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Mean Amplitudes of Vibration for Cyclobutane and Cyclobutane-d_8 from Spectroscopic Data

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With 1 Figure

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Mean amplitudes of vibration for cyclobutane and cyclobutane-d_8 are calculated on the basis of spectroscopic data. Results for the bonded distances are compared with data from electron diffraction, and a good agreement is found.

Structural and Spectral Data

Some years ago the cyclobutane molecule in the gas phase was generally assumed to possess the symmetry D_{4h}, i.e. a planar carbon skeleton. Mainly based on this structure *Lord* and *Nakagawa*[1] performed a normal coordinate analysis of cyclobutane and cyclobutane-d_8. *Venkateswarlu* and *Bhamambal*[2] calculated the generalized mean-square amplitudes of vibration assuming the planar-ring model. However, experimental work in electron diffraction[3] and later spectroscopic investigations[4, 5] indicate that cyclobutane has a slightly puckered ring and accordingly possesses the symmetry D_{2d}. As to the magnitude of the dihedral angle *Skancke*[3] arrived at the value of 35° in his electron diffraction work, and *Dows* and *Rich*[4] calculated it from infrared spectral intensities to be 37°. *Wright* and *Salem*[6] carried out ab initio calculations on cyclobutane, but they did not find a satisfactory potential well for the D_{2d} symmetry. We conclude from the foregoing that there is some doubt as to the magnitude of the dihedral angle of cyclobutane, but that the value is somewhere about 35°. The structural parameters adopted for the present normal coordinate analysis are[3, 7]:

Dihedral angle	35°
$<$ CCC	87.3°
$<$ HCH	108.5°
C—C bond length	1.548 Å
C—H bond length	1.092 Å

It is also assumed that the adjacent planes HCH and CCC are perpendicular to each other.

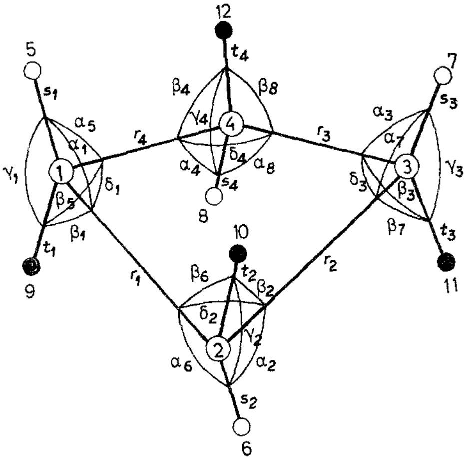

Fig. 1. Cyclobutane (C_4H_8) molecular model. Two sets of symmetrically equivalent H atoms are distinguished. Valence coordinates are indicated. The symbols R, S, and T are used to designate the appropriate equilibrium distances

Spectroscopic frequencies were taken from the work of *Miller* et al.[5] with a few frequencies from the compilations of *Sverdlov* et al.[8].

Symmetry Coordinates

The thirty normal vibrations are distributed among the different symmetry species of D_{2d} in the following way:

$$\Gamma_{\text{vib}} = 6\,A_1 + 2\,A_2 + 3\,B_1 + 5\,B_2 + 7\,E.$$

Thirty independent symmetry coordinates are listed in the following. Also included are some redundant coordinates, which proved to be helpful in the construction of an initial set of force constants. The nomenclature of valence coordinates is shown in Fig. 1.

$$\begin{aligned}
A_1 : S_1 &= \tfrac{1}{2}(r_1 + r_2 + r_3 + r_4) \\
S_2 &= \tfrac{1}{2}(s_1 + s_2 + s_3 + s_4) \\
S_3 &= \tfrac{1}{2}(t_1 + t_2 + t_3 + t_4) \\
S_4 &= (RS/8)^{1/2}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 + \alpha_7 + \alpha_8) \\
S_5 &= (RT/8)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8) \\
S_6 &= R/2(\delta_1 + \delta_2 + \delta_3 + \delta_4) \\
S_{7,\,r} &= (ST/4)^{1/2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)
\end{aligned}$$

$$\begin{aligned}
A_2 : S_1 &= (RS/8)^{1/2}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 - \alpha_5 - \alpha_6 - \alpha_7 - \alpha_8) \\
S_2 &= (RT/8)^{1/2}(\beta_1 + \beta_2 + \beta_3 + \beta_4 - \beta_5 - \beta_6 - \beta_7 - \beta_8)
\end{aligned}$$

$$\begin{aligned}
B_1 : S_1 &= \tfrac{1}{2}(r_1 - r_2 + r_3 - r_4) \\
S_2 &= (RS/8)^{1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 - \alpha_5 + \alpha_6 - \alpha_7 + \alpha_8) \\
S_3 &= (RT/8)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4 - \beta_5 + \beta_6 - \beta_7 + \beta_8)
\end{aligned}$$

$$\begin{aligned}
B_2 : S_1 &= \tfrac{1}{2}(s_1 - s_2 + s_3 - s_4) \\
S_2 &= \tfrac{1}{2}(t_1 - t_2 + t_3 - t_4) \\
S_3 &= (RS/8)^{1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6 + \alpha_7 - \alpha_8) \\
S_4 &= (RT/8)^{1/2}(\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6 + \beta_7 - \beta_8) \\
S_5 &= R/2(\delta_1 - \delta_2 + \delta_3 - \delta_4) \\
S_{6,\,r} &= (ST/4)^{1/2}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)
\end{aligned}$$

$$\begin{aligned}
E_a : S_{1a} &= 2^{-1/2}(r_1 - r_3) \\
S_{2a} &= \tfrac{1}{2}(s_1 + s_2 - s_3 - s_4) \\
S_{3a} &= \tfrac{1}{2}(t_1 + t_2 - t_3 - t_4) \\
S_{4a} &= (RS/8)^{1/2}(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8) \\
S_{5a} &= (RS/8)^{1/2}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 - \alpha_5 + \alpha_6 + \alpha_7 - \alpha_8) \\
S_{6a} &= (RT/8)^{1/2}(\beta_1 + \beta_2 - \beta_3 - \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8) \\
S_{7a} &= (RT/8)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4 - \beta_5 + \beta_6 + \beta_7 - \beta_8) \\
S_{8a,\,r} &= R/2(\delta_1 + \delta_2 - \delta_3 - \delta_4) \\
S_{9a,\,r} &= (ST/4)^{1/2}(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)
\end{aligned}$$

$$\begin{aligned}
E_b : S_{1b} &= 2^{-1/2}(- r_2 + r_4) \\
S_{2b} &= \tfrac{1}{2}(s_1 - s_2 - s_3 + s_4) \\
S_{3b} &= \tfrac{1}{2}(t_1 - t_2 - t_3 + t_4) \\
S_{4b} &= (RS/8)^{1/2}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4 + \alpha_5 - \alpha_6 - \alpha_7 + \alpha_8) \\
S_{5b} &= (RS/8)^{1/2}(- \alpha_1 - \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 - \alpha_7 - \alpha_8) \\
S_{6b} &= (RT/8)^{1/2}(\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8) \\
S_{7b} &= (RT/8)^{1/2}(- \beta_1 - \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8) \\
S_{8b,\,r} &= R/2(\delta_1 - \delta_2 - \delta_3 + \delta_4) \\
S_{9b,\,r} &= (ST/4)^{1/2}(\gamma_1 - \gamma_4 - \gamma_3 + \gamma_4)
\end{aligned}$$

Force Field

A diagonal force-constant matrix based on the redundant set of symmetry coordinates was used as the starting point for further refinement. The final set of force constants was adjusted to reproduce accurately the observed frequencies of the cyclobutane molecule[5]. For the inactive species A_2 frequencies were taken from *Sverdlov* et al.[8]. The force field also reproduces the frequencies of cyclobutane-d_8[5] satisfactorily as Table 1 demonstrates. The force constants are given in Table 2. Potential energy distribution is available on request to the authors.

Table 1. *Observed and Calculated Vibrational Frequencies* (in cm^{-1}) *for Cyclobutane and Cyclobutane*-d_8

	Cyclobutane		Cyclobutane-d_8	
	Observed[a]	Calculated	Observed[b]	Calculated
A_1	2974	2974	2210	2228
	2905	2905	2120	2149.6
	1468.6	1468.6	1169.3	1196.4
	1004.5	1004.5	884.2	834.1
	737	737	615	614.2
	199.4	199.4	157.1	159.8
A_2	1260[b]	1260	—	1015.1
	1104[b]	1104	—	780.9
B_1	1234	1234	1042	1143.3
	1225	1225	925	872.9
	926	926	748	701.8
B_2	2986.7	2986.7	2243	2220.2
	2945	2945	—	2154.3
	1453.9	1453.9	1084	1092.7
	999	999	—	824.6
	625.6	625.6	480	496.6
E	2965	2965	2234	2211.4
	2887	2887	2129	2122.9
	1452	1452	1065	1220.2
	1260	1260	1054	1030.8
	1224	1224	944	947.2
	901.4	901.4	730	657.5
	749	749	556	556

[a] From ref.[5].
[b] Assumed according to ref.[8].

Mean Amplitudes of Vibration

The final set of force constants was used to calculate the mean amplitudes of vibration[9] (u values) for cyclobutane and cyclobutane-d_8. The results are shown in Table 3. The values obtained by *Skancke*[3] from electron diffraction are also given in Table 3; the results from the two methods are found to be in good agreement.

Table 2. *Symmetry Force Constants* (in mdyne/Å) *for Cyclobutane*

Species A_1:						
4.419						
— 0.060	4.554					
0.059	— 0.016	4.571				
0.038	— 0.043	0.061	0.483			
0.289	0.049	0.014	0.390	0.623		
0.016	0.012	0.005	0.194	0.140	0.903	
Species A_2:						
0.427						
— 0.018	0.415					
Species B_1:						
4.051						
0.313	0.484					
0.192	— 0.081	0.568				
Species B_2:						
4.841						
— 0.006	4.866					
— 0.015	— 0.022	0.612				
— 0.002	0.014	0.316	0.676			
0.004	— 0.007	0.261	0.085	0.677		
Species E:						
3.813						
— 0.224	4.708					
— 0.128	— 0.085	4.698				
— 0.125	0.027	0.013	0.625			
0.157	0.037	0.011	— 0.010	0.426		
— 0.061	— 0.009	0.044	0.268	— 0.021	0.699	
— 0.001	0.001	0.033	— 0.064	— 0.061	0.028	0.298

On comparing our calculated u values with those obtained from the data of *Venkateswarlu* et al.[2] we find reasonable correspondence taking into account the effect of the assumption of the planar-ring model that was chosen by these authors. For the nonbonded C—C distance *Venkateswarlu* et al.[2] report a slightly lower mean amplitude than for the bonded C—C distance. Our results show on the contrary a value about 0.0100 Å higher for the nonbonded distance than for bonded one. This may be an effect of the puckering of the ring.

The assumption of a planar-ring model will lead to loss of data for some distances which consequently are classified as symmetrically equivalent, but which are shown by our calculations to have substantial differences in the *u* values. This effect is especially pronounced for the C—H distances 1–7 and 1–11 (see Table 2) where the chain 1–4–3–11 is closer to a linear arrangement than is the case for 1–4–3–7. Hence we may expect a lower mean amplitude in spite of a higher interatomic distance for these two atom pairs in analogy with the familiar effect of cis and trans arrangements. This feature is indeed verified by our calculations.

Table 3. *Mean Amplitudes of Vibration*, *u* (in Å Units) *for Cyclobutane and Cyclobutane*-d_8

Distance type (i–j)[a]		Equilib. distance, Å	Cyclobutane *u* calc.		*u* el. diff.[b]	Cyclobutane-d_8 *u* calc.	
			0 K	298 K		0 K	298 K
C—H	(1–5)	1.092	0.0786	0.0786	0.0716	0.0673	0.0673
C—H	(1–9)	1.092	0.0786	0.0786		0.0673	0.0673
C—C	(1–2)	1.548	0.0498	0.0502	0.0497	0.0495	0.0500
C . . . C	(1–3)	2.135	0.0560	0.0603		0.0552	0.0600
C . . . H	(1–6)	2.238	0.1105	0.1117		0.0957	0.0984
C . . . H	(1–10)	2.238	0.1090	0.1101		0.0943	0.0967
C . . . H	(1–7)	2.685	0.1320	0.1496		0.1142	0.1380
C . . . H	(1–11)	3.079	0.0984	0.0992		0.0857	0.0872
H . . . H	(5–9)	1.772	0.1276	0.1276		0.1074	0.1080
H . . . H	(5–6)	3.127	0.1357	0.1374		0.1154	0.1185
H . . . H	(5–10)	2.505	0.1743	0.1774		0.1472	0.1544
H . . . H	(5—7)	2.817	0.2182	0.2634		0.1857	0.2464
H . . . H	(5–11)	3.752	0.1447	0.1553		0.1232	0.1383
H . . . H	(9–10)	2.912	0.1517	0.1542		0.1285	0.1337
H . . . H	(9–11)	3.883	0.1480	0.1578		0.1253	0.1398

[a] For cyclobutane-d_8, H should be exchanged by D.
[b] From ref.[3].

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