

Table S1: Variational calculations with PES V_A and V_B and CI basis 3 – 6.6 for the vibrational levels of glyoxal (in cm^{-1})

CI 3 – 6.6			Potential A			Potential B		
Assignment	C_{2h}	τ	1-mode	2-mode	3-mode	1-mode	2-mode	3-mode
Zero Point	a_g	0	8115	8146	8144	8115	8026	8026
ν_7 torsion	a_u	1	116	117	118	116	115	115
	a_g	2	247	246	246	247	242	242
	a_u	3	376	373	373	376	367	367
	a_g	4	492	495	495	492	501	501
	a_u	5	618	622	623	618	623	623
	a_g	6	736	742	743	736	744	743
ν_{12} C-C=O bend	b_u	0	358	362	361	358	359	359
	b_g	1	476	488	487	476	496	497
	b_u	2	610	621	620	610	626	627
	b_g	3	743	757	756	743	754	755
ν_5 C-C=O bend	a_g	0	544	548	547	544	546	546
	a_u	1	656	665	664	656	669	670
	a_g	2	784	786	785	784	784	785
	a_u	3	906	908	908	906	897	898
ν_6 C-H wag	a_u	0	860	919	918	860	888	887
	a_g	1	973	1012,1069	1006,1071	973	1007,1057	1001,1056
	a_u	2	1103	1126,1228	1119,1232	1103	1115,1136	1116
	a_g	3	1232	1249,1362	1240,1368	1232	1241	1241
ν_4 C-C stretch	a_g	0	1057	1012,1069	1006,1071	1057	1057	1057
	a_u	1	1175	1126,1228	1119,1232	1175	1191,1223	1192,1223
	a_g	2	1308	1249,1362	1240,1368	1308	1351	1350
	a_u	3	1440	1372,1493	1362,1501	1440	1480	1478

CI 3 – 6.6			Potential A			Potential B		
Assignment	C_{2h}	τ	1-mode	2-mode	3-mode	1-mode	2-mode	3-mode
ν_8 C-H wag	b_g	0	1094	1131	1132	1094	1055	1055
	b_u	1	1208	1249	1250	1208	1185	1186
	b_g	2	1337	1373	1374	1337	1310	1310
	b_u	3	1464	1497	1498	1464	1434	1435
ν_{11} C-H rock	b_u	0	1351	1374	1362,1387	1351	1319	1319
	b_g	1	1468	1501	1489,1515	1468	1458	1458
	b_u	2	1600	1631	1616,1643	1600	1587	1586
	b_g	3	1730	1760	1742,1770	1730	1714	1713
ν_3 C-H rock	a_g	0	1386	1406	1405	1386	1355	1356
	a_u	1	1495	1522	1524	1495	1484	1487
	a_g	2	1635	1656,1660	1656,1662	1635	1619	1621
	a_u	3	1777	1798	1799	1777	1756	1756
ν_{10} C-O stretch	b_u	0	1803	1762	1764	1803	1766	1766
	b_g	1	1920	1881	1885	1920	1898	1898
	b_u	2	2050	2009	2013	2050	2024	2024
	b_g	3	2180	2144	2146	2180	2156	2156
ν_2 C-O stretch	a_g	0	1782	1760	1759	1782	1762	1762
	a_u	1	1897	1879	1880	1897	1893	1893
	a_g	2	2029	2007	2005,2022	2029	2022	2022
	a_u	3	2159	2146	2147,2151	2159	2151	2151
ν_9 C-H stretch	b_u	0	3013	3021	3022	3013	2771	2771
	b_g	1	3129	3144	3146	3129	2888	2888
	b_u	2	3261	3273	3275	3261	3017	3017
	b_g	3	3390	3402	3404	3390	3181	3181
ν_1 C-H stretch	a_g	0	2884	2890	2892	2884	2808	2808
	a_u	1	2996	3011	3012	2996	2928	2929
	a_g	2	3130	3143	3145	3130	3063	3063
	a_u	3	3262	3273	3275	3262	3208	3208

Table S2: Perturbation calculations for the vibrational levels of glyoxal (in cm^{-1}) with the full potential and the potential depending on the level of mode-coupling, using the basis in Table 1

SCF-PT			n-mode Potential			Full Potential		
Assignment	C_{2h}	τ	1-mode	2-mode	3-mode	1-mode	2-mode	3-mode
Zero Point	a_g	0	8093	7969	7990	7969	7989	7990
ν_7 torsion	a_u	1	119	122	121	120	120	121
	a_g	2	261	264	262	261	260	262
	a_u	3	409	412	409	407	406	409
	a_g	4	574	577	577	573	570	577
	a_u	5	757	770	767	760	761	767
	a_g	6	973	979	987	978	969	987
ν_{12} C-C=O bend	b_u	0	360	343	341	339	340	341
	b_g	1	482	467	463	460	462	463
	b_u	2	625	612	605	602	603	605
	b_g	3	777	764	755	750	752	755
ν_5 C-C=O bend	a_g	0	545	552	548	536	547	548
	a_u	1	660	671	664	651	662	664
	a_g	2	794	806	798	783	793	798
	a_u	3	931	946	941	915	928	941
ν_6 C-H wag	a_u	0	865	818	806	780	809	806
	a_g	1	980	945	926	900	930	926
	a_u	2	1119	1091	1067	1044	1071	1067
	a_g	3	1264	1243	1213	1192	1217	1213
ν_4 C-C stretch	a_g	0	1057	1041	1035	1026	1034	1035
	a_u	1	1178	1168	1160	1150	1159	1160
	a_g	2	1321	1314	1308	1294	1302	1308
	a_u	3	1472	1466	1463	1443	1450	1463

SCF-PT			n-mode Potential			Full Potential		
Assignment	C_{2h}	τ	1-mode	2-mode	3-mode	1-mode	2-mode	3-mode
ν_8 C-H wag	b_g	0	1095	1080	1064	1053	1063	1064
	b_u	1	1211	1202	1183	1171	1182	1183
	b_g	2	1350	1342	1321	1310	1319	1321
	b_u	3	1494	1486	1463	1451	1461	1463
ν_{11} C-H rock	b_u	0	1351	1327	1312	1309	1312	1312
	b_g	1	1471	1450	1434	1430	1433	1434
	b_u	2	1613	1590	1574	1571	1572	1574
	b_g	3	1763	1737	1719	1716	1718	1719
ν_3 C-H rock	a_g	0	1387	1362	1353	1349	1352	1353
	a_u	1	1498	1478	1468	1461	1465	1468
	a_g	2	1651	1627	1618	1611	1613	1618
	a_u	3	1806	1780	1772	1762	1764	1772
ν_{10} C-O stretch	b_u	0	1804	1753	1765	1763	1765	1765
	b_g	1	1923	1875	1886	1882	1885	1886
	b_u	2	2063	2016	2026	2023	2025	2026
	b_g	3	2211	2164	2172	2167	2170	2172
ν_2 C-O stretch	a_g	0	1782	1767	1761	1759	1761	1761
	a_u	1	1901	1891	1883	1879	1882	1883
	a_g	2	2044	2033	2023	2020	2020	2023
	a_u	3	2193	2183	2171	2166	2168	2171
ν_9 C-H stretch	b_u	0	3016	2641	2785	2778	2785	2785
	b_g	1	3135	2761	2904	2896	2904	2904
	b_u	2	3277	2901	3047	3038	3045	3047
	b_g	3	3425	3046	3194	3184	3191	3194
ν_1 C-H stretch	a_g	0	2875	2798	2792	2785	2792	2792
	a_u	1	2991	2916	2910	2901	2909	2910
	a_g	2	3135	3059	3055	3045	3052	3055
	a_u	3	3284	3206	3202	3191	3199	3202