Mean Amplitudes of Vibration for 1,3-Butadiene
from Spectroscopic Data

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The mean amplitudes of vibrations have been calculated from spectroscopic data for 1,3-butadiene, 1-3-butadiene-2-d and 1,3-butadiene-d_6. The results are compared with recent electron diffraction data.

Structures of conjugated non-aromatic hydrocarbon molecules have been studied in a great number of works. By modern gas electron-diffraction methods in particular, the butadiene,[5,13] hexatriene,[6] and cyclooctatetraene [5] molecules have been studied. For all these molecules the mean amplitudes of vibration have been established with fairly good accuracy during several electron-diffraction investigations; the first work of this category is due to Karle,[1] who reported structural data including the mean amplitudes for cyclooctatetraene (and benzene). At that time (1952) a rigorous calculation of the mean amplitudes from spectroscopic data for molecules of that size was hardly foreseen, although the results from such calculations would be of prime interest. Today the access to high-speed electronic computers and the existence of suitable programs has made this sort of calculations practically feasible, as far as the approximation of small harmonic vibrations is concerned. If a sufficiently reliable harmonic force field can be set up as the starting point, the computations in fact reduce to almost mere routine.

In the present work the mean amplitudes of vibration for butadiene have been computed according to a harmonic force-field analysis. Similar calculations are in progress for 1,3,5,7-cyclooctatetraene and for the *cis* and *trans* isomers of 1,3,5-hexatriene.

The structure of 1,3-butadiene has been studied both by gas electron diffraction,[2,5,13] high-resolution Raman spectroscopy,[3] and infrared.[4] In the

present calculations we have adopted as equilibrium parameters the structural data from a reinvestigation by electron diffraction.[5] More or less complete vibrational assignments for 1,3-butadiene and some of its deuterated compounds have been published several times. The work of Popov et al.[7] to this effect also includes trans-1,3,5-hexatriene. The present calculations are based on the work of Koptev et al.,[8] who gave complete assignments for both 1,3-butadiene and 1,3-butadiene-d_6; for the original sources of experimental frequencies, see Panchenko et al.[9,10] We have also performed the calculation of mean amplitudes for 1,3-butadiene-2-d, for which an almost complete assignment was proposed by Borshagovskaya et al.[11]

An initial force field for the butadiene molecules was produced by transferring compliants from ethylene and benzene. Most of the interaction terms were neglected. It is not intended to give a lengthy description of details of this procedure; here we only give reference [12] to other calculations (for naphthalene), where the same principles were followed. The calculated frequencies from the initial force field were judged to be close enough to the observed frequencies that the force field could be used with confidence as a starting point for refinements. After several steps of iteration a refined force field was produced, and gave the calculated frequencies in the columns I of Table 1.

Table 1. Calculated (I) and observed (II) frequencies (cm^{-1}) for isotopic 1,3-butadiene molecules.

C_{2h}		C_4H_6 I	C_4H_6 II	C_4D_6 I	C_4D_6 II	C_s		2-C_4H_5D I	2-C_4H_5D II
A_g	1	3072	3101	2367	2345	A'	1	3100	3095
	2	3026	3014	2265	2274		2	3092	3067
	3	3020	3014	2211	2217		3	3041	3033
	4	1663	1645	1572	1590		4	3001	3022
	5	1419	1442	1198	1190		5	2984	3011
	6	1280	1291	1070	1051		6	2246	2305
	7	1208	1205	918	921		7	1655	1633
	8	913	890	723	739		8	1587	1579
	9	522	513	431	440		9	1415	1418
B_{3g}	1	940	965	808	795		10	1380	1400
	2	895	910	718	700		11	1292	1267
	3	726	686	525	560		12	1224	1244
A_u	1	991	1014	754	731		13	1073	1020
	2	886	908	728	718		14	975	939
	3	529	523	385	390		15	828	891
	4	179	175	147	150		16	508	498
B_u	1	3097	3088	2327	2335		17	310	—
	2	3050	3044	2266	2270	A''	1	992	981
	3	3011	2998	2205	2215		2	924	937
	4	1594	1595	1521	1520		3	908	891
	5	1401	1381	1027	1042		4	878	791
	6	1322	1282	976	1009		5	635	681
	7	973	988	781	770		6	498	521
	8	313	310	257	260		7	171	—

Table 2. 1,3-Butadiene and 1,3-butadiene-d_6: calculated and observed mean amplitudes of vibration (Å units).

Distance[a] (equil.)		C_4H_6 Spectr.		C_4H_6 Electron diffrac.		C_4D_6 Spectr.	
		$T=0$	298°K	Ref. 5	Ref. 13[b]	$T=0$	298°K
C_1-H_1	(1.094)	0.0775	0.0775			0.0661	0.0661
C_1-H_1'	(1.094)	0.0773	0.0773	0.082₁	0.077	0.0661	0.0661
C_2-H_2	(1.094)	0.0777	0.0777			0.0664	0.0664
$C_1=C_2$	(1.344)	0.0423	0.0424	0.043₆	0.0412	0.0420	0.0421
C_2-C_3	(1.467)	0.0480	0.0486	0.051₃	0.0467	0.0477	0.0483
C_1-C_3	(2.469)	0.0567	0.0611	0.064₆	0.0603	0.0553	0.0600
C_1-C_4	(3.695)	0.0578	0.0610	0.059₁	0.062	0.0564	0.0597
C_2-H_1	(2.110)	0.0994	0.1005			0.0854	0.0875
C_2-H_1'	(2.110)	0.0993	0.1003	0.069₁	0.100	0.0851	0.0871
C_1-H_2	(2.110)	0.1020	0.1044	0.127₅		0.0875	0.0910
C_2-H_3	(2.201)	0.1019	0.1026	0.050₀		0.0874	0.0887
C_3-H_1	(3.456)	0.0953	0.0963	0.089₅		0.0829	0.0843
C_3-H_1'	(2.692)	0.1387	0.1496	0.122₄		0.1184	0.1340
C_1-H_3	(2.709)	0.1308	0.1375	0.144₂		0.1121	0.1213
C_1-H_4	(4.577)	0.1060	0.1101	0.134₃		0.0916	0.0973
C_1-H_4'	(4.031)	0.1380	0.1486	0.127₀		0.1181	0.1330
H_1-H_1'	(1.905)	0.1243	0.1244			0.1046	0.1050
H_1-H_2	(2.422)	0.1687	0.1765			0.1415	0.1536
$H_1'-H_2$	(3.081)	0.1221	0.1226			0.1033	0.1042
H_2-H_3	(3.151)	0.1261	0.1266			0.1067	0.1078
H_1-H_3	(3.798)	0.1479	0.1531			0.1250	0.1324
$H_1'-H_3$	(2.469)	0.1982	0.2150			0.1665	0.1904
H_1-H_4	(5.536)	0.1283	0.1291			0.1081	0.1096
$H_1'-H_4$	(4.724)	0.1839	0.2031			0.1564	0.1831
$H_1'-H_4'$	(4.610)	0.1651	0.1705			0.1386	0.1475

[a] The numbering of atoms is consistent with Fig. 1 of Ref. 5.

[b] These data became available when the present study was finished.

The agreement with observed frequencies (columns II) is quite satisfactory for all the three isotopic molecules.

The calculated mean amplitudes of vibration for C_4H_6 and C_6D_4 (see Table 2) are based on force fields which were adjusted to fit the observed frequencies (columns II) exactly for each of the molecules individually. The two sets of mean amplitudes are therefore strictly speaking not consistent with exactly the same force constants. The effect of these last refinements is certainly not substantial, but may be of the same order of magnitude as the secondary isotope effect for the calculated C—C mean amplitudes (see Table 2); not too much significance should therefore be attached to the secondary isotope effects from the present calculations. The calculated mean amplitudes for 1,3-butadiene are compared with electron-diffraction values,[5,13] in Table 2. The agreement is satisfactory for bonded C—H, it is excellent for all the C—C distances and quite good for most of the non-bonded C—H distances. The agreement is about as it could be expected when taking into account the reported uncertainties of the electron-diffraction values.[5] There seem to be

Table 3. 1,3-Butadiene, 1,3-butadiene-2-*d*, and 1,3-butadiene-d_6: calculated mean amplitudes (in Å units) at 298°K for distances involving the H_2 or D_2 atom.

Distance[a] (equil.)		C_4H_6	2-C_4H_5D	C_4D_6
$C_2 - H_2$	(1.094)	0.0777	0.077_7	
$C_2 - D_2$			0.066_4	0.0664
$C_1 - H_2$	(2.110)	0.1044	0.103_8	
$C_1 - D_2$			0.091_7	0.0910
$C_3 - H_2$	(2.110)	0.1026	0.102_1	
$C_3 - D_2$			0.089_1	0.0887
$C_4 - H_2$	(2.709)	0.1375	0.136_2	
$C_4 - D_2$			0.122_5	0.1213
$H_1 - H_2$		0.1765		
$H_1 - D_2$	(2.422)		0.165_8	
$D_1 - D_2$				0.1536
$H_1' - H_2$		0.1226		
$H_1' - D_2$	(3.081)		0.113_8	
$D_1' - D_2$				0.1042
$H_2 - H_3$		0.1266		
$D_2 - H_3$	(3.151)		0.117_5	
$D_2 - D_3$				0.1078
$H_2 - H_4$		0.1531		
$D_2 - H_4$	(3.798)		0.140_1	
$D_2 - D_4$				0.1324
$H_2 - H_4'$		0.2150		
$D_2 - H_4'$	(2.469)		0.203_7	
$D_2 - D_4'$				0.1904

[a] See fotnote to Table 2.

only two serious discrepancies, namely for the C_2H_1 and C_2H_3 distances, where in both cases the electron-diffraction values probably are too low.

The complete set of mean amplitudes of vibration was also calculated for 1,3-butadiene-2-*d*; these calculations were based on the force constants consistent with the frequencies of column I in Table 1. There were not found any significant secondary isotope effects; therefore it is sufficient to list only the results for the distances involving the D atom; see Table 3. The table also contains the calculated mean amplitudes for the corresponding distances in 1,3-butadiene and 1,3-butadiene-d_6. For the sake of brevity only the results at 298°K are listed. The tabulated values for C—H and C—D distances show examples of the lack of significant secondary isotope effects. For the H—D distances the values of mean amplitudes are found to lie in-between the corresponding H—H and D—D values, as could be expected.

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