

O-H STRETCH OVERTONE EXCITATION OF ETHYL HYDROPEROXIDE CONFORMERS

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SUPPLEMENTARY INFORMATION

Table 1. Kinetic energy parameters (cm^{-1}) for the *anti* conformer.

Vibrational level	$\nu = 0$	$\nu = 3$	$\nu = 4$	$\nu = 5$	$\nu = 6$
α_0	20.35	16.72	15.61	14.55	13.52
α_1	0.675	0.671	0.674	0.680	0.687

Table 2. Kinetic energy parameters (cm^{-1}) for the *gauche* conformer^a.

Vibrational level	$\nu = 0$	$\nu = 3$	$\nu = 4$	$\nu = 5$	$\nu = 6$
α_0	20.35	16.71	15.60	14.55	13.54
α_1	0.684	0.670	0.669	0.672	0.678

^a*Gauche* values are averages for the two potential minima.

Table 3. Coefficients for Fourier series (seven cosine terms, cm^{-1}) fits to torsional potentials for *anti* conformer.

Vibrational level	$\nu = 0$	$\nu = 3$	$\nu = 4$	$\nu = 5$	$\nu = 6$
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V_0	18708.189	22323.46	25739.034	28954.888	31971.045
V_1	776.463	726.031	671.541	612.994	550.388
V_2	468.23	494.181	523.267	555.486	590.84
V_3	84.702	101.114	118.595	137.148	156.771
V_4	21.8523	27.5457	33.804	40.628	48.0165
V_5	8.91899	11.2107	13.7783	16.6199	19.7375
V_6	-1.00115	-0.360752	0.367342	1.18478	2.0894

Table 4. Coefficients for Fourier series (seven cosine and three sine terms, cm^{-1}) fits to torsional potentials for *gauche* conformer.

Vibrational level	$v = 0$	$v = 3$	$v = 4$	$v = 5$	$v = 6$
V_0	18781.585	22405.008	25829.188	29054.069	32079.797
V_1	660.285	649.508	646.288	652.269	668.597
V_2	898.696	853.106	803.847	750.918	694.319
V_3	510.029	534.236	561.389	591.489	624.536
V_4	77.6282	89.8122	102.666	116.189	130.382
V_5	21.2898	25.7251	30.5757	35.8415	41.5227
V_6	6.90892	9.01134	11.3662	13.9736	16.8334
V_7	-0.161664	0.577702	1.42915	2.39269	3.46831
V_8	-47.2057	-57.9047	-69.3248	-81.4661	-94.3285
V_9	-28.3275	-38.7073	-49.7494	-61.4539	-73.8207

Table 5. First eight torsional energies (cm^{-1}) for *anti* conformer, for each vibrational level v .

$v = 0$	$v = 3$	$v = 4$	$v = 5$	$v = 6$
72.1	85.4	88.6	91.6	94.5
97.3	103.2	105.8	108.4	110.8
215.3	282.1	301.1	314.4	325.0
288.8	294.9	305.4	316.1	325.9

382.1	382.7	413.0	447.7	477.3
510.2	472.2	483.4	503.0	524.7
622.2	563.1	576.1	613.4	670.0
769.0	671.3	665.7	676.8	702.2

Table 6. First eight torsional energies (cm^{-1}) for *gauche* conformer, for each vibrational level ν .

$\nu = 0$	$\nu = 3$	$\nu = 4$	$\nu = 5$	$\nu = 6$
92.6	120.6	134.1	150.5	169.8
118.9	139.0	151.9	167.7	186.6
244.9	319.2	348.8	375.8	402.2
321.8	336.9	355.8	378.4	403.3
422.2	428.7	461.5	504.4	547.6
557.8	526.4	540.8	566.4	598.9
676.9	624.6	637.9	673.3	731.5
832.0	741.7	738.0	750.5	779.1

Table 7. First six derivatives of the dipole moment x -component for the *anti* conformer.

Torsional angle ($^{\circ}$)	1st	2nd	3rd	4th	5th	6th
0	-0.244	1.544	0.409	-4.848	-51.80	204.15
10	-0.237	1.587	0.597	-3.065	-48.35	25.06
20	-0.223	1.713	1.061	-1.978	-40.16	-1.49
30	-0.214	1.879	1.875	-2.065	-63.61	199.74
40	-0.221	2.045	2.588	-2.152	-79.89	274.08
50	-0.247	2.194	3.151	0.001	-72.96	-197.26
60	-0.292	2.338	3.817	-0.709	-90.18	-112.94
70	-0.349	2.459	4.431	-0.041	-99.90	-198.24
80	-0.414	2.557	4.925	-0.592	-108.35	-23.83

90	-0.484	2.605	5.194	1.301	-90.35	-278.09
100	-0.546	2.559	5.204	1.952	-77.25	-230.52
110	-0.628	2.553	5.214	2.603	-64.15	-182.95
120	-0.696	2.470	4.878	1.348	-47.48	6.23
130	-0.756	2.365	4.416	-1.252	-43.56	334.55
140	-0.806	2.257	3.893	-4.578	-41.03	519.51
150	-0.845	2.154	3.404	-7.414	-51.62	637.86
160	-0.872	2.071	2.894	-8.899	-50.88	480.30
170	-0.887	2.019	2.527	-9.587	-42.83	192.39
180 ^a	-0.893	2.011	2.619	-12.942	-76.76	746.59

^aDerivatives beyond 180 degrees are omitted, since they are symmetric about 180.

Table 8. First six derivatives of the dipole moment y-component for the *anti* conformer.

Torsional angle (°)	1st	2nd	3rd	4th	5th	6th
0	0.570	-1.315	-2.578	13.860	46.66	-430.32
10	0.565	-1.354	-2.809	14.685	55.47	-715.49
20	0.550	-1.439	-3.356	13.729	65.84	-828.57
30	0.532	-1.519	-3.822	10.728	58.86	-528.11
40	0.516	-1.546	-4.270	9.178	64.51	-409.14
50	0.501	-1.458	-4.460	6.718	70.19	-244.67
60	0.476	-1.240	-4.207	3.860	69.31	-164.49
70	0.421	-0.924	-3.342	0.205	43.65	178.51
80	0.314	-0.612	-2.156	0.016	37.97	-27.59
90	0.143	-0.399	-0.872	-0.584	18.05	143.77
100	-0.071	-0.300	0.397	-0.501	6.02	151.47
110	-0.282	-0.243	0.999	-0.419	-6.00	159.17
120	-0.453	-0.126	1.758	-1.044	-1.86	148.06

130	-0.567	0.029	2.441	-0.811	-6.04	21.55
140	-0.632	0.205	2.879	-4.385	-22.37	363.08
150	-0.661	0.347	2.990	-7.014	-22.96	392.18
160	-0.671	0.444	2.904	-8.753	-19.33	348.63
170	-0.671	0.492	2.893	-9.505	-27.53	378.46
180 ^a	-0.673	0.515	2.882	-10.256	-35.73	408.29

^aDerivatives beyond 180 degrees are omitted, since they are symmetric about 180.

Table 9. First six derivatives of the dipole moment z -component for the *anti* conformer.

Torsional angle (°)	1st	2nd	3rd	4th	5th	6th
0	0.000	0.000	0.000	0.000	0.000	0.000
10	-0.060	-0.324	-0.206	2.856	5.556	-221.832
20	-0.114	-0.674	-0.471	5.642	3.980	-272.908
30	-0.153	-1.053	-0.910	8.094	10.545	-266.402
40	-0.163	-1.448	-1.597	10.884	30.186	-275.638
50	-0.130	-1.820	-2.481	13.306	50.129	-309.118
60	-0.043	-2.121	-3.567	14.442	62.609	-223.823
70	0.101	-2.268	-4.819	13.518	82.907	-205.522
80	0.286	-2.216	-5.628	10.838	79.728	-106.886
90	0.476	-1.988	-5.948	8.983	83.366	-166.879
100	0.616	-1.664	-5.597	7.294	69.688	-107.877
110	0.691	-1.431	-5.245	5.604	56.011	-48.875
120	0.682	-1.225	-4.633	5.545	43.747	-178.464
130	0.614	-1.029	-3.776	5.870	32.133	-265.265
140	0.511	-0.824	-2.875	6.920	29.925	-447.243
150	0.390	-0.602	-1.906	4.909	17.156	-196.250
160	0.262	-0.394	-1.191	4.374	16.677	-238.621
170	0.132	-0.198	-0.620	3.335	20.546	-322.745

180	0.000	0.000	0.000	0.000	0.000	0.000
190	-0.132	0.198	0.620	-3.335	-20.546	322.745
200	-0.262	0.394	1.191	-4.374	-16.677	238.621
210	-0.390	0.602	1.906	-4.909	-17.156	196.250
220	-0.511	0.824	2.875	-6.920	-29.925	447.243
230	-0.614	1.029	3.776	-5.870	-32.133	265.265
240	-0.682	1.225	4.633	-5.545	-43.747	178.464
250	-0.691	1.431	5.245	-5.604	-56.011	48.875
260	-0.616	1.664	5.597	-7.294	-69.688	107.877
270	-0.476	1.988	5.948	-8.983	-83.366	166.879
280	-0.286	2.216	5.628	-10.838	-79.728	106.886
290	-0.101	2.268	4.819	-13.518	-82.907	205.522
300	0.043	2.121	3.567	-14.442	-62.609	223.823
310	0.130	1.820	2.481	-13.306	-50.129	309.118
320	0.163	1.448	1.597	-10.884	-30.186	275.638
330	0.153	1.053	0.910	-8.094	-10.545	266.402
340	0.114	0.674	0.471	-5.642	-3.980	272.908
350	0.060	0.324	0.206	-2.856	-5.556	221.832
360	0.000	0.000	0.000	0.000	0.000	0.000

Table 10. First six derivatives of the dipole moment *x*-component for the *gauche* conformer.

Torsional angle (°)	1st	2nd	3rd	4th	5th	6th
0	0.130	0.609	-0.921	4.392	-9.08	-220.59
10	0.212	0.676	-0.702	5.872	-13.56	-289.00
20	0.298	0.821	-0.205	7.956	-16.82	-398.33
30	0.358	0.948	0.148	9.443	-8.91	-609.40
40	0.367	0.971	0.342	9.036	-29.61	-473.80

50	0.320	0.897	0.170	6.222	-42.80	-125.52
60	0.234	0.791	-0.166	5.460	-26.42	-200.55
70	0.124	0.752	-0.104	4.860	-19.93	-183.72
80	0.008	0.813	0.356	5.883	-18.61	-305.65
90	-0.109	0.963	0.992	6.476	-2.95	-549.92
100	-0.229	1.150	1.995	4.148	-40.69	-2.28
110	-0.351	1.320	2.601	4.035	-29.60	-81.46
120	-0.475	1.454	3.142	2.249	-38.45	127.54
130	-0.596	1.545	3.344	-0.577	-32.95	339.59
140	-0.711	1.598	3.324	-3.559	-26.80	418.68
150	-0.816	1.631	3.282	-7.195	-37.08	508.58
160	-0.906	1.660	3.198	-11.563	-52.90	758.91
170	-0.981	1.691	3.144	-12.823	-53.27	524.08
180	-1.040	1.754	3.393	-15.621	-80.17	909.46
190	-1.079	1.846	3.672	-15.726	-67.78	909.12
200	-1.102	1.974	4.822	-18.861	-152.04	2113.28
210	-1.099	2.110	4.850	-14.506	-58.23	1632.07
220	-1.064	2.197	4.203	6.813	108.43	-1626.85
230	-1.018	2.364	4.222	12.947	251.20	-3627.05
240	-0.952	2.482	5.310	10.853	152.11	-2671.54
250	-0.859	2.529	4.794	18.779	245.86	-4378.88
260	-0.762	2.575	6.765	-0.112	-86.77	-80.32
270	-0.644	2.490	6.258	-0.446	-88.43	-181.68
280	-0.521	2.328	5.553	-1.435	-99.09	-20.97
290	-0.397	2.107	4.503	-1.091	-76.52	-180.46
300	-0.282	1.851	3.578	-1.745	-85.40	163.02
310	-0.180	1.577	2.404	0.429	-42.04	-181.54
320	-0.099	1.308	1.580	1.041	-46.97	6.63
330	-0.036	1.049	0.710	2.784	-33.29	-128.15

340	0.015	0.829	-0.088	2.427	-21.05	-30.56
350	0.066	0.666	-0.669	3.434	-17.23	-93.65
360	0.130	0.609	-0.921	4.392	-9.08	-220.59

Table 11. First six derivatives of the dipole moment y-component for the *gauche* conformer.

Torsional angle (°)	1st	2nd	3rd	4th	5th	6th
0	-0.540	1.362	1.756	-9.794	-67.09	516.20
10	-0.534	1.513	1.770	-11.141	-59.98	536.87
20	-0.507	1.717	1.977	-11.368	43.75	413.86
30	-0.475	1.950	2.468	-10.697	-49.62	346.96
40	-0.448	2.181	2.218	-4.130	-74.56	-1435.02
50	-0.451	2.414	3.853	-12.122	-74.80	471.17
60	-0.478	2.583	5.102	-14.057	-154.66	1191.43
70	-0.522	2.650	5.294	-7.279	-78.34	-77.22
80	-0.581	2.630	5.913	-4.967	-97.16	-18.41
90	-0.642	2.517	6.129	-3.369	-90.90	0.65
100	-0.688	2.307	5.829	-0.869	-62.61	-389.90
110	-0.711	2.052	5.277	-1.159	-52.10	-178.33
120	-0.700	1.775	4.414	0.398	-45.61	158.27
130	-0.655	1.514	3.492	-1.543	-48.74	477.16
140	-0.576	1.285	2.357	-1.365	-30.25	284.58
150	-0.473	1.109	1.270	-1.558	-2.93	16.40
160	-0.360	0.983	0.645	-3.283	-25.06	315.46
170	-0.247	0.884	0.124	-3.344	-31.56	388.53
180	-0.142	0.801	-0.426	-0.625	-5.18	-73.87
190	-0.051	0.731	-0.700	0.602	-7.23	-28.43
200	0.025	0.682	-0.601	-1.442	-51.82	650.16

210	0.088	0.644	-1.137	-1.783	-1.16	735.43
220	0.136	0.625	-0.355	-5.379	-97.90	1333.27
230	0.177	0.588	-0.380	-5.670	-145.44	2093.65
240	0.203	0.584	-0.704	-2.747	-97.91	1351.34
250	0.207	0.614	-0.237	-5.635	-158.48	2070.93
260	0.196	0.643	-1.026	3.228	-6.34	-114.63
270	0.155	0.720	-0.653	2.990	-13.26	-135.91
280	0.088	0.811	-0.235	2.547	-9.39	-208.21
290	-0.001	0.911	0.461	-0.176	-44.39	249.29
300	-0.102	0.988	0.882	0.411	-33.68	5.68
310	-0.207	1.059	1.382	-0.546	-46.75	66.36
320	-0.307	1.116	1.697	-1.414	-50.45	111.47
330	-0.396	1.164	1.855	-2.828	-47.72	151.14
340	-0.469	1.206	1.813	-5.011	-44.36	279.14
350	-0.519	1.264	1.714	-6.976	-42.70	241.50
360	-0.540	1.362	1.756	-9.794	-67.09	516.20

Table 12. First six derivatives of the dipole moment z -component for the *gauche* conformer.

Torsional angle (°)	1st	2nd	3rd	4th	5th	6th
0	0.255	-1.137	-1.338	10.796	23.408	-355.56
10	0.194	-0.966	-0.944	8.324	9.661	-117.71
20	0.136	-0.797	-0.777	6.950	14.002	-191.37
30	0.088	-0.598	-0.525	4.171	8.935	-20.22
40	0.053	-0.396	-0.226	2.192	7.796	-10.12
50	0.017	-0.126	0.073	0.212	6.658	-0.01
60	-0.039	0.158	0.549	-1.992	-1.362	12.06
70	-0.094	0.382	1.025	-4.196	-9.382	24.12

80	-0.166	0.604	1.509	-6.240	3.014	-91.57
90	-0.249	0.776	2.185	-7.456	-24.156	168.39
100	-0.339	0.889	2.705	-6.852	-20.403	-20.93
110	-0.429	0.940	3.211	-8.529	-39.078	360.69
120	-0.509	0.912	3.431	-7.528	-31.701	207.35
130	-0.572	0.834	3.417	-8.425	-26.538	380.08
140	-0.610	0.711	3.190	-7.867	-19.205	292.73
150	-0.615	0.574	2.927	-7.955	-27.628	358.61
160	-0.583	0.445	2.487	-7.138	-14.404	155.74
170	-0.517	0.335	2.167	-7.085	-23.494	259.32
180	-0.422	0.235	1.821	-6.997	-22.770	360.05
190	-0.304	0.112	1.007	-0.468	47.927	-765.72
200	-0.175	-0.026	0.712	0.286	20.039	-605.89
210	-0.049	-0.195	0.417	1.041	-7.850	-446.06
220	0.074	-0.400	-0.806	1.696	57.865	-550.19
230	0.183	-0.655	-1.190	-0.397	-4.690	188.69
240	0.279	-0.965	-2.282	2.253	23.238	-105.88
250	0.356	-1.287	-3.027	1.956	0.861	351.13
260	0.414	-1.606	-4.095	4.068	42.092	190.41
270	0.453	-1.890	-4.855	6.701	71.859	30.80
280	0.472	-2.098	-5.249	7.921	80.839	146.41
290	0.473	-2.232	-5.374	12.463	98.377	-394.39
300	0.461	-2.249	-5.155	12.707	90.904	-262.26
310	0.441	-2.172	-4.707	12.925	77.839	-280.61
320	0.417	-2.013	-4.138	13.829	73.068	-599.91
330	0.390	-1.797	-3.387	13.865	50.802	-636.00
340	0.355	-1.550	-2.553	11.790	33.446	-425.12
350	0.311	-1.328	-1.934	12.036	38.453	-552.73
360	0.255	-1.137	-1.338	10.796	23.408	-355.56

