Appendices

Appendix 1: Fluorocarbons Supplementary Information

Appendix 1.1 Atomic data: G3 energies and heats of formation at 0 K of atoms, and thermal corrections to enthalpies of elements in their standard states, as used in this work.

	E_0 (G3) / E_h	$\Delta_f H_0^0$ / kcal mol^{-1}	$\left(H_{298}^0 - H_0^0\right)$ / kcal mol^{-1}
H	−0.5010	51.63	1.01
C	−37.8277	169.98	0.25
O	−75.0310	58.99	1.04
F	−99.6842	18.47	1.05

Appendix 1.2 C_1 Hydrofluorocarbons: Rotational constants, vibrational frequencies (scaled by 0.8929), obtained at MP2(Full)/6-31G(*d*) and HF/6-31G(*d*) levels of theory respectively and the resulting zero point energies and thermal corrections[a] to the heats of formation.

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_4	5.2850	5.2850	5.2848	1328	1328	1329	1520	1520	2856	26.78	2.39
				2947	2949	2952					
CH_3F	5.2414	0.8490	0.8490	1061	1172	1172	1475	1476	1476	23.78	2.42
				2886	2957	2957					
CH_2F_2	1.6481	0.3479	0.3045	510	1106	1123	1164	1259	1464	20.16	2.56
				1530	2941	3005					
CHF_3	0.3408	0.3407	0.1868	491	492	680	1126	1185	1187	15.76	2.78
				1414	1414	3036					
CF_4	0.1883	0.1883	0.1883	422	422	610	610	610	896	10.74	3.08
				1315	1315	1315					
CH_3	9.5909	9.5909	4.7955	275	1375	1375	2933	3090	3090	17.35	2.66
CH_2F	8.7668	1.0151	0.9215	770	1133	1143	1443	2962	3088	15.07	2.46
CHF_2	2.2359	0.3603	0.3152	521	1041	1150	1181	1343	3005	11.78	2.55
CF_3	0.3573	0.3573	0.1850	491	491	677	1086	1286	1286	7.60	2.77
CH_2	20.0859	11.2493	7.2108	1397	2794	2850				10.06	2.37
CHF	15.669	1.2090	1.1224	1189	1405	2727				7.61	2.39
CF_2	2.8441	0.4132	0.3608	651	1155	1240				4.35	2.48
CH	14.4520			2733						3.91	2.07
CF	1.3802			1259						1.80	2.08

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_2O	9.5774	1.2666	1.1187	1193	1235	1500	1811	2822	2886	16.36	2.39
CHFO	3.0430	0.3836	0.3406	659	1051	1115	1375	1878	2996	12.97	2.49
CF_2O	0.3879	0.3823	0.1925	563	610	779	976	1305	1953	8.85	2.67
CHO	23.3086	1.4662	1.3794	1118	1913	2601				8.05	2.39
CFO	6.2938	0.3751	0.3540	632	1081	1912				5.18	2.48
CH_3OH	4.2466	0.8251	0.7954	311	1040	1061	1151	1346	1462	31.01	2.69
				1475	1485	2844	2885	2951	3677		
CH_2FOH	1.5160	0.3413	0.3011	351	529	1020	1070	1132	1245	27.49	2.80
				1363	1447	1522	2903	2990	3658		
CHF_2OH	0.3347	0.3327	0.1864	303	498	532	640	1025	1119	23.03	3.05
				1192	1310	1384	1438	3040	3629		
CF_3OH	0.1890	0.1857	0.1852	234	428	441	583	607	617	17.94	3.41
				888	1123	1234	1323	1414	3654		
CH_3OF	1.4291	0.3576	0.3028	244	437	922	1090	1154	1206	26.10	2.93
				1433	1445	1484	2891	2971	2976		
CH_2FOF	0.6195	0.1865	0.1597	159	396	587	936	1087	1135	22.34	3.15
				1157	1290	1429	1485	2949	3017		
CHF_2OF	0.2531	0.1570	0.1290	146	275	506	525	789	945	17.85	3.46
				1124	1176	1195	1386	1406	3016		
CF_3OF	0.1833	0.1034	0.1014	133	262	424	430	572	597	12.84	3.81
				676	887	1083	1283	1298	1337		
CH_3O	5.2530	0.9136	0.9097	727	990	1083	1414	1423	1488	22.56	2.49
				2841	2900	2917					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_2FO	1.8277	0.3572	0.3172	528	912	1047	1109	1198	1413	19.26	2.58
				1440	2885	2938					
CHF_2O	0.3559	0.3434	0.1903	443	500	645	1014	1147	1154	15.17	2.82
				1356	1391	2959					
CF_3O	0.1995	0.1933	0.1847	225	411	572	583	607	884	10.21	3.26
				1275	1278	1310					
CH_2OH	6.3381	0.9898	0.8696	368	763	1032	1149	1324	1452	22.54	2.68
				2936	3059	3682					
CHFOH	2.1107	0.3613	0.3132	198	515	1021	1045	1186	1253	18.88	2.92
				1379	2928	3678					
CF_2OH	0.3591	0.3474	0.1828	257	483	491	674	1040	1113	14.83	3.09
				1287	1363	3665					
CH_2OF	1.7795	0.3801	0.3162	204	463	762	935	1117	1169	17.34	2.99
				1409	2973	3098					
CHFOF	1.6064	0.1461	0.1349	80	341	499	1017	1051	1159	13.83	3.30
				1194	1327	3008					
CH_3OOH	1.3976	0.3511	0.3029	182	240	445	926	1107	1155	33.53	3.31
				1201	1397	1440	1453	1484	2873		
				2938	2961	3650					
CF_3OOH	0.1824	0.1041	0.1030	139	256	288	429	437	572	20.43	4.08
				604	674	879	1067	1263	1294		
				1319	1438	3631					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_3OO	1.7316	0.3821	0.3332	162	478	950	1143	1143	1200	26.16	2.99
				1439	1457	1470	2896	2972	2987		
CF_3OO	0.1848	0.1091	0.1076	122	279	420	442	571	593	12.86	3.80
				687	879	1124	1251	1289	1341		
HCOOH	2.5687	0.3968	0.3437	618	639	1065	1138	1286	1386	20.76	2.60
				1817	2965	3609					
FCOOH	0.3934	0.3757	0.1922	545	557	607	791	965	1215	16.59	2.80
				1398	1881	3642					
HCOO - A_1	5.3878	0.3786	0.3537	509	821	1060	1218	1693	2010	10.45	2.58
FCOO - B_2	0.4666	0.3636	0.2043	540	568	811	993	1561	2457	9.91	2.68
CH_2OHOH	1.3806	0.3410	0.3013	367	391	552	984	1042	1101		
				1178	1345	1365	1437	1515	2897	34.91	2.99
				2941	3653	3654					
CF_2OHOH	0.1884	0.1839	0.1823	162	338	432	449	583	595	25.21	3.73
				606	880	1101	1153	1158	1408		
				1451	3659	3659					
OCH_2OH	1.6489	0.3549	0.3147	301	532	877	1006	1110	1132	26.54	2.86
				1329	1410	1444	2832	2930	3659		
OCF_2OH	0.1974	0.1950	0.1803	228	319	406	567	583	597	17.49	3.53
				877	1092	1216	1287	1414	3647		

[a] $\Delta\Delta_f H^0_{298} = \Delta_f H^0_{298} - \Delta_f H^0_0$

Appendix 1.3 C_2 Hydrofluorocarbons: Rotational constants and vibrational frequencies (scaled by 0.8929) obtained at MP2(Full)/6-31G(*d*) and HF/6-31G(*d*) levels of theory respectively and the resulting zero point energies and thermal corrections[a] to the heats of formation.

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
C_2H_6	2.6863	0.6695	0.6695	292	794	794	947	1194	1194	44.69	2.81
				1382	1410	1468	1468	1473	1473		
				2857	2862	2901	2901	2923	2923		
CH_3CH_2F	1.1984	0.3144	0.2749	244	392	784	867	1044	1107	40.98	3.04
				1169	1270	1381	1418	1452	1469		
				1503	2869	2896	2924	2930	2948		
CH_2FCH_2F	1.0612	0.1293	0.1205	129	273	444	787	1045	1065	37.16	3.41
				1068	1157	1211	1268	1338	1444		
				1500	1506	2914	2916	2951	2975		
CH_3CHF_2	0.3115	0.3017	0.1721	230	364	449	548	846	957	36.71	3.33
				1120	1145	1158	1376	1391	1432		
				1455	1458	2883	2947	2952	2966		
CHF_2CH_2F	0.3012	0.1222	0.0939	114	235	413	465	559	896	32.81	3.71
				1081	1111	1124	1154	1238	1332		
				1402	1457	1486	2923	2971	2986		
CH_3CF_3	0.1807	0.1724	0.1724	224	350	350	522	522	577	31.87	3.66
				811	977	977	1263	1263	1277		
				1429	1453	1453	2898	2974	2974		

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CHF_2CHF_2	0.1679	0.1063	0.0689	85	196	348	406	476	523	28.35	4.09
				607	1094	1123	1139	1148	1165		
				1306	1362	1390	1480	2985	2994		
CH_2FCF_3	0.1767	0.0934	0.0923	105	209	341	398	516	530	27.94	4.07
				646	828	980	1101	1200	1217		
				1303	1314	1448	1485	2935	2990		
CHF_2CF_3	0.1210	0.0814	0.0671	72	201	235	351	406	505	23.45	4.48
				559	569	706	859	1130	1169		
				1217	1256	1324	1385	1466	2995		
CF_3CF_3	0.0931	0.0618	0.0618	62	205	205	337	370	370	18.46	4.88
				504	504	602	602	691	793		
				1110	1274	1274	1280	1280	1453		
CH_3CH_2	3.4574	0.7584	0.7040	148	407	778	967	994	1169	35.49	3.10
				1386	1436	1455	1460	2822	2883		
				2914	2960	3047					
CH_2FCH_2	1.3690	0.3355	0.2866	157	383	440	831	956	1061	31.83	3.27
				1101	1228	1388	1426	1486	2857		
				2909	2974	3071					
CH_3CHF	1.5509	0.3172	0.2791	184	389	640	879	1023	1088	32.42	3.13
				1152	1338	1405	1442	1458	2839		
				2903	2935	3000					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_2FCHF	1.2642	0.1306	0.1217	101	276	449	648	1005	1065	28.59	3.46
				1075	1137	1208	1290	1426	1491		
				2875	2933	3019					
CHF_2CH_2	0.3276	0.3174	0.1759	127	367	376	470	615	909	27.62	3.57
				957	1142	1152	1369	1391	1427		
				2928	2993	3096					
CH_3CF_2	0.3328	0.3074	0.1693	186	354	443	520	837	973	28.53	3.38
				1081	1248	1250	1408	1447	1450		
				2863	2936	2966					
CH_2FCF_2	0.3162	0.1234	0.0930	96	226	412	443	558	883	24.67	3.74
				1047	1095	1208	1232	1292	1422		
				1481	2896	2967					
CHF_2CHF	0.3131	0.1241	0.0937	87	238	415	459	560	713	24.31	3.77
				993	1127	1136	1174	1297	1389		
				1432	2945	3039					
CF_3CH_2	0.1834	0.1817	0.1774	120	314	361	460	519	569	22.84	3.89
				594	832	933	1183	1267	1284		
				1429	3001	3110					
CHF_2CF_2	0.1724	0.1068	0.0684	70	194	345	392	476	524	20.27	4.11
				617	1002	1127	1165	1240	1261		
				1379	1433	2954					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
C_2F_4H	0.1815	0.0939	0.0923	79	204	339	403	506	537	19.46	4.13
				653	713	844	1161	1193	1219		
				1289	1424	3049					
CF_3CF_2	0.1233	0.0809	0.0661	58	197	216	350	408	501	15.37	4.51
				571	582	697	830	1134	1238		
				1271	1286	1418					
CH_2CH_2	4.9089	0.9996	0.8305	801	978	982	1032	1208	1337	30.69	2.51
				1438	1658	2964	2985	3030	3053		
CH_2CHF	2.1652	0.3509	0.3020	468	715	916	922	977	1148	26.70	2.71
				1301	1393	1691	3002	3059	3085		
CHFCHF–*Z*	1.8979	0.1329	0.1242	309	338	538	846	932	1127	22.44	3.10
				1143	1275	1275	1745	3079	3088		
CHFCHF–*E*	0.6950	0.1960	0.1529	225	492	748	804	906	1005	22.66	3.04
				1112	1255	1381	1760	3071	3095		
CH_2CF_2	0.3601	0.3459	0.1764	423	528	630	713	865	918	22.35	2.95
				951	1332	1386	1748	3027	3115		
$CHFCF_2$	0.3492	0.1280	0.0937	223	307	469	586	605	816	18.06	3.42
				922	1145	1265	1369	1824	3105		
CF_2CF_2	0.1792	0.1078	0.0673	199	200	382	431	530	540	13.44	3.90
				563	777	1164	1341	1355	1915		
CH_3CH	4.0717	0.8832	0.8312	356	646	915	1021	1231	1335	28.23	2.75
				1395	1473	2775	2804	2864	2930		

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_3CF	1.7801	0.3549	0.3129	98	485	751	923	1045	1192	24.87	3.12
				1356	1412	1444	2831	2903	2955		
CH_2FCH	1.6163	0.3499	0.3038	259	449	798	905	1056	1105	24.57	2.97
				1249	1351	1384	2861	2871	2901		
CH_2FCF	1.4920	0.1385	0.1299	147	333	496	712	993	1117	21.10	3.30
				1162	1218	1380	1422	2867	2913		
CHF_2CH	0.3603	0.3458	0.1764	366	414	499	536	798	1006	20.50	3.15
				1120	1170	1340	1374	2831	2884		
CHF_2CF	0.3285	0.1391	0.1034	58	260	420	540	556	860	16.96	3.69
				1133	1164	1224	1361	1377	2912		
CF_3CH	0.2050	0.1898	0.1731	153	339	420	521	528	580	15.83	3.65
				821	1047	1182	1268	1319	2900		
CF_3CF	0.1823	0.0990	0.0985	11	267	363	398	520	529	12.34	4.07
				675	827	1223	1227	1261	1327		
CH_2CH	7.8272	1.1191	0.9791	740	790	856	1068	1257	1460	21.69	2.55
				2927	3012	3062					
CHFCH–*Z*	2.3878	0.3837	0.3306	437	629	825	853	1053	1253	18.11	2.75
				1452	3062	3100					
CHFCH–*E*	3.0421	0.3641	0.3252	481	644	756	810	1080	1247	18.03	2.74
				1475	3017	3104					
CH_2CF	3.9358	0.3430	0.3155	427	614	797	905	1093	1367	18.29	2.75
				1537	2975	3077					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CHFCF–*Z*	0.8850	0.1829	0.1516	204	402	719	727	945	1120	14.46	3.09
				1325	1577	3099					
CHFCF–*E*	2.8566	0.1322	0.1264	296	298	518	685	1049	1163	14.14	3.15
				1260	1569	3052					
CF_2CH	0.3880	0.3650	0.1881	416	519	528	624	819	904	14.02	3.00
				1279	1586	3130					
CF_2CF	0.3742	0.1260	0.0943	204	279	414	459	588	864	10.00	3.51
				1204	1317	1663					
CH_3C	5.3133	0.9550	0.9485	662	774	997	1334	1362	1433	21.59	2.54
				2797	2859	2887					
CH_2FC	1.8557	0.3715	0.3287	441	511	914	1060	1159	1339	17.93	2.75
				1388	2845	2885					
CHF_2C	0.3723	0.3384	0.1916	362	421	527	811	1115	1125	14.15	2.99
				1307	1362	2868					
CF_3C	0.2087	0.1974	0.1795	280	299	515	524	570	816	9.60	3.36
				1201	1218	1293					
HCCH	1.1605			710	710	789	789	2006	3219	16.50	2.31
				3320							
HCCF	0.3167			442	442	684	684	1043	2262	12.65	2.58
				3294							
FCCF	0.1156			291	291	408	408	771	1321	8.57	3.06
				2502							
CH_2C	9.5141	1.3022	1.1454	505	828	1235	1650	2970	3045	14.63	2.56

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CHFC	3.4765	0.3821	0.3443	360	780	1044	1157	1691	3018	11.51	2.68
CF_2C	0.4245	0.3592	0.1946	351	494	585	928	1297	1706	7.67	2.88
CCH	1.5328			496	496	1654	3234			8.41	2.36
CCF	0.3697			218	218	1003	2072			5.02	2.77
CH_2CO	9.4884	0.3370	0.3254	439	555	646	993	1131	1399	19.17	2.79
				2124	3015	3105					
CHFCO	1.7613	0.1517	0.1396	242	472	561	668	1024	1169	15.44	3.07
				1408	2152	3106					
CF_2CO	0.3491	0.1288	0.0941	207	273	378	442	673	794	11.07	3.52
				1315	1451	2209					
CHCO	27.3099	0.3613	0.3565	485	553	606	1172	2207	3013	11.49	2.75
CFCO	37.0140	0.1318	0.1314	204	433	590	940	1691	2286	8.78	3.03
CH_3CHO	1.8856	0.3366	0.3016	136	488	764	861	1099	1129	33.58	3.08
				1371	1398	1434	1443	1815	2812		
				2863	2912	2964					
CH_2FCHO	1.3230	0.1429	0.1322	85	315	515	721	1019	1078	29.72	3.38
				1105	1222	1328	1392	1461	1821		
				2858	2911	2960					
CHF_2CHO	0.3075	0.1291	0.0998	76	316	369	416	592	978	25.57	3.70
				1082	1128	1131	1312	1369	1395		
				1841	2875	3003					
CF_3CHO	0.1806	0.0993	0.0977	71	251	309	423	515	515	20.73	4.05
				688	835	981	1225	1225	1330		
				1383	1858	2894					

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
CH_3CFO	0.3606	0.3236	0.1761	130	394	561	585	837	1002	29.72	3.32
				1059	1222	1398	1438	1444	1894		
				2887	2945	2991					
CH_2FCFO	0.3440	0.1286	0.0953	112	243	443	528	635	870	25.84	3.62
				1034	1121	1167	1238	1421	1468		
				1925	2913	2960					
CHF_2CFO	0.1786	0.1107	0.0745	53	224	311	427	542	586	21.50	4.02
				747	924	1116	1183	1211	1381		
				1424	1932	2975					
CF_3CFO	0.1256	0.0834	0.0686	47	219	233	375	417	501	16.57	4.41
				578	678	763	801	1122	1244		
				1293	1373	1944					
CH_3CO	2.7440	0.3313	0.3128	87	454	826	938	1037	1356	26.08	3.12
				1432	1433	1911	2871	2946	2950		
CH_2FCO	1.6312	0.1424	0.1343	137	312	496	842	895	1100	22.29	3.30
				1215	1346	1451	1925	2908	2964		
CHF_2CO	0.3213	0.1323	0.1002	57	367	407	411	590	947	18.11	3.65
				1133	1150	1319	1366	1940	2977		
CF_3CO	0.1856	0.1000	0.1000	57	234	388	412	523	531	13.27	4.01
				667	795	1203	1241	1268	1960		

[a] $\Delta\Delta_f H^0_{298} = \Delta_f H^0_{298} - \Delta_f H^0_0$

[b] Computed from HF/6-31G(*d*) geometry.

Appendix 1.4 C_3 Hydrofluorocarbons: Rotational constants and vibrational frequencies (scaled by 0.8929) obtained at MP2(Full)/6-31G(*d*) and HF/6-31G(*d*) levels of theory respectively and the resulting zero point energies and thermal corrections[a] to the heats of formation.

Species	Rotational Constants (cm^{-1})			Vibrational frequencies (cm^{-1})						ZPE (kcal mol^{-1})	$\Delta\Delta_f H^0_{298}$ (kcal mol^{-1})
C_3H_6	1.5495	0.3109	0.2720	189	407	572	880	919	954	47.88	3.21
				1008	1060	1158	1289	1389	1424		
				1451	1464	1679	2852	2895	2923		
				2964	2976	3039					
C_3H_7	1.0384	0.2983	0.2674	118	241	314	481	713	855	52.93	3.76
				860	997	1049	1171	1277	1315		
				1388	1432	1458	1466	1475	2853		
				2858	2881	2912	2917	2952	3039		
C_3F_6	0.0840	0.0419	0.0328	36	125	170	238	245	351	21.39	5.61
				358	457	497	566	586	638		
				660	751	1025	1198	1228	1254		
				1342	1404	1832					
C_3F_6H	0.0760	0.0460	0.0398	34	89	143	204	234	287	28.08	5.82
				348	447	509	517	567	623		
				740	840	924	1123	1176	1239		
				1247	1296	1314	1379	1403	2963		

[a] $\Delta\Delta_f H^0_{298} = \Delta_f H^0_{298} - \Delta_f H^0_0$

Appendix 2: Phosphorus Compounds Supplementary Information

Appendix 2.1 Geometric data for molecules in **Table 4.1**. Bond lengths in Å, angles in degrees, rotational constants and vibrational frequencies in cm^{-1}.

H_2 - $^1\Sigma_g$ - $D_{\infty h}$

G3

Z-matrix

H(1)
H(2) 1 0.7375

Rotational Constant

61.5135

Vibrational Frequency

4149

G3X

Z-matrix

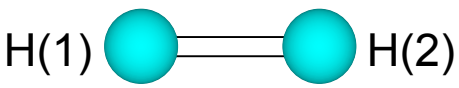
H(1)
H(2) 1 0.7427

Rotational Constant

60.6414

Vibrational Frequency

4401



O_2 - $^3\Sigma_g$ - $D_{\infty h}$

G3

Z-matrix

O(1)
O(2) 1 1.2460

Rotational Constant

1.3578

Vibrational Frequency

1784

G3X

Z-matrix

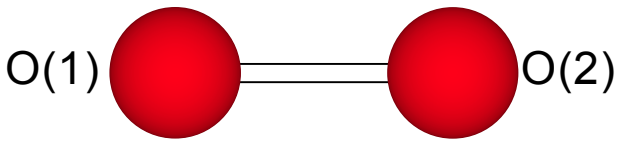
O(1)
O(2) 1 1.2064

Rotational Constant

1.4484

Vibrational Frequency

1640



P_2 - $^1\Sigma_g$ - $D_{\infty h}$

G3

Z-matrix

P(1)
P(2) 1 1.9324

Rotational Constant
0.2915

Vibrational Frequency

811

G3X

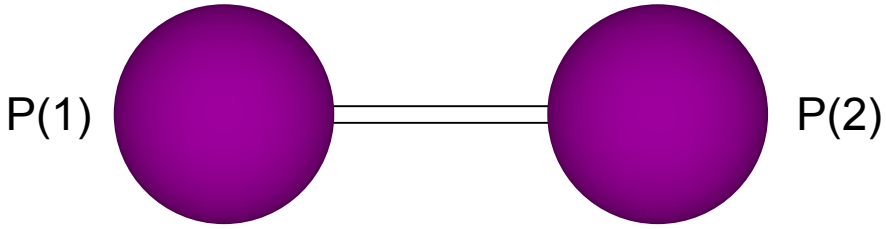
Z-matrix

P(1)
P(2) 1 1.8952

Rotational Constant
0.3031

Vibrational Frequency

793



P_4 - $^1A_1$ - T_d

G3

Z-matrix

P(1)
P(2) 1 2.1948
P(3) 1 2.1948 2 60.0
P(4) 1 2.1948 2 60.0 3 -70.5

Rotational Constants

0.1130, 0.1130, 0.1130

Vibrational Frequencies

363, 363, 466, 466, 466, 615

G3X

Z-matrix

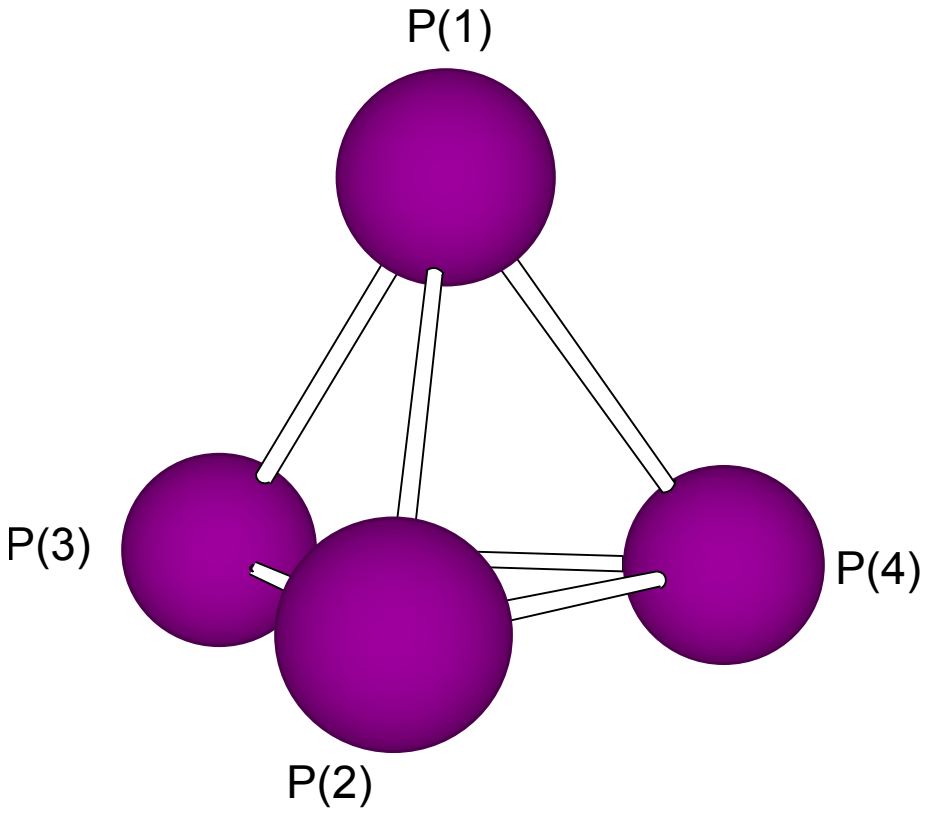
P(1)
P(2) 1 2.2112
P(3) 1 2.2112 2 60.0
P(4) 1 2.2112 2 60.0 3 -70.5

Rotational Constants

0.1113, 0.1113, 0.1113

Vibrational Frequencies

363, 363, 454, 454, 454, 599



HO - $^2\Pi$ - $C_{\infty v}$

G3

Z-matrix

O(1)
H(2) 1 0.9790

Rotational Constant

18.5531

Vibrational Frequency

3569

G3X

Z-matrix

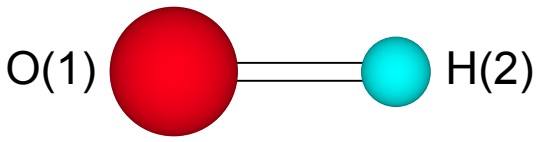
O(1)
H(2) 1 0.9761

Rotational Constant

18.6606

Vibrational Frequency

3642



H_2O - $^1A_1$ - C_{2v}

G3

Z-matrix

O(1)
H(2) 1 0.9686
H(3) 1 0.9686 2 103.9

Rotational Constants

26.4131, 14.3801, 9.3109

Vibrational Frequencies

1631, 3635, 3740

G3X

Z-matrix

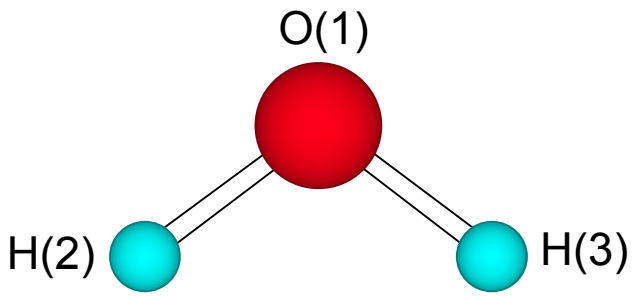
O(1)
H(2) 1 0.9620
H(3) 1 0.9620 2 103.7

Rotational Constants

26.6798, 14.6088, 9.4399

Vibrational Frequencies

1647, 3749, 3852



HO_2 - $^2A''$ - C_s

G3

Z-matrix

O(1)
H(2) 1 0.9835
O(3) 1 1.3247 2 104.6

Rotational Constants

20.2165, 1.1318, 1.0718

Vibrational Frequencies

1117, 1450, 3583

G3X

Z-matrix

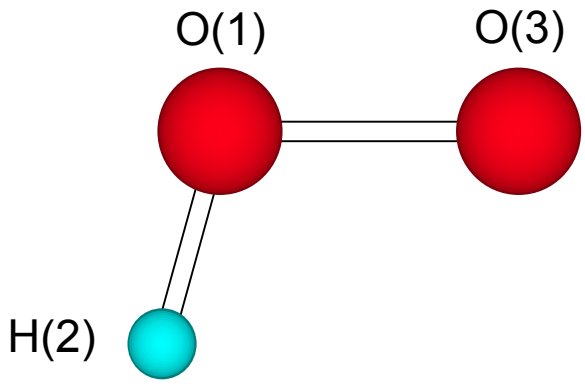
O(1)
H(2) 1 0.9774
O(3) 1 1.3238 2 105.4

Rotational Constants

20.6569, 1.1316, 1.0728

Vibrational Frequencies

1168, 1428, 3529



PH - $^3\Sigma$ - $C_{\infty v}$

G3

Z-matrix

P(1)
H(2) 1 1.4256

Rotational Constant

8.4977

Vibrational Frequency

2283

G3X

Z-matrix

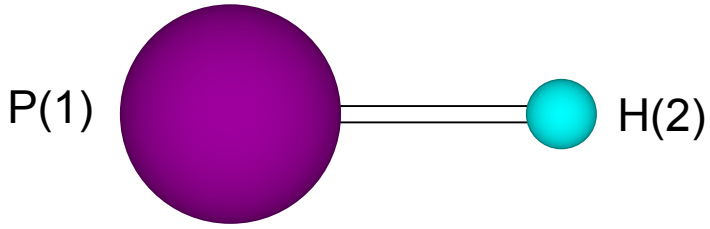
P(1)
H(2) 1 1.4321

Rotational Constant

8.4209

Vibrational Frequency

2302



PH_2 - $^2B_1$ - C_{2v}

G3

Z-matrix

P(1)
H(2) 1 1.4199
H(3) 1 1.4199 2 92.5

Rotational Constants

9.2479, 7.9442, 4.2733

Vibrational Frequencies

1123, 2302, 2303

G3X

Z-matrix

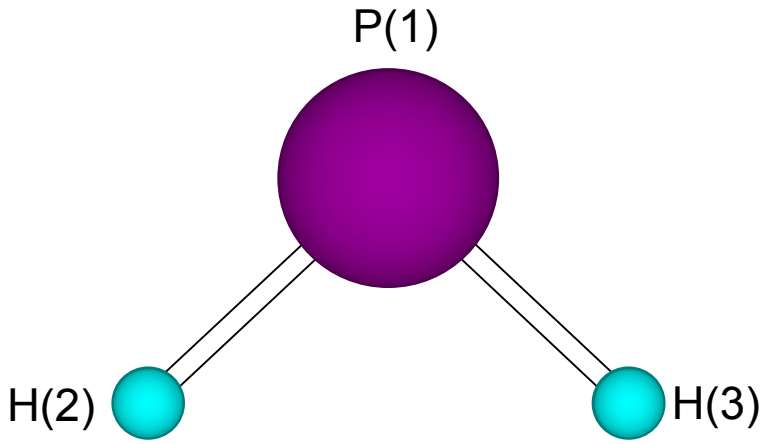
P(1)
H(2) 1 1.4265
H(3) 1 1.4265 2 91.6

Rotational Constants

9.0041, 7.9990, 4.2359

Vibrational Frequencies

1113, 2328, 2338



PH_3 - $^1A'$ - C_s

G3

Z-matrix

P(1)
H(2) 1 1.4146
H(3) 1 1.4146 2 94.6
H(4) 1 1.4146 2 94.6 3 95.0

Rotational Constants

4.5307, 4.5304, 3.8680

Vibrational Frequencies

1018, 1135, 1135, 2323, 2325, 2330

G3X

Z-matrix

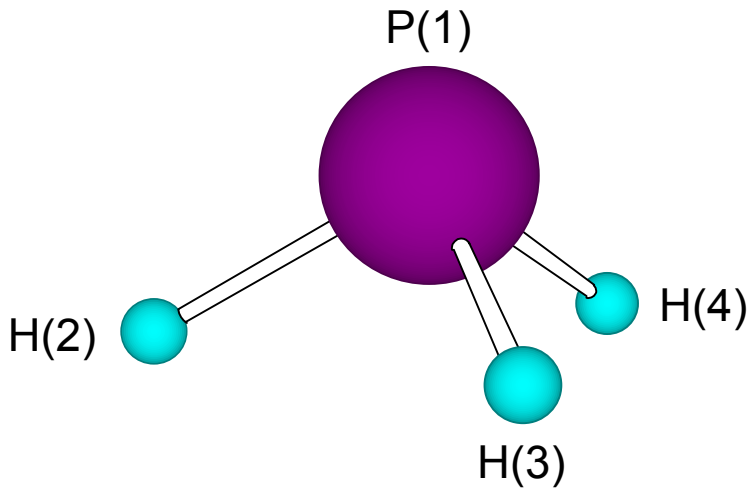
P(1)
H(2) 1 1.4219
H(3) 1 1.4219 2 93.3
H(4) 1 1.4219 2 93.3 3 93.5

Rotational Constants

4.4376, 4.4374, 3.9147

Vibrational Frequencies

1010, 1126, 1126, 2355, 2364, 2367



P_2H_2 - ^1A_g - C_s

G3

Z-matrix

P(1)
P(2) 1 2.0429
H(3) 1 1.4221 2 94.7
H(4) 2 1.4221 1 94.7 3 180.0

Rotational Constants

4.3429, 0.2501, 0.2364

Vibrational Frequencies

626, 686, 775, 961, 2299, 2311

G3X

Z-matrix

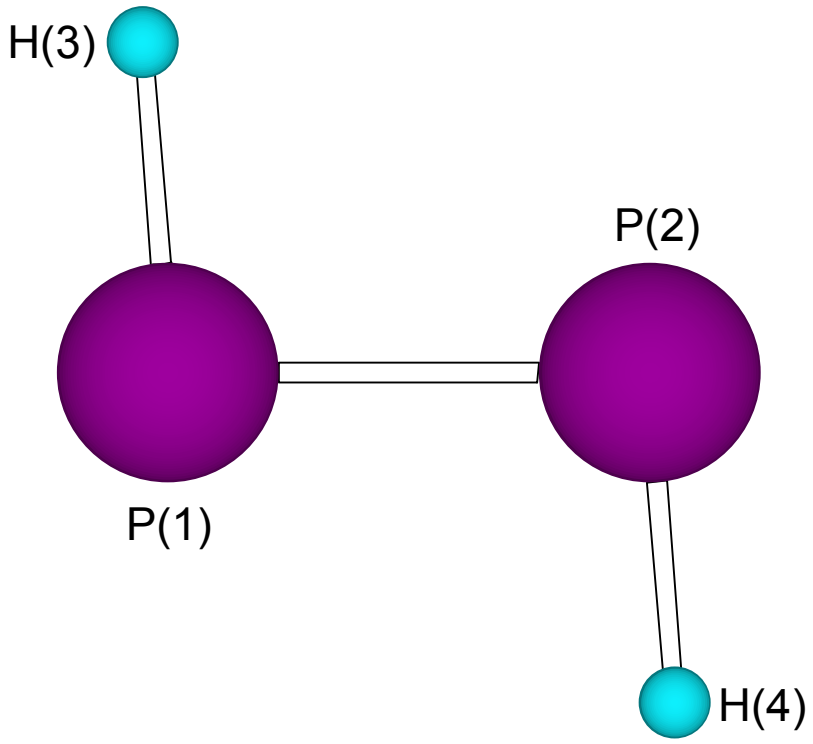
P(1)
P(2) 1 2.0351
H(3) 1 1.4294 2 94.2
H(4) 2 1.4294 1 94.2 3 180.0

Rotational Constants

4.2893, 0.2522, 0.2382

Vibrational Frequencies

611, 678, 766, 962, 2298, 2313



P_2H_4 - ^1A_g - C_s

G3

Z-matrix

P(1)
P(2) 1 2.2311
H(3) 1 1.4170 2 95.2
H(4) 1 1.4170 2 95.2 3 -94.1
H(5) 2 1.4170 1 95.2 3 -85.9
H(6) 2 1.4170 1 95.2 3 180.0

Rotational Constants

2.1786, 0.1937, 0.1917

Vibrational Frequencies

58, 436, 622, 649, 869, 908,
1103, 1106, 2311, 2319, 2321,
2324

G3X

Z-matrix

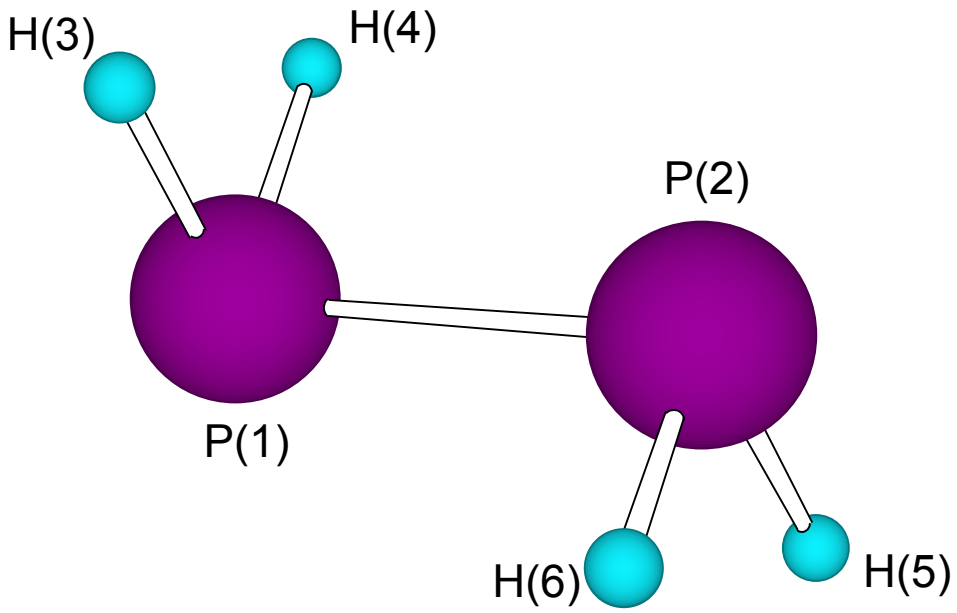
P(1)
P(2) 1 2.2594
H(3) 1 1.4242 2 93.8
H(4) 1 1.4242 1 93.8 3 -92.4
H(4) 2 1.4242 1 93.8 3 -87.6
H(4) 2 1.4242 1 93.8 3 180.0

Rotational Constants

2.1468, 0.1894, 0.1881

Vibrational Frequencies

103, 422, 613, 629, 854, 896,
1084, 1093, 2333, 2338, 2340,
2351



PO - $^2\Pi$ - $C_{\infty v}$

G3

Z-matrix

P(1)
O(2) 1 1.4715

Rotational Constant

0.7381

Vibrational Frequency

1254

G3X

Z-matrix

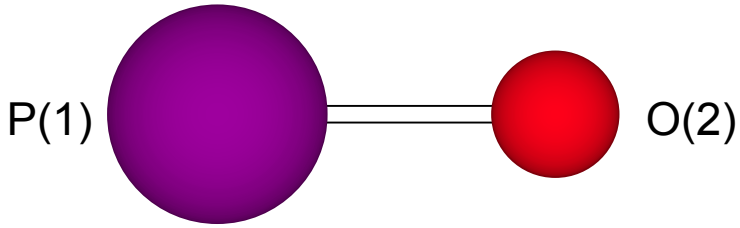
P(1)
O(2) 1 1.4831

Rotational Constant

0.7266

Vibrational Frequency

1241



PO_2 - $^2A_1$ - C_{2v}

G3

Z-matrix

P(1)
O(2) 1 1.4924
O(3) 1 1.4924 2 136.4

Rotational Constants

3.4850, 0.2745, 0.2544

Vibrational Frequencies

409, 1079, 1301

G3X

Z-matrix

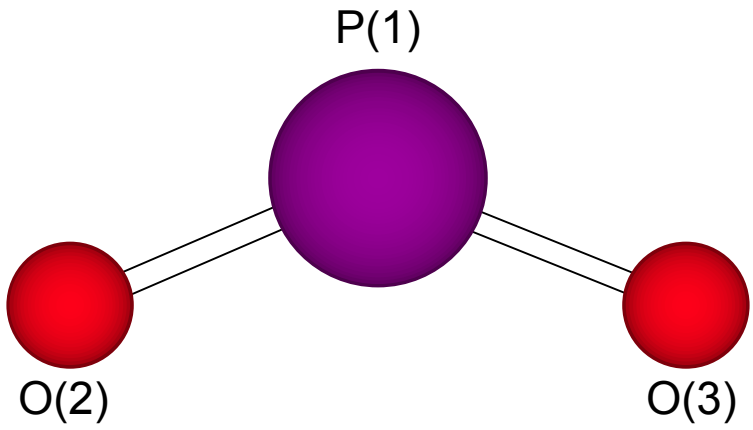
P(1)
O(2) 1 1.4743
O(3) 1 1.4743 2 134.4

Rotational Constants

3.2851, 0.2852, 0.2625

Vibrational Frequencies

378, 1061, 1314



PO_3 - $^2A_2'$ - D_{3h}

G3

Z-matrix

P(1)
O(2) 1 1.5025
O(3) 1 1.5025 2 120.0
O(4) 1 1.5025 2 120.0 3 180.0

Rotational Constants

0.3112, 0.3112, 0.1556

Vibrational Frequencies

442, 442, 443, 1028, 1690, 1690

G3X

Z-matrix

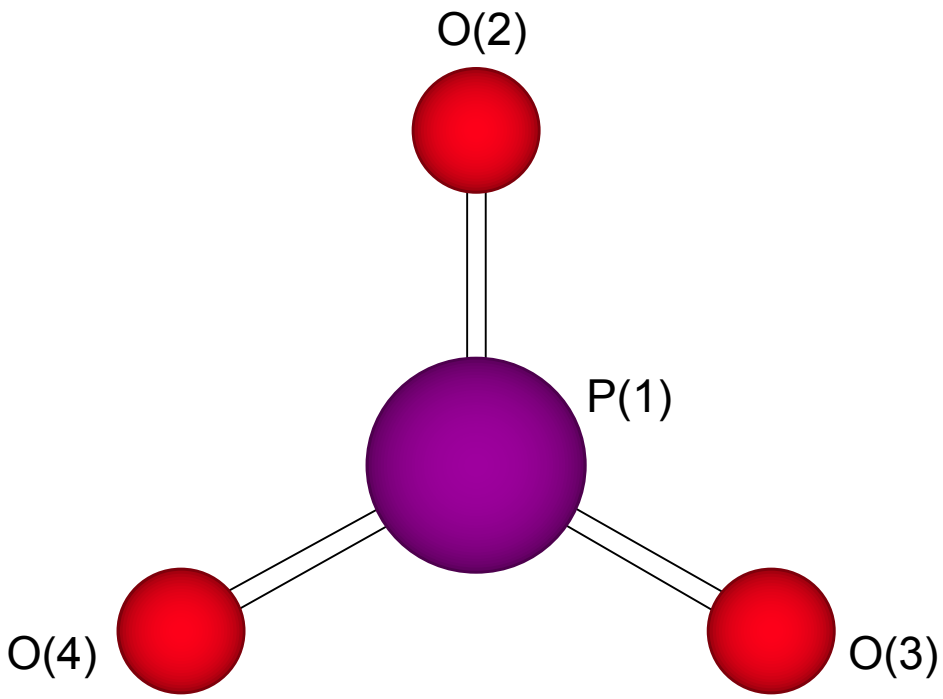
P(1)
O(2) 1 1.4792
O(3) 1 1.4792 2 120.0
O(4) 1 1.4792 2 120.0 3 180.0

Rotational Constants

0.3211, 0.3211, 0.1606

Vibrational Frequencies

152, 152, 424, 1009, 1107, 1108



PO_3 - $^2B_2$ - C_{2v}

Z-matrix

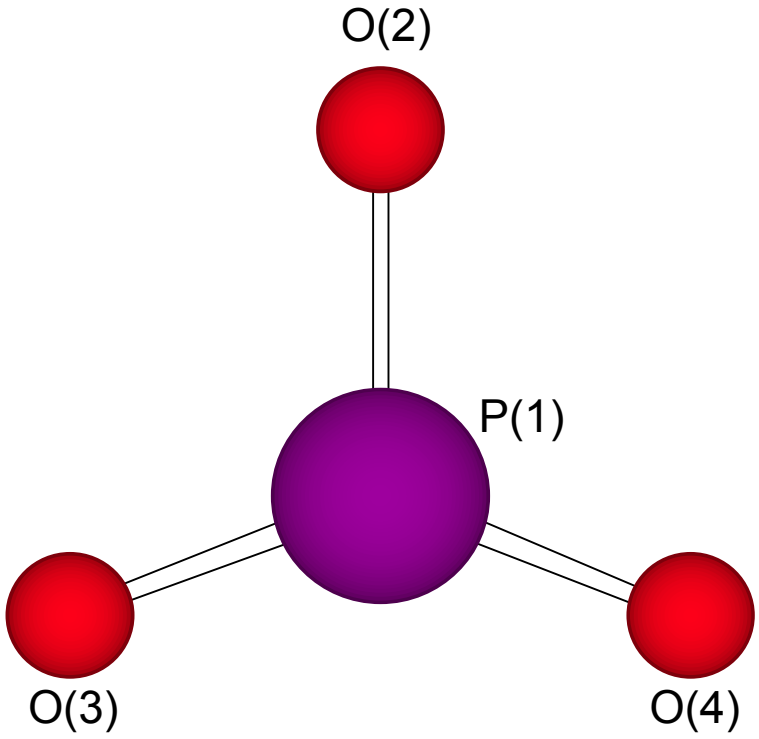
P(1)
O(2) 1 1.6076
O(3) 1 1.4726 2 111.4
O(4) 1 1.4726 2 111.4 3 180.0

Rotational Constants

0.3394, 0.2804, 0.1535

Vibrational Frequencies

343, 431, 434, 856, 1176, 1465



PPO - $^1\Sigma$ - $C_{\infty v}$

G3

Z-matrix

P(1)
P(2) 1 1.9217
O(3) 1 1.5029 2 180.0

Rotational Constant

0.1255

Vibrational Frequencies

179, 179, 669, 1275

G3X

Z-matrix

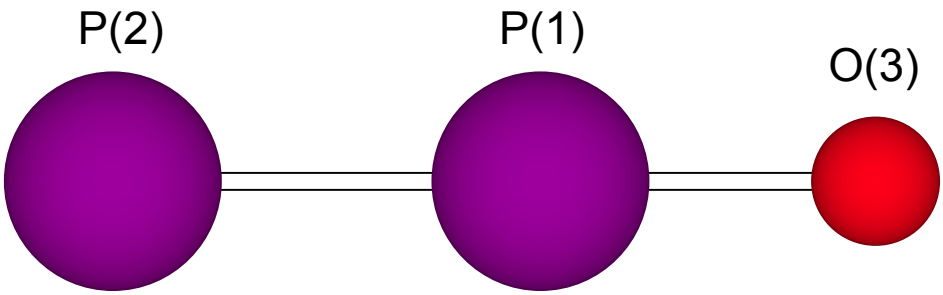
P(1)
P(2) 1 1.8926
O(3) 1 1.4730 2 180.0

Rotational Constant

0.1298

Vibrational Frequencies

214, 215, 657, 1294



P_2O - $^1A_1$ - C_{2v}

Z-matrix

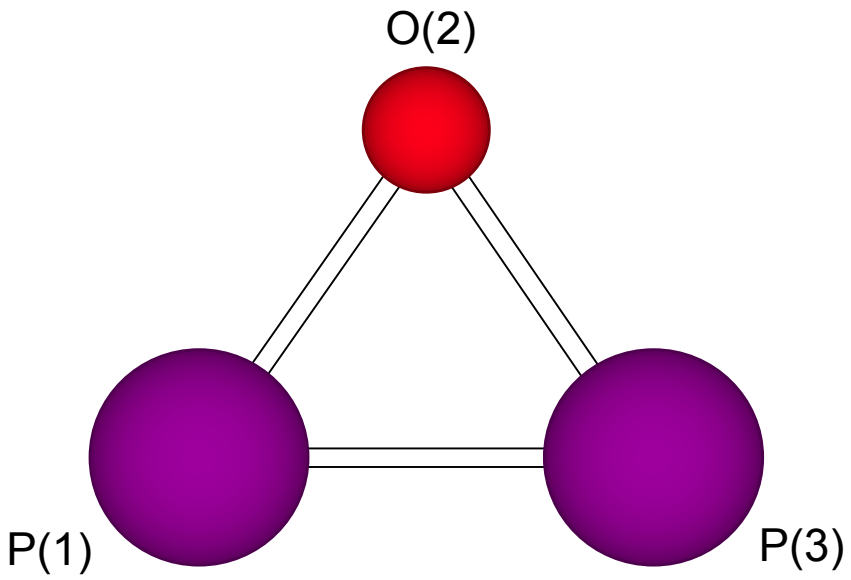
P(1)
O(2) 1 1.7755
P(3) 2 1.7755 1 69.0

Rotational Constants

0.6193, 0.2691, 0.1876

Vibrational Frequencies

241, 655, 825



P_2O_2 - ^1A_g - D_{2h}

G3

Z-matrix

P(1)
O(2) 1 1.6916
P(3) 2 1.6916 1 96.6
O(4) 3 1.6916 2 83.4 1 0.0

Rotational Constants

0.4158, 0.1707, 0.1210

Vibrational Frequencies

24, 446, 615, 720, 759, 912

G3X

Z-matrix

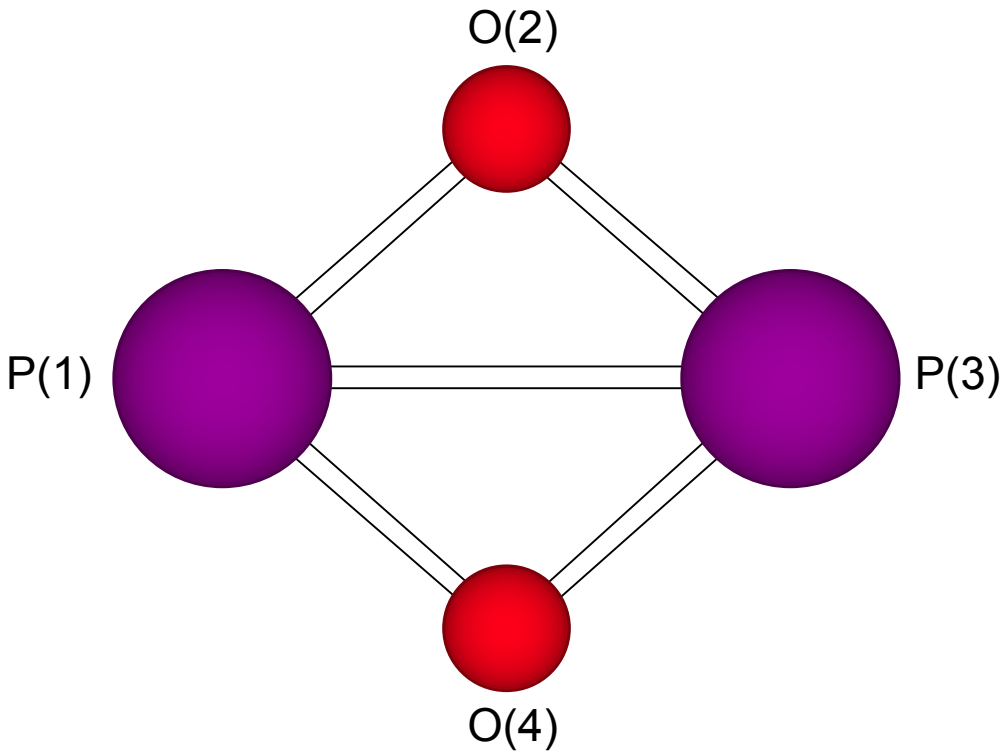
P(1)
O(2) 1 1.6611
P(3) 2 1.6611 1 96.5
O(4) 3 1.6620 2 83.6 1 0.0

Rotational Constants

0.4298, 0.1773, 0.1255

Vibrational Frequencies

445, 552, 619, 708, 731, 876



P_2O_2 - C_1

Z-matrix

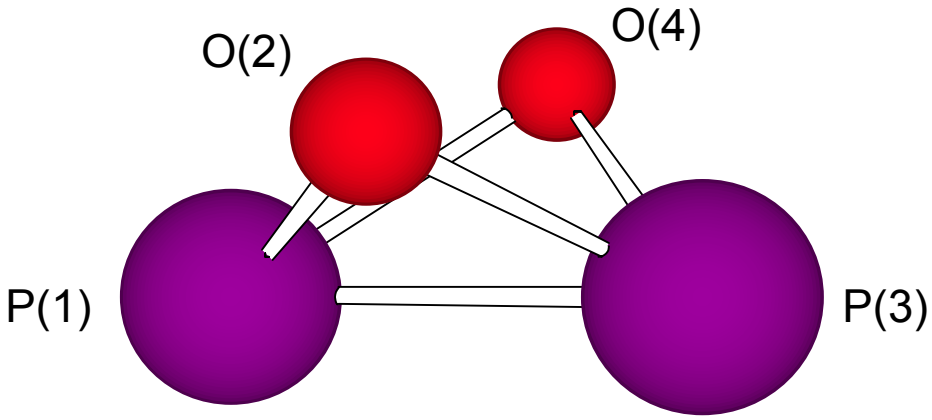
P(1)
O(2) 1 1.7500
P(3) 2 1.7479 1 70.9
O(4) 3 1.7491 2 83.9 1 50.2

Rotational Constants

0.2922, 0.2168, 0.1569

Vibrational Frequencies

385, 396, 513, 652, 785, 877



P_2O_2 - $^3A''$ - C_s

Z-matrix

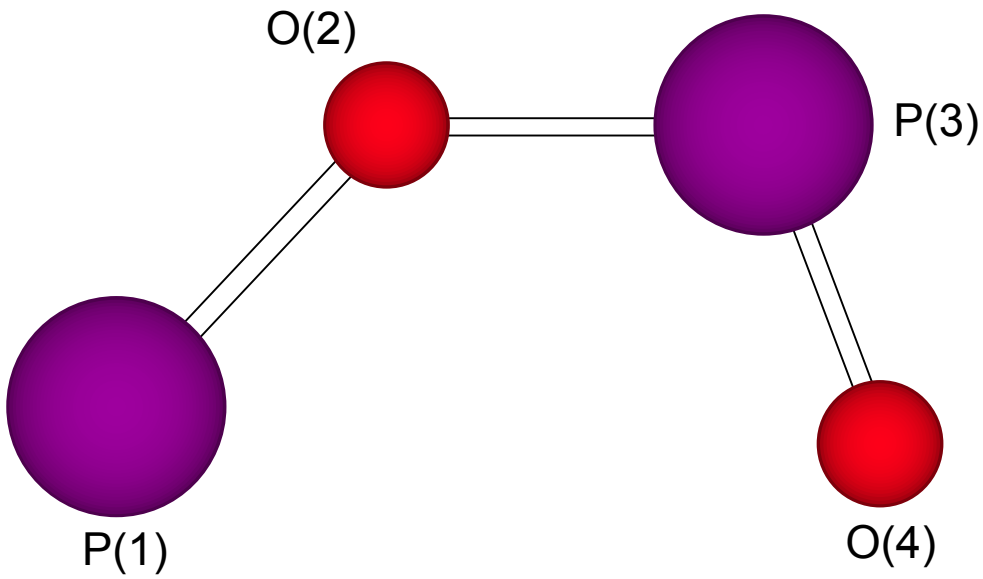
P(1)
O(2) 1 1.6977
P(3) 2 1.6559 1 129.6
O(4) 3 1.4938 2 111.5 1 0.0

Rotational Constants

0.4799, 0.0959, 0.0799

Vibrational Frequencies

129, 168, 463, 591, 875, 1275



P_2O_2 - $^3A''$ - C_s

Z-matrix

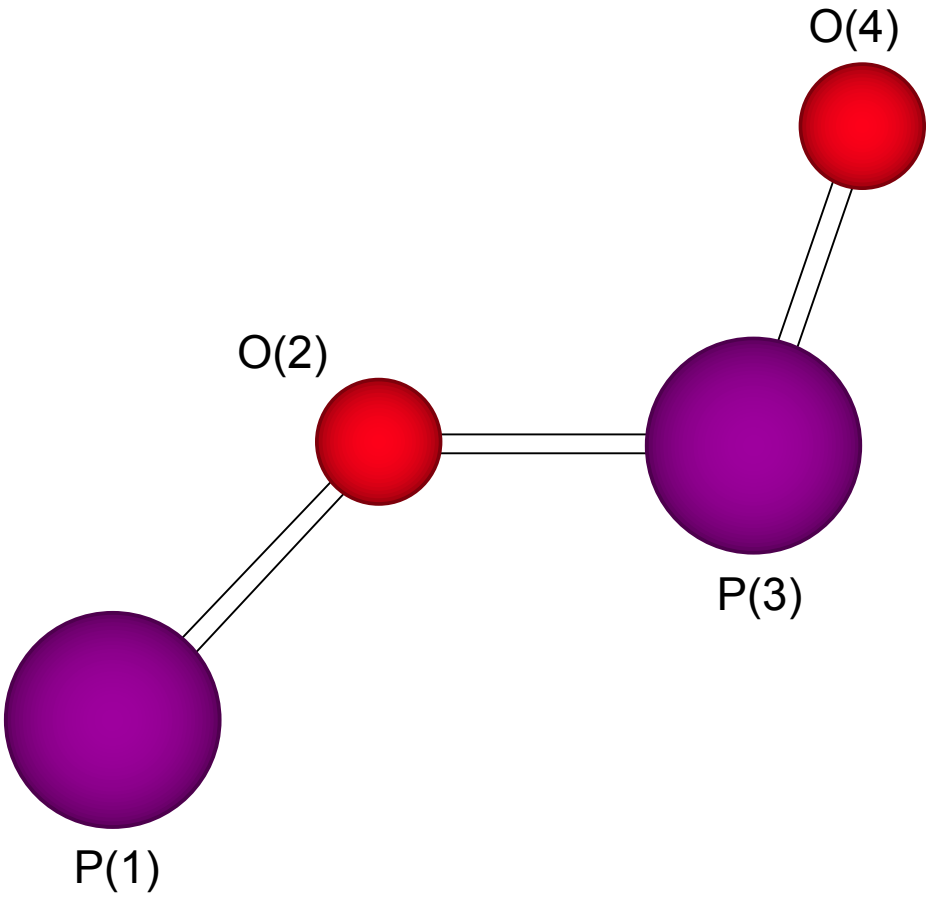
P(1)
O(2) 1 1.6836
P(3) 2 1.6645 1 128.0
O(4) 3 1.4895 2 108.6 1 180.0

Rotational Constants

1.2663, 0.0729, 0.0690

Vibrational Frequencies

93, 137, 346, 646, 893, 1291



P_2O_3 - ^1A - C_2

G3

Z-matrix

O(1)
P(2) 1 1.4920
O(3) 2 1.6787 1 111.1
P(4) 3 1.6787 2 135.3 1 28.3
O(5) 4 1.4920 3 111.1 2 28.3

Rotational Constants

0.2676, 0.0693, 0.0584

Vibrational Frequencies

76, 86, 98, 389, 497, 571, 833, 1279, 1296

G3X

Z-matrix

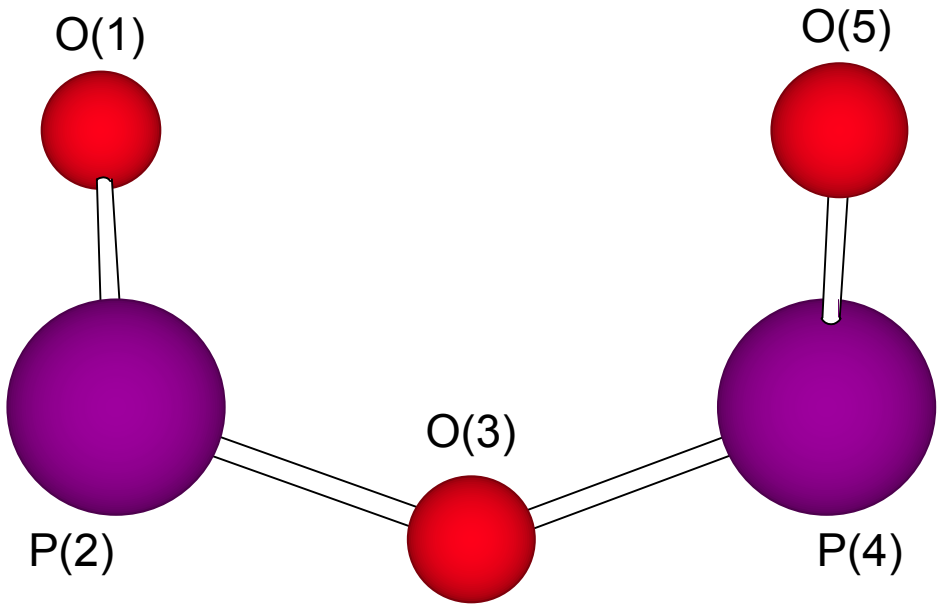
O(1)
P(2) 1 1.4665
O(3) 2 1.6499 1 110.6
P(4) 3 1.6499 2 143.8 1 34.5
O(5) 4 1.4665 3 110.6 2 34.5

Rotational Constants

0.3024, 0.0636, 0.0567

Vibrational Frequencies

52, 72, 94, 390, 459, 555, 841, 1267, 1282



HPO - $^1A'$ - C_s

G3

Z-matrix

P(1)
O(2) 1 1.5170
H(3) 1 1.4530 2 105.6

Rotational Constants

9.0393, 0.6702, 0.6239

Vibrational Frequencies

1007, 1228, 2153

G3X

Z-matrix

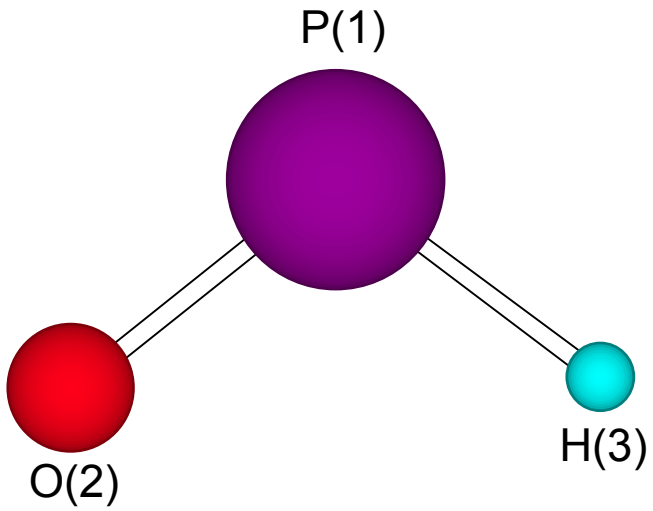
P(1)
O(2) 1 1.4851
H(3) 1 1.4727 2 104.9

Rotational Constants

8.7388, 0.6994, 0.6475

Vibrational Frequencies

998, 1212, 2052



POH - $^3A''$ - C_s

Z-matrix

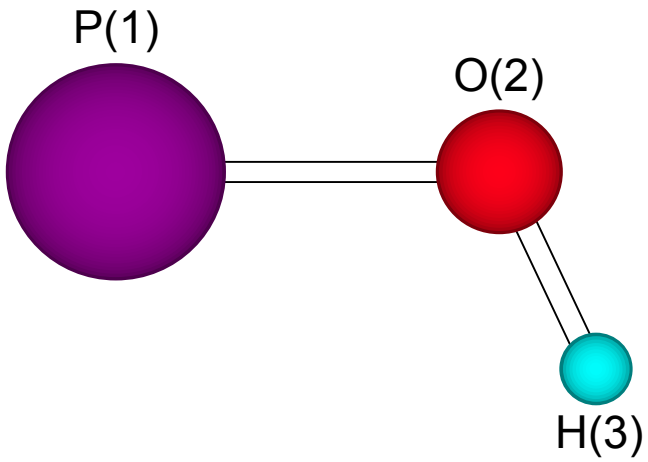
P(1)
O(2) 1 1.6668
H(3) 2 0.9741 1 112.6

Rotational Constants

22.6958, 0.5352, 0.5228

Vibrational Frequencies

798, 928, 3651



HPOH - $^2A''$ - C_s

G3

Z-matrix

P(1)
O(2) 1 1.6759
H(3) 1 1.4161 2 93.8
H(4) 2 0.9730 1 108.9 3 180.0

Rotational Constants

6.2768, 0.5224, 0.4823

Vibrational Frequencies

364, 795, 891, 1091, 2322, 3669

G3X

Z-matrix

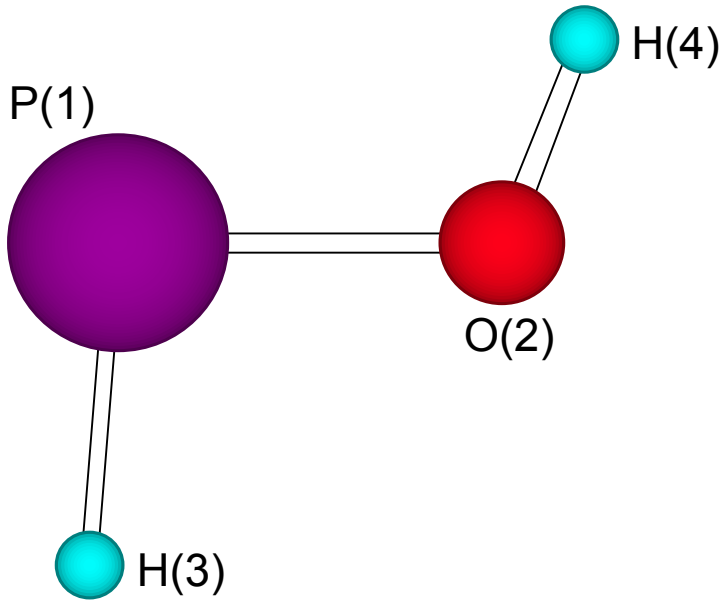
P(1)
O(2) 1 1.6585
H(3) 1 1.4276 2 93.9
H(4) 2 0.9637 1 109.7 3 180.0

Rotational Constants

6.2639, 0.5326, 0.4909

Vibrational Frequencies

441, 812, 913, 1115, 2312, 3772



HPOH - $^2A''$ - C_s

Z-matrix

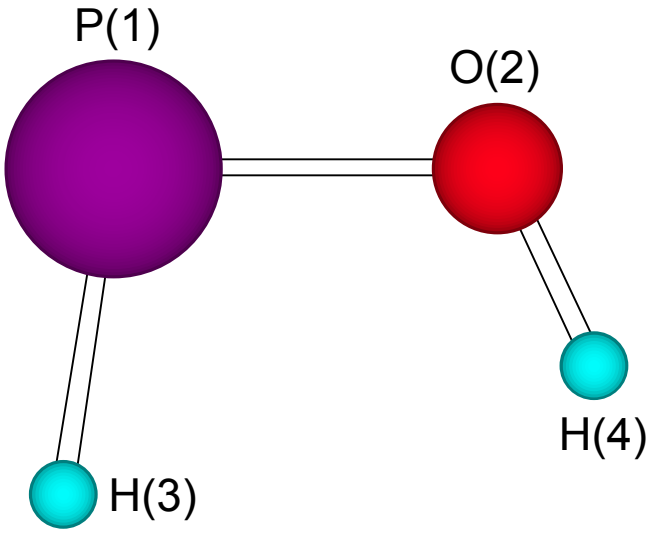
P(1)
O(2) 1 1.6701
H(3) 1 1.4284 2 98.8
H(4) 2 0.9714 1 113.7 3 0.0

Rotational Constants

6.2564, 0.5222, 0.4820

Vibrational Frequencies

178, 797, 878, 1069, 2248, 3685



H_3PO - $^1A_1$ - C_{3v}

G3

Z-matrix

P(1)
O(2) 1 1.4977
H(3) 1 1.4112 2 117.5
H(4) 1 1.4112 2 117.5 3 120.0
H(5) 1 1.4112 2 117.5 3 -120.0

Rotational Constants

3.5612, 0.5645, 0.565

Vibrational Frequencies

855, 855, 1112, 1112, 1147, 1247, 2380, 2380, 2405

G3X

Z-matrix

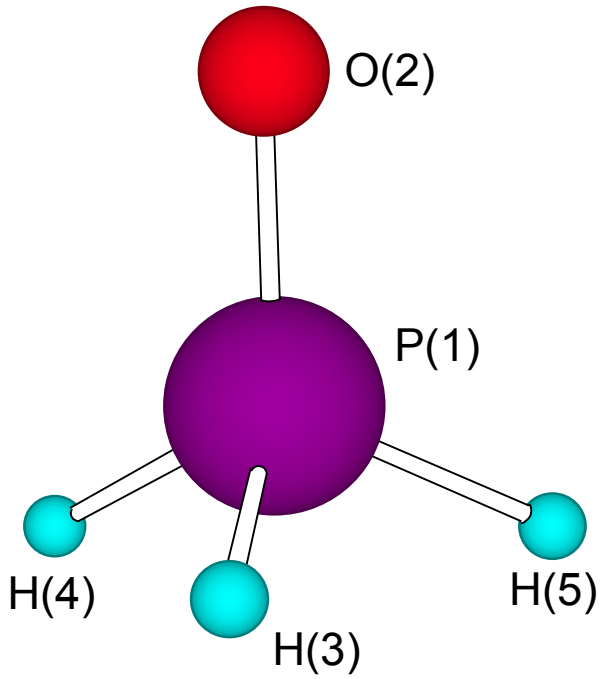
P(1)
O(2) 1 1.4787
H(3) 1 1.4187 2 117.3
H(4) 1 1.4187 2 117.3 3 120.0
H(5) 1 1.4187 2 117.3 3 -120.0

Rotational Constants

3.5060, 0.5764, 0.5764

Vibrational Frequencies

834, 834, 1104, 1104, 1143, 1264, 2345, 2345, 2366



H_2POH - $^1A'$ - C_s

G3

Z-matrix

P(1)
O(2) 1 1.6803
H(3) 2 0.9705 1 108.0
H(4) 1 1.4159 2 99.1 3 132.5
H(5) 1 1.4159 2 99.1 3 -132.5

Rotational Constants

3.7301, 0.4754, 0.4722

Vibrational Frequencies

262, 785, 895, 899, 1117, 1142, 2321, 2331, 3688

G3X

Z-matrix

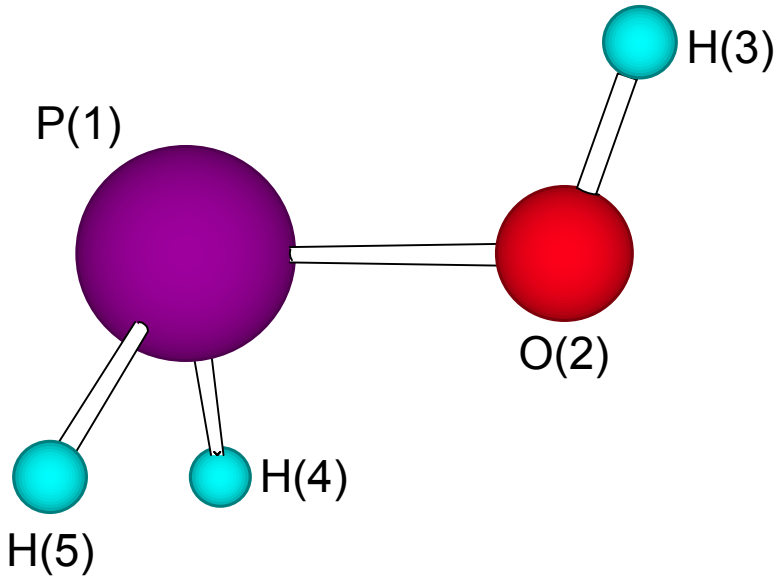
P(1)
O(2) 1 1.6634
H(3) 2 0.9610 1 108.6
H(4) 1 1.4267 2 98.8 3 133.4
H(5) 1 1.4267 2 98.8 3 -133.4

Rotational Constants

3.6995, 0.4845, 0.4801

Vibrational Frequencies

257, 788, 912, 925, 1137, 1144, 2313, 2313, 3804



H_2POH - $^1A'$ - C_s

Z-matrix

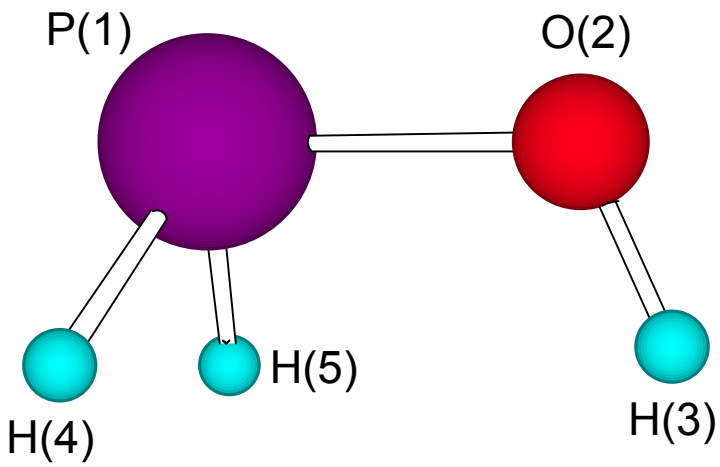
P(1)
O(2) 1 1.6701
H(3) 2 0.9721 1 113.4
H(4) 1 1.4234 2 101.8 3 47.7
H(5) 1 1.4234 2 101.8 3 -47.7

Rotational Constants

3.6989, 0.4778, 0.4741

Vibrational Frequencies

410, 793, 892, 893, 1096, 1144, 2274, 2285, 3663



HOPO - $^1A'$ - C_s

G3

Z-matrix

P(1)
O(2) 1 1.6380
O(3) 1 1.4960 2 110.5
H(4) 2 0.9816 1 112.1 3 0.0

Rotational Constants

1.1834, 0.3082, 0.2445

Vibrational Frequencies

394, 546, 848, 956, 1274, 3591

G3X

Z-matrix

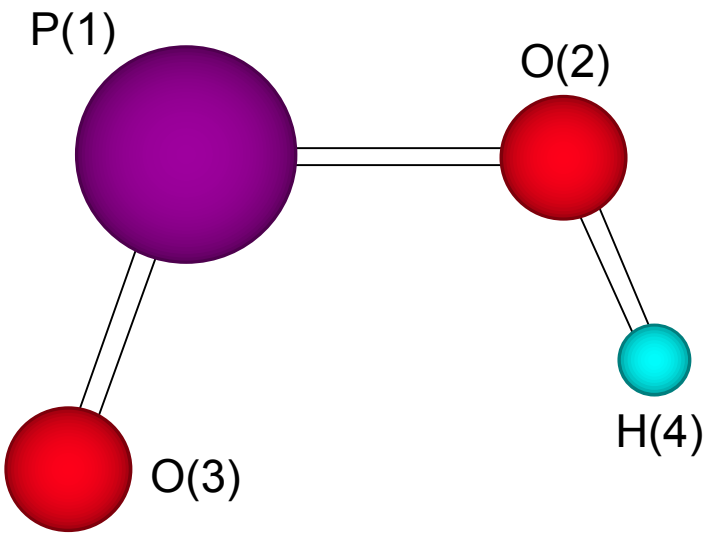
P(1)
O(2) 1 1.6163
O(3) 1 1.4726 2 111.0
H(4) 2 0.9706 1 113.6 3 0.0

Rotational Constants

1.2306, 0.3150, 0.2508

Vibrational Frequencies

379, 556, 837, 944, 1263, 3681



HOPO - $^1A'$ - C_s

Z-matrix

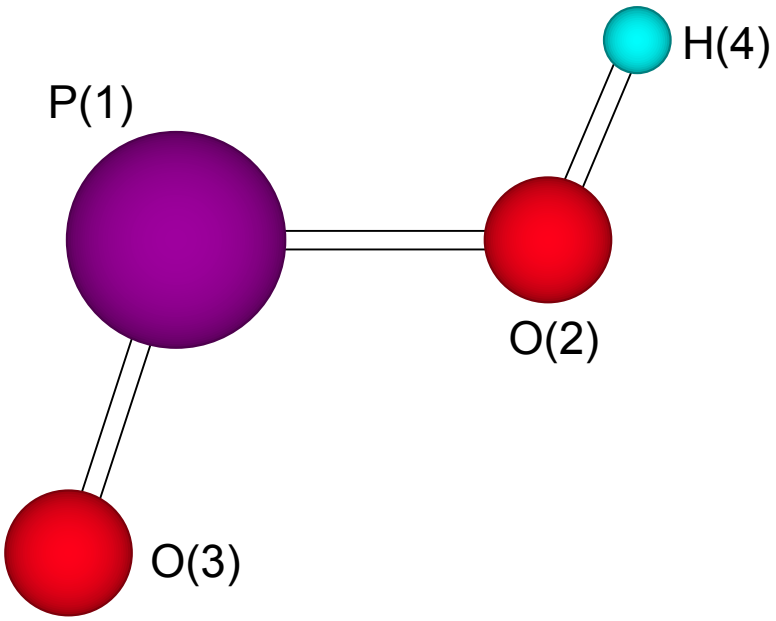
P(1)
O(2) 1 1.6432
O(3) 1 1.4900 2 108.8
H(4) 2 0.9771 1 110.6 3 180.0

Rotational Constants

1.2970, 0.2980, 0.2423

Vibrational Frequencies

408, 450, 828, 952, 1296, 3637



HPO_2 - $^1A_1$ - C_{2v}

Z-matrix

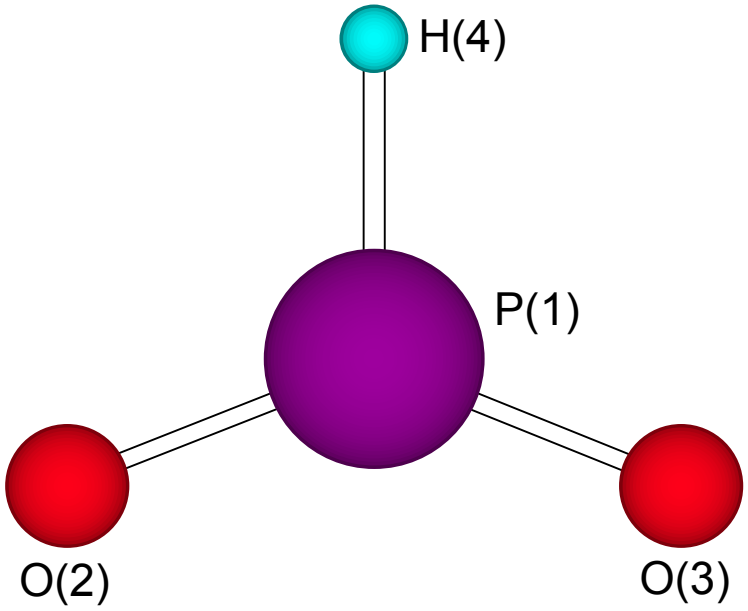
P(1)
O(2) 1 1.4793
O(3) 1 1.4793 2 134.9
H(4) 1 1.4034 2 112.5 3 180.0

Rotational Constants

2.1344, 0.2823, 0.2493

Vibrational Frequencies

475, 663, 1053, 1151, 1454, 2476



$HOPO_2$ - $^1A'$ - C_s

G3

Z-matrix

P(1)
O(2) 1 1.6047
O(3) 1 1.4728 2 112.1
O(4) 1 1.4788 2 113.5 3 180.0
H(5) 2 0.9779 1 110.5 3 180.0

Rotational Constants

0.3110, 0.2799, 0.1473

Vibrational Frequencies

391, 433, 450, 515, 899, 1028, 1180, 1445, 3623

G3X

Z-matrix

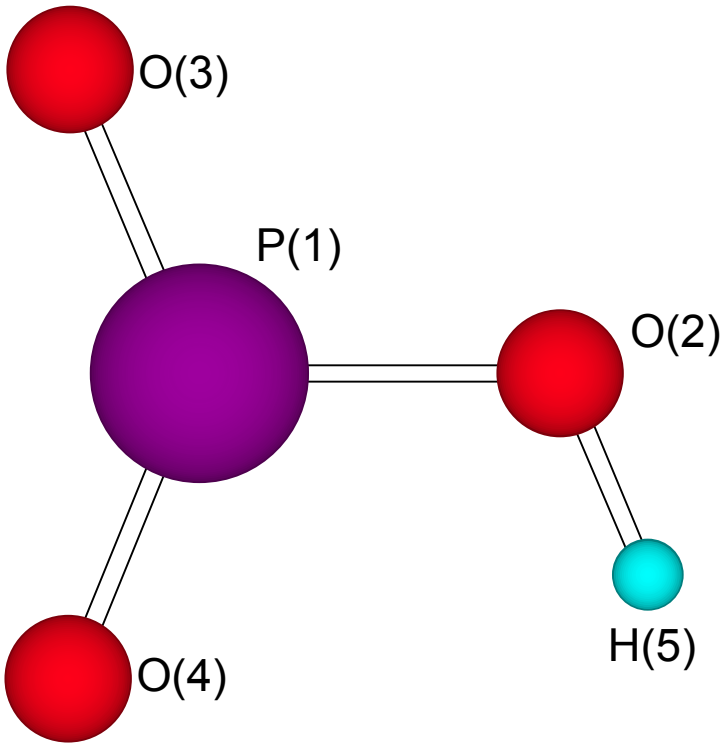
P(1)
O(2) 1 1.5846
O(3) 1 1.4536 2 112.0
O(4) 1 1.4591 2 113.9 3 180.0
H(5) 2 0.9677 1 111.2 3 180.0

Rotational Constants

0.3175, 0.2883, 0.1511

Vibrational Frequencies

391, 424, 435, 502, 889, 1036, 1179, 1452, 3736



Appendix 2.2 Computed Heats of Reaction for Twarowski's[a] data set.

Reaction No.	Reaction	$\Delta_r H^0_{298}$ (kcal mol^{-1})			
		G3	G3X[b]	Literature[c]	Diff(G3X–Lit)
1	$H + H \rightarrow H_2$	–104.7	–104.6	–104.2	–0.4
2	$O + O \rightarrow O_2$	–118.0	–119.1	–119.1	0.0
3	$H + O \rightarrow OH$	–103.2	–103.2	–102.8	–0.4
4	$H + OH \rightarrow H_2O$	–118.0	–118.0	–118.7	0.7
5	$H + O_2 \rightarrow HO_2$	–49.9	–48.9	–48.8	–0.1
6	$H + O_2 \rightarrow OH + O$	14.8	15.9	16.3	–0.4
7	$H_2 + OH \rightarrow H_2O + H$	–13.3	–13.4	–14.5	1.1
8	$OH + OH \rightarrow O + H_2O$	–14.7	–14.8	–15.9	1.1
9	$O + H_2 \rightarrow OH + H$	1.4	1.4	1.4	0.0
10	$HO_2 + H \rightarrow OH + OH$	–38.6	–38.4	–37.7	–0.7
11	$HO_2 + H \rightarrow H_2 + O_2$	–54.8	–55.7	–55.4	–0.3
12	$HO_2 + O \rightarrow O_2 + OH$	–53.3	–54.3	–54.0	–0.3
13	$HO_2 + OH \rightarrow H_2O + O_2$	–68.1	–69.1	–69.9	0.8
14	$H + PO \rightarrow HPO$	–65.1	–65.4	–66.9	1.5
15	$H + PO_2 \rightarrow HOPO$	–92.9	–92.2	–94.2	2.0
16	$H + PO_3 \rightarrow HOPO_2$	–115.2	–113.2	–116.0	2.8
17	$H + HPO \rightarrow HPOH$	–54.1	–53.5		
18	$H + P \rightarrow PH$	–71.7	–72.0		
19	$PH_2 + H \rightarrow PH_3$	–81.6	–81.8		
20	$PH + H \rightarrow PH_2$	–75.5	–75.6		
21	$HPOH + H \rightarrow H_2POH$	–76.5	–77.3		
22	$O + PO \rightarrow PO_2$	–119.5	–120.9	–122.0	1.1
23	$PO_2 + O \rightarrow PO_3$	–93.7	–95.8	–96.8	1.0
24	$HOPO + O \rightarrow HOPO_2$	–116.0	–116.7	–118.6	1.9
25	$P + O \rightarrow PO$	–142.7	–143.9	–143.0	–0.9
26	$P_2 + O \rightarrow P_2O$	–89.5	–72.5		
27	$PH + O \rightarrow HPO$	–136.1	–137.3		
28	$O + P_2O \rightarrow P_2O_2$	–124.8	–126.2		
29	$OH + PO \rightarrow HOPO$	–109.1	–110.0	–113.4	3.5
30	$OH + PO_2 \rightarrow HOPO_2$	–105.7	–105.7	–109.9	4.2
31	$OH + PH_2 \rightarrow H_2POH$	–87.9	–89.2		
32	$PH + OH \rightarrow HPOH$	–86.9	–87.5		
33	$PO + PO \rightarrow P_2O_2$	–44.6	–46.0		
34	$PO + PO_2 \rightarrow P_2O_3$	–76.0	–76.4		
35	$PO + P \rightarrow P_2O$	–62.5	–63.6		
36	$P + P \rightarrow P_2$	–115.8	–135.0		

Reaction No.	Reaction	$\Delta_r H^0_{298}$ (kcal mol^{-1})			
		G3	G3X[b]	Literature[c]	Diff(G3X–Lit)
37	$P_2 + P_2 \rightarrow P_4$	–52.7	–52.3		
38	$H_2O + PO_3 \rightarrow OH + HOPO_2$	2.8	4.9	2.7	2.1
39	$H_2 + PO_3 \rightarrow HOPO_2 + H$	–10.5	–8.6	–11.8	3.2
40	$O_2 + PO \rightarrow O + PO_2$	–1.5	–1.8	–2.9	1.1
41	$P + O_2 \rightarrow O + PO$	–24.8	–24.8	–23.9	–0.9
42	$O_2 + PH \rightarrow O + HPO$	–18.1	–18.2		
43	$H + HOPO \rightarrow H_2O + PO$	–8.8	–8.0	–5.3	–2.7
44	$H + HOPO \rightarrow H_2 + PO_2$	–11.8	–12.4	–10.0	–2.4
45	$H + HOPO_2 \rightarrow H_2O + PO_2$	–12.3	–12.3	–8.8	–3.5
46	$H + PO_3 \rightarrow O + HOPO$	0.9	3.5	2.5	1.0
47	$H + PO_3 \rightarrow OH + PO_2$	–9.5	–7.4	–6.1	–1.4
48	$H + P_2O_3 \rightarrow HOPO + PO$	–16.9	–15.8		
49	$H + HPO \rightarrow H_2 + PO$	–39.6	–39.2	–37.3	–1.9
50	$H + PH_3 \rightarrow H_2 + PH_2$	–23.0	–22.8		
51	$H + PH_2 \rightarrow H_2 + PH$	–29.2	–29.0		
52	$H + PH \rightarrow H_2 + P$	–32.9	–32.6		
53	$H + P_2O \rightarrow OH + P_2$	–13.7	–30.7		
54	$H + P_2O \rightarrow PO + PH$	–9.2	–8.4		
55	$H + P_2O \rightarrow HPO + P$	–2.5	–1.8		
56	$H + P_2O_2 \rightarrow PO + HPO$	–20.4	–19.5		
57	$H + H_2POH \rightarrow H_2O + PH2$	–30.0	–28.8		
58	$H + H_2POH \rightarrow H_2 + HPOH$	–28.2	–27.3		
59	$H + HPOH \rightarrow H_2O + PH$	–31.0	–30.5		
60	$H + HPOH \rightarrow H_2 + HPO$	–50.6	–51.1		
61	$O + HOPO \rightarrow OH + PO_2$	–10.4	–11.0	–8.6	–2.4
62	$O + HOPO_2 \rightarrow O_2 + HOPO$	–1.9	–2.4	–0.6	–1.8
63	$O + PO_3 \rightarrow O_2 + PO_2$	–24.3	–23.3	–22.3	–1.0
64	$O + P_2O_3 \rightarrow PO + PO_3$	–17.7	–19.4		
65	$O + P_2O_3 \rightarrow PO_2 + PO_2$	–43.6	–44.5		
66	$O + HPO \rightarrow H + PO_2$	–54.5	–55.5	–55.1	–0.4
67	$O + HPO \rightarrow OH + PO$	–38.2	–37.8	–35.9	–1.9
68	$O + P_2 \rightarrow P + PO$	–27.0	–8.9		
69	$O + PH_3 \rightarrow OH + PH_2$	–21.6	–21.4		
70	$O + PH_2 \rightarrow H + HPO$	–60.6	–61.6		
71	$O + PH_2 \rightarrow OH + PH$	–27.8	–27.6		
72	$O + PH \rightarrow H + PO$	–71.0	–71.9		
73	$O + PH \rightarrow OH + P$	–31.5	–31.2		

Reaction No.	Reaction	$\Delta_r H^0_{298}$ (kcal mol^{-1})			
		G3	G3X[b]	Literature[c]	Diff(G3X–Lit)
74	$O + P_2O \rightarrow O_2 + P_2$	–28.5	–46.6		
75	$O + P_2O \rightarrow PO + PO$	–80.2	–80.3		
76	$O + P_2O \rightarrow PO_2 + P$	–57.0	–57.3		
77	$O + P_2O_2 \rightarrow O_2 + P_2O$	6.8	7.1		
78	$O + P_2O_2 \rightarrow PO + PO_2$	–74.9	–75.0		
79	$O + H_2POH \rightarrow OH + HPOH$	–26.8	–25.9		
80	$O + HPOH \rightarrow H + HOPO$	–93.2	–94.3		
81	$O + HPOH \rightarrow OH + HPO$	–49.1	–49.7		
82	$OH + PO \rightarrow H + PO_2$	–16.3	–17.7	–19.2	1.5
83	$OH + HOPO \rightarrow H_2O + PO_2$	–25.1	–25.8	–24.5	–1.3
84	$OH + HOPO \rightarrow H + HOPO_2$	–12.8	–13.5	–15.7	2.2
85	$OH + PO_3 \rightarrow O + HOPO_2$	–12.0	–10.0	–13.2	3.2
86	$OH + P_2O_3 \rightarrow PO + HOPO_2$	–29.7	–29.3		
87	$OH + P_2O_3 \rightarrow PO_2 + HOPO$	–33.2	–33.6		
88	$OH + HPO \rightarrow H_2O + PO$	–52.9	–52.6	–51.8	–0.8
89	$OH + HPO \rightarrow H + HOPO$	–44.1	–44.6	–46.5	2.0
90	$OH + P \rightarrow H + PO$	–39.5	–40.7	–40.1	–0.5
91	$OH + PH_3 \rightarrow H_2O + PH_2$	–36.4	–36.2		
92	$OH + PH_3 \rightarrow H + H_2POH$	–6.3	–7.3		
93	$OH + PH_2 \rightarrow H_2O + PH$	–42.5	–42.4		
94	$OH + PH_2 \rightarrow H + HPOH$	–11.5	–11.9		
95	$OH + PH \rightarrow H_2O + P$	–46.3	–46.0		
96	$OH + PH \rightarrow H + HPO$	–32.8	–34.1		
97	$OH + P_2O \rightarrow H + P_2O_2$	–21.6	–23.0		
98	$OH + P_2O \rightarrow P + HOPO$	–46.6	–46.4		
99	$OH + P_2O_2 \rightarrow PO + HOPO$	–64.5	–64.0		
100	$OH + H_2POH \rightarrow H_2O + HPOH$	–41.5	–40.7		
101	$OH + HPOH \rightarrow H_2O + HPO$	–63.9	–64.6		
102	$HO_2 + PO \rightarrow O_2 + HPO$	–15.1	–16.5	–18.1	1.6
103	$HO_2 + PO \rightarrow O + HOPO$	–44.5	–45.2	–48.4	3.2
104	$HO_2 + PO \rightarrow OH + PO_2$	–54.9	–56.2	–57.0	0.8
105	$HO_2 + PO_2 \rightarrow O_2 + HOPO$	–42.9	–43.4	–45.4	2.1
106	$HO_2 + PO_2 \rightarrow O + HOPO_2$	–41.0	–41.0	–44.9	3.9
107	$HO_2 + PO_2 \rightarrow OH + PO_3$	–29.1	–31.0	–31.7	0.7
108	$HO_2 + HOPO \rightarrow OH + HOPO_2$	–51.4	–51.9	–53.5	1.6
109	$HO_2 + PO_3 \rightarrow O_2 + HOPO_2$	–65.3	–64.3	–67.2	2.9
110	$HO_2 + HPO \rightarrow O_2 + HPOH$	–4.2	–4.6		

Reaction No.	Reaction	$\Delta_r H^0_{298}$ (kcal mol^{-1})			
		G3	G3X[b]	Literature[c]	Diff(G3X–Lit)
111	$HO_2 + P \rightarrow O_2 + PH$	–21.8	–23.1		
112	$HO_2 + P \rightarrow OH + PO$	–78.1	–79.1	–77.9	–1.2
113	$HO_2 + P_2 \rightarrow OH + P_2O$	–24.9	–7.7		
114	$HO_2 + PH_2 \rightarrow O_2 + PH_3$	–31.7	–32.9		
115	$HO_2 + PH_2 \rightarrow O + H_2POH$	–23.3	–24.4		
116	$HO_2 + PH \rightarrow O_2 + PH_2$	–25.6	–26.8		
117	$HO_2 + PH \rightarrow O + HPOH$	–22.3	–22.8		
118	$HO_2 + PH \rightarrow OH + HPO$	–71.4	–72.5		
119	$HO_2 + P_2O \rightarrow OH + P_2O_2$	–60.2	–61.4		
120	$HO_2 + HPOH \rightarrow O_2 + H_2POH$	–26.6	–28.4		
121	$PO + HOPO_2 \rightarrow HOPO + PO_2$	–3.5	–4.2	–3.5	–0.7
122	$PO + PO_3 \rightarrow PO_2 + PO_2$	–25.8	–25.2	–25.3	0.1
123	$PO + P_2O \rightarrow PO_2 + P_2$	–30.0	–48.4		
124	$PO + P_2O_2 \rightarrow PO_2 + P_2O$	5.3	5.3		
125	$PO + H_2POH \rightarrow HOPO + PH_2$	–21.2	–20.8		
126	$PO + HPOH \rightarrow HOPO + PH$	–22.2	–22.4		
127	$PO + HPOH \rightarrow HPO + HPO$	–11.0	–11.9		
128	$PO_2 + HPO \rightarrow H + P_2O_3$	–10.9	–11.0		
129	$PO_2 + HPO \rightarrow PO + HOPO$	–27.8	–26.8	–27.3	0.5
130	$PO_2 + P \rightarrow PO + PO$	–23.2	–23.0	–20.9	–2.0
131	$PO_2 + PH_3 \rightarrow HOPO + PH_2$	–11.2	–10.4		
132	$PO_2 + PH_2 \rightarrow HOPO + PH$	–17.4	–16.6		
133	$PO_2 + PH \rightarrow PO + HPO$	–16.6	–16.3		
134	$PO_2 + PH \rightarrow HOPO + P$	–21.1	–20.2		
136	$PO_2 + P_2O \rightarrow PO_3 + P_2$	–4.2	–23.3		
136	$PO_2 + P_2O \rightarrow P_2O_3 + P$	–13.4	–12.8		
137	$PO_2 + P_2O \rightarrow PO + P_2O_3$	–31.4	–30.5		
138	$PO_2 + H_2POH \rightarrow HOPO + HPOH$	–16.4	–15.0		
139	$PO_2 + H_2POH \rightarrow HOPO_2 + PH_2$	–17.7	–16.6		
140	$PO_2 + HPOH \rightarrow HOPO + HPO$	–38.8	–38.8		
141	$PO_2 + HPOH \rightarrow HOPO_2 + PH$	–18.7	–18.2		
142	$HOPO + PO_3 \rightarrow PO_2 + HOPO_2$	–22.3	–20.9	–21.8	0.9
143	$HOPO + P_2O \rightarrow HOPO_2 + P_2$	–26.5	–44.2		
145	$HOPO + P_2O_2 \rightarrow HOPO_2 + P_2O$	8.8	9.5		
145	$HOPO_2 + P \rightarrow PO + HOPO$	–26.7	–27.2	–24.4	–2.8
146	$HOPO_2 + PH \rightarrow HOPO + HPO$	–20.0	–20.6		
147	$PO_3 + HPO \rightarrow PO + HOPO_2$	–50.1	–47.8	–49.1	1.3

Reaction No.	Reaction	$\Delta_r H^0_{298}$ (kcal mol^{-1})			
		G3	G3X[b]	Literature[c]	Diff(G3X–Lit)
148	$PO_3 + P \rightarrow PO + PO_2$	–49.0	–48.1	–46.2	–1.9
149	$PO_3 + PH_3 \rightarrow HOPO_2 + PH_2$	–33.6	–31.3		
150	$PO_3 + PH_2 \rightarrow HOPO_2 + PH$	–39.7	–37.5		
152	$PO_3 + PH \rightarrow HPO + PO_2$	–42.4	–41.5		
152	$PO_3 + PH \rightarrow HOPO_2 + P$	–43.5	–41.1		
153	$PO_3 + P_2O \rightarrow PO_2 + P_2O_2$	–31.1	–30.4		
154	$PO_3 + H_2POH \rightarrow HOPO_2 + HPOH$	–38.7	–35.9		
156	$PO_3 + HPOH \rightarrow HOPO_2 + HPO$	–61.1	–59.7		
156	$HPO + P \rightarrow PO + PH$	–6.7	–6.6		
157	$HPO + PH_2 \rightarrow PO + PH_3$	–16.6	–16.4		
158	$HPO + PH \rightarrow PO + PH_2$	–10.4	–10.2		
159	$HPO + HPOH \rightarrow PO + H_2POH$	–11.4	–11.9		
161	$P + PH \rightarrow H + P_2$	–44.0	–63.0		
161	$P + P_2O \rightarrow PO + P_2$	–53.2	–71.4		
162	$P + P_2O_2 \rightarrow PO + P_2O$	–17.9	–17.7		
164	$P + HPOH \rightarrow HPO + PH$	–17.6	–18.6		
164	$PH + PH_3 \rightarrow PH_2 + PH_2$	6.1	6.2		
165	$PH_3 + HPOH \rightarrow PH_2 + H_2POH$	5.1	4.6		
166	$PH_2 + PH \rightarrow P + PH_3$	–9.9	–9.8		
168	$PH_2 + HPOH \rightarrow HPO + PH_3$	–27.5	–28.4		
168	$PH + PH \rightarrow P + PH_2$	–3.7	–3.6		
169	$PH + P_2O \rightarrow HPO + P_2$	–46.5	–64.8		
170	$PH + P_2O_2 \rightarrow HPO + P_2O$	–11.3	–11.1		
171	$PH + H_2POH \rightarrow PH_2 + HPOH$	1.0	1.6		
172	$PH + HPOH \rightarrow HPO + PH_2$	–21.4	–22.2		
173	$PH + HPOH \rightarrow P + H_2POH$	–4.7	–5.3		
174	$P_2O + P_2O \rightarrow P_2 + P_2O_2$	–35.3	–53.7		
175	$HPOH + HPOH \rightarrow HPO + H_2POH$	–22.4	–23.8		

[a] A. Twarowski, *Combustion and Flame*, **1995**, *102*, 41.

[b] Using experimental $\Delta_f H^0_{298}$ for H, O and P and G3X(RAD) type $\Delta_f H^0_{298}$ for PO and PO_2.

[c] Using experimental $\Delta_f H^0_{298}$ for H, O, P, OH, H_2O and Bauschlicher's CBS data for PO, PO_2, PO_3, HPO, HOPO, $HOPO_2$ (C. W. Bauschlicher, Jr., *J. Phys. Chem. A*, **1999**, *103*, 11126.).

Appendix 2.3 Transition State Geometries (Z-matrices with bond lengths in Å and angles in degrees).

1a: H + PO_2 → HOPO

1000, 1250 K

P						
O	1	1.497				
O	1	1.464	2	129.0		
H	2	2.501	1	95.6	3	0.0

1500, 1750, 2000 K

P						
O	1	1.500				
O	1	1.464	2	128.1		
H	2	2.426	1	96.8	3	0.0

1b: HOPO + H → PO_2 + H_2

P						
O	1	1.564				
O	1	1.491	2	121.4		
H	2	1.310	1	122.2	3	0.0
H	4	0.858	2	178.9	1	0.0

1c: H_2 + OH → H_2O + H

O						
H	1	0.979				
H	1	1.293	2	98.8		
H	3	0.841	1	167.3	2	0.0

2a: PO_2 +OH → $HOPO_2$

1000 K

P						
O	1	1.481				
O	1	1.482	2	129.4		
O	1	2.927	2	118.7	3	–180.0
H	4	0.961	1	112.0	2	180.0

1250 K

P						
O	1	1.480				
O	1	1.482	2	129.3		
O	1	2.839	2	117.8	3	–180.0
H	4	0.962	1	110.7	2	180.0

1500 K

P						
O	1	1.480				
O	1	1.482	2	129.2		
O	1	2.794	2	117.4	3	–180.0
H	4	0.962	1	110.3	2	180.0

1750 K

P						
O	1	1.479				
O	1	1.481	2	129.2		
O	1	2.747	2	116.9	3	–180.0
H	4	0.963	1	110.0	2	180.0

2000 K

P						
O	1	1.479				
O	1	1.481	2	129.3		
O	1	2.699	2	116.5	3	–180.0
H	4	0.963	1	110.0	2	180.0

2b: $HOPO_2$ + H → PO_2 + H_2O

P						
O	1	1.483				
O	1	1.487	2	135.7		
O	1	1.761	2	112.3	3	156.1
H	4	0.989	1	107.2	2	21.3
H	4	1.285	1	135.3	2	–106.8

Appendix 2.4 Transition State Vibrational Frequencies and Rotational Constants (in cm^{-1}).

Reaction	Temperature(s)	Rotational Constants			Vibrational Frequencies					
1a: $H + PO_2 \rightarrow HOPO$	1000, 1250 K	1.2566	0.2936	0.2380	340*i*	82	152	406	1022	1329
	1500, 1750, 2000 K	1.2632	0.2946	0.2389	444*i*	81	169	407	997	1321
1b: $HOPO + H \rightarrow PO_2 + H_2$	All	1.0019	0.2722	0.2140	2668*i*	224	270	469	774	787
					899	1276	1477			
1c: $H_2 + OH \rightarrow H_2O + H$	All	18.5846	2.9867	2.5732	2813*i*	628	675	1283	1443	3602
2a: $PO_2 + OH \rightarrow HOPO_2$	1000 K	0.2919	0.1124	0.0812	200*i*	86	126	164	426	470
					1087	1212	3982			
	1250 K	0.2918	0.1154	0.0827	211*i*	93	134	175	428	504
					1089	1211	3978			
	1500 K	0.2916	0.1219	0.0860	236*i*	108	152	199	432	579
					1095	1207	3967			
	1750 K	0.2915	0.1255	0.0877	250*i*	117	162	212	434	620
					1097	1201	3961			
	2000 K	0.2914	0.1294	0.0896	265*i*	127	173	226	437	663
					1100	1193	3953			
2b: $HOPO_2 + H \rightarrow PO_2 + H_2O$	All	0.2708	0.2481	0.1321	3665*i*	244	279	327	438	531
					632	738	1115	1238	1405	3530

Appendix 3: NNH + O Supplementary Information

Appendix 3.1 B3LYP/6-31G(2*df*,*p*) geometries (Z-matrices) for minima and first order saddle points on the N_2OH potential energy surface (in Å and degrees).

N_2 - $^1\Sigma_g$

```
N
N     1   1.099
```

NH - $^3\Sigma$

```
N
H     1   1.045
```

NO - $^2\Pi$

```
N
O     1   1.151
```

OH - $^2\Pi$

```
O
H     1   0.976
```

NNH - $^2A'$

```
N
N     1   1.175
H     1   1.059   2   117.3
```

NNO - $^1\Sigma$

```
N
N     1   1.128
O     1   1.186   2   180.0
```

HNO - $^1A'$

```
N
O     1   1.201
H     1   1.069   2   108.7
```

NN-H - $^2A'$

```
N
N     1   1.117
H     1   1.542   2   119.0
```

trans-ONNH - ^{2}A′

N						
N	1	1.245				
O	1	1.201	2	132.2		
H	2	1.024	1	107.5	3	180.0

cis-ONNH - ^{2}A′

N						
N	1	1.229				
O	1	1.210	2	139.3		
H	2	1.037	1	110.0	3	0.0

ONHN - ^{2}A′

N						
N	1	1.251				
O	1	1.242	2	129.7		
H	1	1.045	2	112.7	3	180.0

ONN-H - ^{2}A′

N						
N	1	1.142				
O	1	1.188	2	173.0		
H	2	1.650	1	113.7	3	0.0

ON_2-H - ^{2}A′

N						
N	1	1.163				
O	1	1.207	2	155.6		
H	1	1.512	2	100.3	3	180.0

NNOHsq - ^{2}A′

N						
N	1	1.215				
O	1	1.408	2	96.8		
H	2	1.268	1	89.0	3	0.0

NNOHtr - ^{2}A′

N						
N	1	1.155				
O	1	1.420	2	141.8		
H	1	1.171	3	61.6	2	180.0

ONNH _c-t_ TS - ^{2}A

N						
N	1	1.259				
O	1	1.201	2	133.0		
H	2	1.019	1	116.7	3	90.9

ONHN-ONNH*t* - ^{2}A′

N						
N	1	1.251				
O	1	1.212	2	142.3		
H	1	1.216	2	65.7	3	180.0

Appendix 3.2 B3LYP/6-31G(2*df*,*p*) rotational constants and harmonic vibrational frequencies for minima and first order saddle points on the N_2OH potential energy surface (in cm^{-1}).

Species	Rotational Constant(s)			Scaled Vibrational Frequencies					
N_2	1.9942			2395					
NH	16.4281			3199					
NO	1.7036			1956					
HO	18.6606			3642					
NNH	22.0461	1.5489	1.4472	1108	1854	2757			
NNO	0.4207			615	615	1321	2328		
HNO	18.4723	1.4287	1.3262	1549	1658	2768			
trans-ONNH	6.3081	0.4135	0.3881	653	770	1258	1348	1711	3383
cis-ONNH	5.5599	0.4162	0.3872	573	755	1211	1331	1724	3190
ONHN	3.6496	0.4427	0.3948	550	939	1249	1404	1536	3077
NN-H	11.6966	1.5727	1.3863	1100*i*	641	2191			
ONN-H	7.3044	0.3850	0.3657	946*i*	381	617	663	1284	2213
ON_2-H	4.9909	0.4196	0.3871	1479*i*	668	727	815	1274	1949
NNOHsq	2.0273	0.5747	0.4477	1868*i*	689	905	1000	1605	2030
NNOHtr	5.9012	0.3731	0.3509	1635*i*	498	514	714	1803	2211
ONNH *c*-*t* TS	5.3473	0.4073	0.3910	1133*i*	629	832	1244	1637	3464
ONHN-ONNH*t*	6.0159	0.4075	0.3816	2225*i*	445	665	1257	1689	2255

Appendix 3.3 B3LYP/6-31G(2*df*,*p*) geometries (Z-matrices) for variational transition states on the N_2OH potential energy surface (in Å and degrees).

***trans*-ONNH → NNH + O - ^{2}A′**

1000 K

N						
N	1	1.170				
O	1	2.799	2	107.2		
H	2	1.055	1	118.0	3	180.0

1500 K

N						
N	1	1.169				
O	1	2.574	2	107.0		
H	2	1.053	1	117.8	3	180.0

2000 K

N						
N	1	1.169				
O	1	2.374	2	106.5		
H	2	1.051	1	117.3	3	180.0

2500 K

N						
N	1	1.170				
O	1	2.199	2	106.3		
H	2	1.047	1	116.2	3	180.0

***cis*-ONNH → NNH + O - ^{2}A′**

1000 K

N						
N	1	1.170				
O	1	3.001	2	112.7		
H	2	1.054	1	118.9	3	0.0

1500 K

N						
N	1	1.169				
O	1	2.901	2	111.4		
H	2	1.053	1	119.1	3	0.0

2000 K

N						
N	1	1.168				
O	1	2.751	2	110.1		
H	2	1.051	1	119.5	3	0.0

2500 K

N						
N	1	1.167				
O	1	2.551	2	108.3		
H	2	1.049	1	119.9	3	0.0

ONHN → NNH + O - ^{2}A′

1000 K

N						
N	1	1.168				
O	1	3.024	2	134.9		
H	1	1.055	2	119.5	3	180.0

1500 K

N						
N	1	1.165				
O	1	2.799	2	134.6		
H	1	1.052	2	120.7	3	180.0

2000 K

N						
N	1	1.157				
O	1	2.393	2	134.3		
H	1	1.045	2	124.9	3	180.0

2200 K

N						
N	1	1.147				
O	1	2.093	2	131.4		
H	1	1.035	2	131.2	3	180.0

***trans*-ONNH → NO + NH - ^{2}A**

1000 K

N						
N	1	2.349				
O	1	1.142	2	110.0		
H	2	1.042	1	89.6	3	154.8

1500 K

N						
N	1	2.224				
O	1	1.141	2	110.1		
H	2	1.042	1	90.9	3	145.0

2000 K

N						
N	1	2.124				
O	1	1.141	2	110.1		
H	2	1.041	1	92.2	3	140.9

2400 K

N						
N	1	2.099				
O	1	1.147	2	110.2		
H	2	1.041	1	92.3	3	139.2

cis-ONNH → NO + NH - ^{2}A

1000 K

N						
N	1	2.324				
O	1	1.142	2	109.9		
H	2	1.042	1	90.3	3	154.0

1500 K

N						
N	1	2.199				
O	1	1.141	2	110.1		
H	2	1.041	1	91.3	3	144.9

2000 K

N						
N	1	2.099				
O	1	1.141	2	110.1		
H	2	1.041	1	92.4	3	139.9

2500 K

N						
N	1	2.074				
O	1	1.141	2	110.1		
H	2	1.041	1	92.7	3	141.5

ONHN → HNO + N - ^{4}A

1000 K

N						
N	1	2.169				
O	1	1.207	2	117.4		
H	1	1.051	2	99.5	3	121.5

1500 K

N						
N	1	2.119				
O	1	1.208	2	117.0		
H	1	1.050	2	99.8	3	122.0

2000 K

N						
N	1	2.069				
O	1	1.200	2	116.6		
H	1	1.048	2	100.2	3	122.5

2500 K

N						
N	1	2.044				
O	1	1.211	2	116.4		
H	1	1.047	2	100.4	3	122.8

NNH + O → N_2 + OH - $^2A'$

1000 K

N						
N	1	1.165				
O	1	3.991	2	119.0		
H	1	1.075	2	119.0	3	0.0

1500 K

N						
N	1	1.162				
O	1	3.841	2	119.5		
H	1	1.081	2	119.5	3	0.0

2000 K

N						
N	1	1.158				
O	1	3.691	2	120.4		
H	1	1.091	2	120.4	3	0.0

2500 K

N						
N	1	1.156				
O	1	3.641	2	120.6		
H	1	1.095	2	120.6	3	0.0

Appendix 3.4 B3LYP/6-31G(2*df*,*p*) rotational constants and harmonic vibrational frequencies for variational transition states on the N_2OH potential energy surface (in cm^{-1}).

Reaction	Temp. /K	Rotational Constants			Scaled Vibrational Frequencies					
NNH + O → *trans*-ONNH	1000	2.2571	0.1664	0.1550	118*i*	124	253	1064	1874	2826
	1500	2.3111	0.1918	0.1771	130*i*	164	334	1051	1882	2866
	2000	2.3510	0.2200	0.2012	146*i*	210	408	1041	1885	2920
	2500	2.4076	0.2490	0.2256	216*i*	260	499	1038	1878	2988
NNH + O → *cis*-ONNH	1000	1.9769	0.1492	0.1387	118*i*	100	242	1068	1878	2838
	1500	1.9520	0.1597	0.1476	129*i*	106	290	1064	1884	2855
	2000	1.9367	0.1768	0.1620	139*i*	122	319	1059	1892	2881
	2500	1.9186	0.2042	0.1846	155*i*	142	392	1052	1902	2923
NNH + O → ONHN	1000	3.0576	0.1308	0.1254	102*i*	103	171	1057	1875	2822
	1500	3.0968	0.1488	0.1420	115*i*	129	227	1038	1892	2858
	2000	3.2448	0.1919	0.1812	119*i*	199	312	998	1941	2968
	2200	3.1956	0.2403	0.2235	177*i*	303	448	991	1996	3120
trans-ONNH → NO + NH	1000	2.3006	0.2307	0.2105	155*i*	97	256	575	1944	3223
	1500	2.3483	0.2510	0.2287	227*i*	116	300	651	1935	3226
	2000	2.3895	0.2693	0.2446	306*i*	131	343	722	1923	3231
	2400	2.4007	0.2740	0.2489	325*i*	129	355	738	1918	3232
cis-ONNH → NO + NH	1000	2.3069	0.2347	0.2140	166*i*	103	264	590	1943	3223
	1500	2.3584	0.2555	0.2325	245*i*	116	310	668	1933	3228
	2000	2.3990	0.2742	0.2489	326*i*	134	355	738	1919	3232
	2500	2.4147	0.2791	0.2530	346*i*	134	368	763	1914	3235

Reaction	Temp. /K	Rotational Constants			Scaled Vibrational Frequencies					
ONHN → HNO + N	1000	2.1767	0.2518	0.2296	248*i*	252	614	1392	1586	2957
	1500	2.1734	0.2615	0.2375	290*i*	273	658	1382	1573	2977
	2000	2.1686	0.2717	0.2457	336*i*	295	698	1373	1555	2999
	2500	2.1656	0.2770	0.2500	358*i*	306	717	1368	1545	3011
NNH + O → N_2 + OH	1000	2.6851	0.0879	0.0851	118*i*	103	307	1065	1844	2532
	1500	2.7579	0.0940	0.0909	133*i*	125	361	1059	1849	2454
	2000	2.8617	0.1006	0.0972	155*i*	147	424	1053	1847	2338
	2500	2.8909	0.1030	0.0994	166*i*	153	453	1053	1840	2287