949087	0.000009
6	-2.396220	1.112296	0.000004
6	-3.086906	2.428310	-0.000005
1	-3.722823	2.538587	-0.881019
1	-3.722862	2.538580	0.880983
6	-4.543100	-0.240342	-0.000011
1	-4.738319	-1.311421	-0.000028
1	-4.998647	0.202889	-0.887693
6	-2.206783	-1.129043	0.000014
8	-2.516647	-2.307463	0.000012
1	-2.336367	3.213327	0.000015
1	-4.998658	0.202862	0.887679
1	5.390036	0.258926	-0.000000
8	3.749853	2.288959	0.000010
1	4.714805	-2.106088	-0.000001

4.4 Z2 Neutral

Atomic number	x	y	z
6	3.341549	1.066128	0.000001
6	2.653421	-1.652820	-0.000001
6	1.619382	-0.693232	-0.000000
6	1.960395	0.645619	0.000001
6	4.356862	0.035444	0.000000
6	4.002796	-1.284406	-0.000001
1	2.391503	-2.702987	-0.000002
1	1.200896	1.413095	0.000001

Atomic number	x	y	z
6	0.244719	-1.178068	-0.000000
1	0.114036	-2.254828	-0.000000
6	-0.896479	-0.477656	-0.000001
7	-3.107539	-0.061275	-0.000000
7	-1.078329	0.907842	-0.000002
6	-2.353735	1.097983	-0.000002
6	-3.007432	2.428655	-0.000001
1	-3.641898	2.545374	-0.879928
1	-3.641891	2.545376	0.879930
6	-4.544354	-0.180883	0.000003
1	-4.778779	-1.242916	0.000002
1	-4.977138	0.278176	-0.888537
6	-2.232634	-1.141142	-0.000002
8	-2.542350	-2.307574	0.000002
1	-2.244465	3.200497	-0.000005
1	-4.977134	0.278173	0.888547
1	5.389360	0.355558	0.000000
8	3.647101	2.272527	0.000002
1	4.761634	-2.054848	-0.000002

4.5 E1 Anion

Atomic number	x	y	z
6	-2.708871	-1.059122	0.000001
6	-1.584495	-0.223935	-0.000000
6	-1.740803	1.173314	-0.000001
6	-3.034958	1.674544	-0.000000
6	-4.148779	0.854924	0.000000
6	-4.058660	-0.578518	0.000001
1	-2.574961	-2.135662	0.000001
1	-0.882616	1.823685	-0.000001
6	-0.311836	-0.901027	-0.000000
1	-0.401295	-1.983751	0.000000
6	0.991559	-0.518274	-0.000001
7	3.011310	0.462229	-0.000003
7	1.993106	-1.519239	-0.000001
6	3.123092	-0.916364	-0.000001
6	4.453466	-1.580699	0.000001
1	5.035023	-1.299656	-0.880708
1	5.035020	-1.299655	0.880711
6	4.068493	1.432969	0.000005
1	3.597876	2.414479	-0.000030
1	4.697025	1.340781	-0.887999
6	1.654121	0.798189	-0.000003
8	1.258834	1.949375	-0.000001
1	4.305492	-2.656922	0.000001
1	4.696977	1.340823	0.888049
1	-5.144423	1.284810	0.000001
1	-3.176962	2.750795	-0.000001
8	-5.062839	-1.338956	0.000002

4.6 E1 Neutral

Atomic number	x	y	z
6	-2.698771	-1.096919	-0.000000
6	-1.567538	-0.304861	0.000001
6	-1.731963	1.099054	0.000001
6	-3.007181	1.675495	0.000001
6	-4.134589	0.902373	-0.000000
6	-4.029801	-0.538575	0.000000
1	-2.628764	-2.176832	-0.000001
1	-0.855699	1.729305	0.000002
6	-0.282819	-0.993319	0.000001
1	-0.367446	-2.074854	0.000002
6	0.997310	-0.581838	0.000001
7	2.975023	0.493796	-0.000003
7	2.031160	-1.536669	0.000001
6	3.135666	-0.883884	-0.000000
6	4.488078	-1.492646	-0.000000
1	5.052604	-1.181148	-0.880207
1	5.052604	-1.181148	0.880207
6	4.008525	1.499412	0.000000
1	3.517428	2.469400	-0.000020
1	4.634218	1.417520	-0.888401
6	1.621861	0.776694	0.000000
8	1.154707	1.895648	-0.000000
1	4.389637	-2.573574	0.000000
1	4.634192	1.417543	0.888422
1	-5.127822	1.329178	-0.000001
1	-3.088549	2.753937	0.000001
8	-5.035751	-1.270039	-0.000002

4.7 E2 Anion

Atomic number	x	y	z
6	-2.576955	-1.783684	-0.000002
6	-1.607101	-0.755029	0.000002
6	-1.999219	0.581326	0.000002
6	-3.380903	0.982649	-0.000002
6	-4.315200	-0.112018	-0.000006
6	-3.918265	-1.434443	-0.000006
1	-2.270114	-2.821722	-0.000002
1	-1.255450	1.363540	0.000005
6	-0.239403	-1.219719	0.000005
1	-0.158027	-2.303554	0.000004
6	0.989749	-0.646029	0.000009
7	2.840061	0.629036	-0.000005
7	2.132033	-1.484228	0.000010
6	3.157288	-0.715550	0.000000
6	4.572779	-1.171707	-0.000009
1	5.104826	-0.805255	-0.880587
1	5.104835	-0.805260	0.880566
6	3.736417	1.750010	-0.000010
1	3.119923	2.647286	-0.000027
1	4.371403	1.755828	-0.888238
6	1.445109	0.757138	0.000015
8	0.880093	1.831095	0.000009
1	4.589685	-2.257964	-0.000012
1	4.371385	1.755851	0.888231

Atomic number	x	y	z
1	-5.368796	0.144425	-0.000009
8	-3.746163	2.185364	-0.000002
1	-4.671542	-2.216164	-0.000009

4.8 E2 Neutral

Atomic number	x	y	z
6	-2.609308	-1.735379	-0.000002
6	-1.580293	-0.765447	0.000002
6	-1.939355	0.568976	0.000004
6	-3.327733	0.970754	0.000003
6	-4.331844	-0.069221	-0.000004
6	-3.961843	-1.384880	-0.000005
1	-2.338397	-2.783173	-0.000003
1	-1.194834	1.351070	0.000007
6	-0.216701	-1.281257	0.000004
1	-0.154095	-2.364589	0.000007
6	0.997007	-0.703228	0.000003
7	2.806503	0.636796	-0.000007
7	2.152229	-1.505273	0.000004
6	3.155566	-0.703573	-0.000000
6	4.579279	-1.119418	-0.000001
1	5.094916	-0.732094	-0.880097
1	5.094923	-0.732074	0.880082
6	3.688640	1.777519	-0.000001
1	3.065442	2.668523	-0.000039
1	4.319495	1.784824	-0.888522
6	1.424927	0.728654	-0.000002
8	0.804621	1.768090	-0.000001
1	4.632070	-2.203537	0.000011
1	4.319438	1.784862	0.888561
1	-5.367792	0.239517	-0.000006
8	-3.647363	2.173199	0.000002
1	-4.710406	-2.165309	-0.000009

5 Vibrational Frequencies

This section provides the vibrational frequencies in wavenumbers for the anion and neutrals calculated with the Gaussian16 [1] program package at the ωB97X-D/aug-cc-pVTZ [2, 3] level of theory as presented in the paper.

5.1 Z1

Anion	Neutral
34.055	30.3367
57.0108	59.8534
84.8942	89.9608
114.3623	108.7675
126.9487	120.7423
152.0729	145.8875
179.6575	177.4057
193.4463	192.3204
201.8627	209.4313
217.5767	219.4115

Anion	Neutral
231.4628	234.6459
279.7236	279.8
311.7144	287.9871
338.1105	339.9245
459.951	421.8928
471.4949	469.9937
496.1257	495.0693
535.0944	533.197
568.9896	564.9863
600.1603	592.0079
630.5874	609.2717
634.7018	630.7959
692.498	672.9337
717.2956	693.5057
724.5375	720.1798
765.1672	752.8448
783.258	798.7148
795.2051	813.9075
823.575	820.5448
883.3172	906.8638
885.4439	912.9937
924.072	954.7145
969.7613	969.7126
992.1403	970.3729
999.8687	1004.7893
1010.6621	1024.7427
1023.1581	1027.203
1063.5446	1059.6318
1065.5601	1067.103
1102.4507	1115.7182
1159.4268	1160.7959
1164.0416	1164.0485
1180.4436	1183.7657
1208.0976	1207.903
1233.0551	1223.895
1275.2068	1292.6444
1337.2634	1332.0718
1344.0813	1351.3927
1394.5244	1388.3807
1405.2552	1408.9387
1416.2988	1411.9481
1437.7673	1446.3575
1470.0084	1457.693
1482.1431	1469.3273
1485.3401	1483.9084
1495.2438	1496.7381
1506.7183	1507.0449
1515.802	1516.5665
1563.3816	1524.5242
1587.3939	1581.7505
1639.1575	1598.5139
1649.5547	1659.1318
1704.2442	1735.1162
1782.2788	1827.7735
3033.5916	3055.4771
3042.2582	3057.2355

Anion	Neutral
3090.7831	3118.2495
3097.6428	3123.74
3138.3281	3158.6152
3140.5938	3178.2558
3159.5464	3181.008
3165.2107	3198.5846
3165.9265	3206.1531
3171.8966	3221.4848
3243.5372	3236.3578

5.2 Z2

Anion	Neutral
33.7144	28.8008
53.9111	56.1699
77.2979	81.6833
111.749	111.1097
126.3857	121.5624
148.7091	146.0265
177.4265	178.0242
190.6663	191.6184
196.1429	198.0472
201.4874	209.4243
258.0813	262.0498
286.3817	283.9353
307.8641	286.611
343.0937	344.9633
452.6187	423.9917
471.8146	474.8726
507.9894	499.2115
538.069	537.2142
554.2555	543.3371
596.9563	588.6997
628.4468	605.5813
630.7056	630.643
695.1737	671.37
707.0096	693.0401
724.5236	721.2293
754.9021	758.0226
771.4361	797.6793
796.1016	798.5063
801.4114	816.5972
872.7045	906.4259
909.6577	941.0925
946.4718	952.9284
961.6437	960.6985
982.4937	965.9388
992.2793	1009.4805
1011.1694	1015.4714
1030.8587	1033.4025
1059.319	1054.6555
1064.8859	1066.9779
1105.8701	1114.2449
1160.2539	1161.2477
1165.2231	1166.905

Anion	Neutral
1175.8496	1175.384
1209.5154	1207.9447
1233.4999	1221.9351
1272.3434	1283.6997
1327.1581	1329.7088
1342.6496	1339.5569
1388.8741	1365.6889
1405.0259	1409.8909
1430.5671	1424.2704
1437.5519	1447.1776
1467.9512	1453.0087
1484.5478	1468.2987
1492.7071	1483.2342
1499.3582	1496.057
1506.6488	1508.2751
1515.6212	1512.6049
1557.3699	1516.7124
1585.9066	1584.8849
1630.5325	1592.3979
1657.8252	1659.4862
1707.5594	1738.9108
1778.9359	1825.077
3032.3823	3054.4902
3043.537	3058.1877
3089.0804	3119.3407
3099.0536	3122.2249
3139.9405	3158.5317
3140.5799	3177.1508
3153.9934	3180.8899
3169.0054	3192.0516
3170.7985	3206.8759
3186.7001	3223.7505
3224.654	3240.8823

5.3 E1

Anion	Neutral
35.306	27.9112
50.9087	53.0771
97.9533	90.1137
107.454	117.2395
122.6814	119.6095
153.4073	150.398
181.4715	180.6861
195.3714	192.3065
200.6465	205.6783
209.9178	212.0167
245.0292	249.8108
286.896	293.5193
349.4112	329.5273
360.149	359.8501
430.8235	427.7725
462.2792	442.6177
468.7844	463.4121
538.5138	539.4381

Anion	Neutral
569.205	562.5747
600.195	596.1849
628.1062	602.5303
639.8379	627.9672
670.8348	668.4788
704.3269	675.6095
716.2948	701.248
760.3995	748.2926
793.8568	803.4825
809.4943	816.9516
818.0914	823.1163
881.4059	909.6507
895.5631	910.9712
919.0541	965.2646
975.3421	972.993
997.596	984.3007
1007.2148	1004.6086
1011.4891	1030.9143
1025.1875	1032.2696
1065.567	1068.4304
1066.1717	1073.6638
1105.4114	1116.2951
1159.0029	1160.1496
1164.6046	1165.2995
1186.6291	1188.9921
1205.4706	1210.412
1233.0273	1234.9246
1280.4124	1294.8545
1336.6379	1341.9477
1353.7627	1355.8407
1392.0016	1387.8872
1409.5225	1409.9256
1418.8216	1421.3445
1433.222	1445.0579
1470.6687	1455.3509
1476.7082	1469.1327
1485.1524	1484.5826
1497.169	1493.4438
1506.9198	1507.3924
1515.0861	1517.1711
1562.5337	1524.1419
1583.0918	1586.7962
1627.5788	1593.8852
1638.0107	1661.5226
1709.1023	1727.9507
1775.6972	1797.6731
3032.7576	3055.8385
3041.9872	3057.305
3089.5669	3117.4086
3096.8018	3123.9208
3141.2818	3162.6183
3141.6433	3172.8904
3153.8544	3178.2489
3163.4732	3199.7244
3163.8415	3205.7083
3171.8549	3221.7976

Anion	Neutral
3259.8488	3237.3586

5.4 E2

Anion	Neutral
29.7877	24.7629
47.2322	49.1504
95.0899	102.0885
106.7173	103.0129
126.2954	124.0227
153.8938	149.2999
178.3161	177.5586
189.9852	192.0493
198.7144	203.6906
202.7037	205.6852
259.5686	265.5456
297.2654	303.8401
346.4158	323.0707
353.199	355.986
426.8481	433.2838
462.5711	443.132
481.7462	467.3388
537.5408	537.5825
557.1259	546.0267
597.9293	593.1547
624.4436	598.5271
635.5288	627.5989
672.3638	666.6579
705.14	675.0396
705.2373	702.096
753.4356	754.2348
765.48	787.8868
797.0746	816.3748
808.8688	819.0853
871.8775	909.9704
922.7932	926.5323
930.2992	964.7504
973.7853	972.8401
981.8057	981.4164
998.1868	1010.9887
1013.449	1015.2907
1028.7112	1033.9654
1055.6772	1063.7878
1065.4211	1067.9995
1108.3999	1116.2534
1160.4137	1161.5257
1163.9095	1162.3319
1176.767	1178.303
1206.381	1211.6838
1234.2088	1235.8629
1274.5675	1287.6265
1327.5612	1336.2
1344.0744	1345.937
1385.962	1367.7322
1404.1224	1407.5696

Anion	Neutral
1431.4289	1429.3022
1436.4677	1445.871
1471.447	1454.5724
1484.2212	1469.0632
1497.5999	1483.5956
1501.5684	1495.1465
1508.4697	1508.9353
1515.3502	1511.9795
1554.6455	1517.4838
1582.2231	1582.0354
1625.3061	1590.8063
1645.4751	1661.4809
1708.9146	1728.187
1789.1663	1804.1574
3030.5614	3054.7613
3042.6266	3057.6525
3087.4263	3118.4163
3097.7609	3122.2944
3139.0995	3160.4013
3139.3984	3167.9281
3147.37	3178.4921
3162.8199	3191.5442
3170.7915	3206.6605
3185.9495	3223.7714
3238.7278	3231.2913

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