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Mean Amplitudes of Vibration for Cyclohexene from Spectroscopic Data

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With 1 Figure

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A normal coordinate analysis is performed for cyclohexene (C_6H_{10}). The calculated frequencies for C_6H_{10} and C_6D_{10} are reported. The mean amplitudes of vibration for all types of interatomic distances in these two molecules were also computed. Those of the bonded distances and nonbonded C—C distances in C_6H_{10} are compared with the corresponding data from election diffraction.

Structures of hydrocarbons with C=C double bonds have been studied with much interest. Among these structures are the six-membered ring molecules 1.4-cyclohexadiene and 1.3-cyclohexadiene, for which a number of spectroscopical and electron diffraction works have been published[1–5]. Recently the mean amplitudes of vibration[6] were calculated from spectroscopic data for both of these molecules[7, 8]. In the present work the same approach was used in an analysis of cyclohexene.

Normal Coordinate Analysis

A non-planar carbon atom ring is found in the cyclohexene molecule, which is attributed to the symmetry group C_2. The normal modes of vibration are distributed according to

$$\Gamma \text{ vib} = 22A + 20B$$

The structural parameters from a gas electron diffraction investigation[9]

Table 1. *Calculated and Observed Frequencies* (in cm^{-1}) *for Cyclohexene-d_{10}*

Species *A*		Species *B*	
Calculated	Observed[10]	Calculated	Observed[10]
2251	2264	2284	2302
2207	2221	2211	2206
2173	2140	2156	2182
2114	2105	2121	2115
2103	2087	2085	2093
1582	1621	1379	1170
1397	1206	1282	—
1296	1103	1090	1080
1149	1079	1028	1064
1044	—	985	1048
965	998	960	962
934	923	883	868
888	899	832	—
863	845	779	791
840	799	712	730
767	779	675	710
713	737	513	605
589	727	463	497
570	615	408	378
452	457	143	—
308	327		
228	230		

Table 2. *Mean Amplitudes* (Å) *for the Bonded Distances and Nonbonded* C—C *Distances in Cyclohexene and Cyclohexene-d_{10}*

Distance	(*i*—*j*)	R_{ij}	C_6H_{10} Spectroscopic 0 K	C_6H_{10} Spectroscopic 298 K	C_6H_{10} Electron diffraction[9]	C_6D_{10} Spectroscopic 0 K	C_6D_{10} Spectroscopic 298 K
C—H	(5–13)	1.093	0.0792	0.0792		0.0677	0.0678
C—H	(5–15)	1.093	0.0792	0.0792		0.0678	0.0678
C—H	(3–9)	1.093	0.0792	0.0792	0.078	0.0678	0.0678
C—H	(3–11)	1.093	0.0792	0.0792		0.0678	0.0678
C—H	(1–7)	1.093	0.0772	0.0772		0.0661	0.0661
C—C	(5–6)	1.550	0.0426	0.0427	0.049 ± 0.006	0.0425	0.0426
C—C	(3–5)	1.515	0.0472	0.0476	0.057 ± 0.010	0.0471	0.0475
C—C	(1–3)	1.504	0.0469	0.0471	0.063 ± 0.010	0.0468	0.0471
C=C	(1–2)	1.334	0.0475	0.0480	0.048 ± 0.002	0.0474	0.0479
C···C	(1–5)	2.505	0.0587	0.0619	0.085[a]	0.0582	0.0617
C···C	(1–6)	2.845	0.0639	0.0706	0.085[a]	0.0630	0.0704
C···C	(1–4)	2.501	0.0536	0.0551	0.061[a]	0.0532	0.0549
C···C	(3–6)	2.526	0.0648	0.0781	0.070[a]	0.0635	0.0779
C···C	(3–4)	2.993	0.0610	0.0659	0.080[a]	0.0604	0.0657

[a] Assumed values.

were adopted. Complete sets of assigned vibrational frequencies for cyclohexene and cyclohexene-d_{10} are available from the spectroscopic work of *Neto* et al.[10], who also performed a normal coordinate analysis and reported force constant values.

We shall not claim that our reinvestigation of the force field introduces real improvements. Hence we feel it as unnecessary to give a

Table 3. *Mean Amplitudes* (Å) *for the Nonbonded* C—H (*or* C—D) *Distances in Cyclohexene and Cyclohexene-d_{10} from Spectroscopic Data*

C ··· H (D)		C_6H_{10}		C_6D_{10}	
(*i*—*j*)	R_{ij}	0 K	298 K	0 K	298 K
(5–14)	2.170	0.1059	0.1064	0.0910	0.0925
(5–16)	2.160	0.1064	0.1069	0.0915	0.0930
(5–9)	2.153	0.1067	0.1076	0.0920	0.0940
(5–11)	2.142	0.1073	0.1081	0.0925	0.0944
(5–10)	3.467	0.1021	0.1054	0.0893	0.0938
(5–12)	2.908	0.1509	0.1773	0.1306	0.1654
(5–7)	3.467	0.0991	0.1013	0.0869	0.0900
(5–8)	3.930	0.0970	0.1015	0.0863	0.0920
(3–13)	2.147	0.1067	0.1073	0.0920	0.0936
(3–15)	2.141	0.1071	0.1080	0.0923	0.0943
(3–14)	3.463	0.1016	0.1066	0.0891	0.0954
(3–16)	2.748	0.1492	0.1658	0.1290	0.1526
(3–10)	3.895	0.1140	0.1238	0.0993	0.1126
(3–12)	3.585	0.1417	0.1614	0.1224	0.1493
(3–7)	2.189	0.1044	0.1048	0.0900	0.0912
(3–8)	3.508	0.0959	0.0967	0.0840	0.0854
(1–9)	2.133	0.1071	0.1079	0.0923	0.0942
(1–11)	2.138	0.1065	0.1071	0.0918	0.0935
(1–13)	3.431	0.1019	0.1033	0.0889	0.0912
(1–15)	2.873	0.1433	0.1574	0.1236	0.1440

detailed report on the symmetry coordinates applied, the initial and final force constants and the potential energy distribution. We shall only give the calculated frequencies, which may be used to judge approximately the reliability of the force field. The force constants were adjusted to reproduce accurately all the observed fundamental frequencies for cyclohexene[10] along with four unobserved frequencies for which we adopted the calculated values given in the paper[10] cited. The complete set of frequencies (in cm^{-1}) is: (*A*) 3026, 2940, 2916, 2865, 2839, 1656, (1463), 1436, 1353, 1343, 1241, 1222, (1141), (1095), 1068, 966, 905, 822, 789, 495, 394, 281; (*B*) 3067, 2960, 2898, 2882, 2860, 1450, 1443, 1338, 1321, 1265, (1214), 1139, 1040, 1009, 917, 878, 721, 643, 455 and 175. The unobserved values are given in parantheses. Table 1 shows the

calculated frequencies for cyclohexene-d_{10} from our force constants along with the observes values[10].

Table 4. *Mean Amplitudes* (Å) *for the Nonbonded* H—H (*or* D—D) *Distances in Cyclohexene and Cyclohexene-d_{10} from Spectroscopic Data*

H (D) ··· H (D)		C_6H_{10}		C_6D_{10}	
(*i*—*j*)	R_{ij}	0 K	298 K	0 K	298 K
(13–15)	1.781	0.1553	0.1612	0.1317	0.1420
(13–14)	2.476	0.1527	0.1535	0.1288	0.1309
(13–16)	2.488	0.1664	0.1709	0.1405	0.1488
(9–13)	2.570	0.1510	0.1531	0.1277	0.1314
(11–13)	2.369	0.1679	0.1706	0.1416	0.1477
(7–13)	4.305	0.1368	0.1377	0.1158	0.1181
(11–12)	4.364	0.1608	0.1674	0.1362	0.1479
(11–14)	3.851	0.1690	0.1896	0.1442	0.1724
(11–16)	2.708	0.2252	0.2636	0.1922	0.2449
(15–16)	3.053	0.1290	0.1293	0.1091	0.1101
(9–15)	2.398	0.1722	0.1789	0.1455	0.1571
(11–15)	3.028	0.1293	0.1302	0.1095	0.1112
(7–15)	3.771	0.1744	0.1943	0.1485	0.1765
(9–11)	1.741	0.1608	0.1653	0.1360	0.1456
(9–14)	4.290	0.1402	0.1413	0.1187	0.1214
(9–16)	3.790	0.1631	0.1769	0.1391	0.1590
(9–10)	4.870	0.1342	0.1356	0.1139	0.1171
(9–12)	4.300	0.1994	0.2436	0.1699	0.2273
(7–9)	2.425	0.1629	0.1663	0.1375	0.1437
(7–11)	2.615	0.1570	0.1625	0.1328	0.1414
(7–14)	4.973	0.1223	0.1246	0.1047	0.1080
(7–16)	4.087	0.1859	0.2085	0.1585	0.1910
(7–10)	4.196	0.1477	0.1516	0.1252	0.1322
(7–12)	4.076	0.1530	0.1593	0.1297	0.1402
(7–8)	2.511	0.1610	0.1623	0.1360	0.1396

Mean Amplitudes of Vibration

The force constants were used to calculate the mean amplitudes of vibration of cyclohexene and cyclohexene-d_{10} and are reported here for the first time. Table 2 shows the values pertaining to the bonded distances and the nonbonded C—C distances. They may be compared with the corresponding data from gas electron diffraction for cyclohexene, which are quoted in the table. The agreement is very good. No electron diffraction data are reported for the nonbonded C—H and H—H distances. The calculated values are shown in Tables 3 and 4, respectively.

The numbering of atoms is shown in Fig. 1. The interatomic distances (R_{ij}, in Å) calculated from the adopted structural parameters are included in Tables 2, 3 and 4.

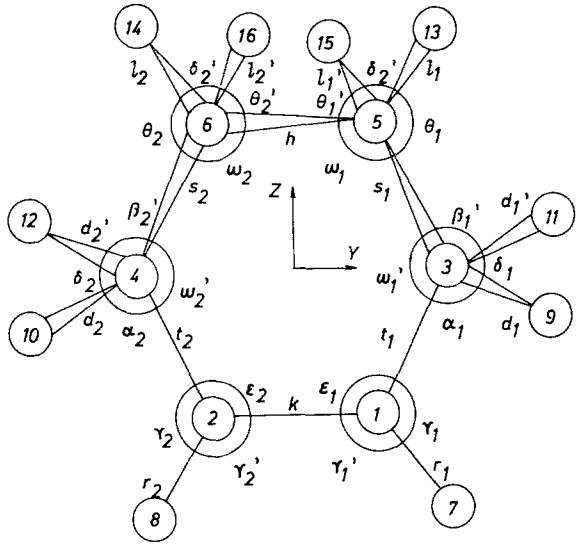

Fig. 1. The cyclohexene model. Symmetrically equivalent atoms are numbered consecutively. The following coordinates are not indicated on the figure: (i) Bends: α_1' (1–3–11), α_2' (2–4–12), φ_1' (3–5–15), φ_2' (4–6–16), θ_1 (6–5–13), θ_2 (5–6–14), β_1 (5–3–9), β_2 (6–4–10); (ii) torsions: τ_1 (2–1–3–5), τ_2 (1–2–4–6); (iii) out-of-plane bendings: ξ_1 (2.3–1–7), ξ_2 (1.4–2–8). The capital letters R, T etc. are fused to designate the appropiate equilibrium distances

Erratum: Read δ_1' (instead of δ_2') at C-atom 5 (between H-atoms 15 and 13)

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