

Harmonic Force Fields for Cyclopropene and Cyclopropane

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A harmonic force field for cyclopropene molecules has been developed on the basis of a recently reported vibrational assignment. Calculated frequencies are given for cyclopropene, cyclopropene-1,2- d_2 , cyclopropene-3,3- d_2 and cyclopropene- d_4 . Also the force field for cyclopropane molecules has been reinvestigated.

The present study of the force fields for cyclopropene and cyclopropane was initiated by the appearance of experimental vibrational frequencies for cyclopropene and cyclopropene-1,2- d_2 recently published by Mitchell *et al.*¹ To the writer's knowledge no harmonic force field for cyclopropene has been developed before. A study of the force field for cyclopropane has been included because of the close relationship of the two molecules, although such analyses have been performed previously by several workers (for ref. see below).

CYCLOPROPENE

Molecular model. According to electron diffraction² and microwave³ studies the cyclopropene molecule belongs to the C_{2v} symmetry group. Its normal vibrations are distributed among the appropriate species in the following way:

$$6A_1 + 2A_2 + 3B_1 + 4B_2$$

It should be noted that the species notation in the present case depends on the choice of cartesian axes for the molecule. The above distribution pertains to the present convention with the x axis perpendicular to the skeletal ring plane; *cf.* Fig. 1. As a consequence the designations B_1 and B_2 are the reverse of those in the paper of Mitchell *et al.*¹

Fig. 1 shows the orientation and numbering of atoms, along with the applied valence coordinates. It was found possible to construct a complete set of symmetry coordinates with no redundants involved. They are specified in the following.

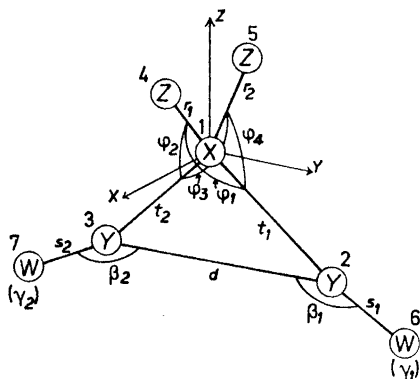


Fig. 1. The $XY_2W_2Z_2$ cyclopropene type molecular model; symmetry C_{2v} . The symbols on the figure indicate valence coordinates of the conventional types: stretchings (r,s,d,t), bendings (β,φ) and out-of-plane bendings (γ). The capital letters R , S , D and T are used to denote the appropriate equilibrium distances, viz. $X-Z$, $Y-W$, $Y-Y$ and $X-Y$, respectively. For further explanations as to the applied system of notation, see, e.g., Ref. 7.

$$\begin{aligned}
 S_1(A_1) &= 2^{-\frac{1}{2}}(r_1 + r_2) \\
 S_2(A_1) &= 2^{-\frac{1}{2}}(s_1 + s_2) \\
 S_3(A_1) &= 2^{-\frac{1}{2}}(t_1 + t_2) \\
 S_4(A_1) &= d \\
 S_5(A_1) &= (SD/2)^{\frac{1}{2}}(\beta_1 + \beta_2) \\
 S_6(A_1) &= \frac{1}{2}(RT)^{\frac{1}{2}}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4) \\
 S_1(A_2) &= [S(DT)^{\frac{1}{2}}/2]^{\frac{1}{2}}(\gamma_1 - \gamma_2) \\
 S_2(A_2) &= \frac{1}{2}(RT)^{\frac{1}{2}}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4) \\
 S_1(B_1) &= 2^{-\frac{1}{2}}(r_1 - r_2) \\
 S_2(B_1) &= \frac{1}{2}(RT)^{\frac{1}{2}}(\varphi_1 + \varphi_2 - \varphi_3 - \varphi_4) \\
 S_3(B_1) &= [S(DT)^{\frac{1}{2}}/2]^{\frac{1}{2}}(\gamma_1 + \gamma_2) \\
 S_1(B_2) &= 2^{-\frac{1}{2}}(s_1 - s_2) \\
 S_2(B_2) &= 2^{-\frac{1}{2}}(t_1 - t_2) \\
 S_3(B_2) &= (SD/2)^{\frac{1}{2}}(\beta_1 - \beta_2) \\
 S_4(B_2) &= \frac{1}{2}(RT)(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4)
 \end{aligned}$$

Structure parameters. The adopted molecular parameters for cyclopropene are:³

$$\begin{array}{ll}
 R(\text{C-H}) &= 1.087 \text{ \AA}, & S(\text{C-H}) &= 1.070 \text{ \AA} \\
 D(\text{C=C}) &= 1.300 \text{ \AA}, & T(\text{C-C}) &= 1.515 \text{ \AA} \\
 2A(\angle \text{HCH}) &= 114^\circ 42', & B(\angle \text{CCH}) &= 149^\circ 55'
 \end{array}$$

Force field. An initial diagonal force field was produced from observed frequencies for cyclopropene¹ by using the approximation⁴

$$F_{ii} \simeq \lambda_i/G_{ii}$$

This rather rough approximation gave remarkable good agreement with the observed frequencies both for cyclopropene and cyclopropene-1,2- d_2 .¹ The initial force field was adjusted to fit accurately the observed frequencies for cyclopropene by a number of iterative steps according to⁴

$$F = \tilde{L}_0^{-1} \lambda L_0^{-1}$$

where observed frequencies were inserted into the diagonal elements of λ every time. The F matrix was accepted as the final solution when it did not change substantially from F_0 of the previous set, *i.e.* the force constant matrix used to determine the normal-coordinate transformation matrix (L) from the familiar secular equation ⁴

$$G F_0 L_0 = \lambda_0 L_0$$

During this process certain interaction terms in the F_0 matrix were maintained as zero. In the final F matrix some small, not necessarily real interaction force constants were introduced; *cf.* Table 1. The observed frequencies

Table 1. Harmonic force field for cyclopropene in terms of symmetrized F matrix blocks. Units: mdyne/Å.

Species A_1	1	4.754	0.000	0.002	-0.003	0.001	0.000					
	2							5.320	-0.001	-0.008	0.000	0.001
	3								3.930	-0.020	0.013	0.006
	4									9.524	-0.005	0.007
	5										0.425	0.001
	6											0.567
Species A_2	1	0.381	-0.010	B_1	1	4.755	0.000	0.000				
	2								0.732	2	0.141	0.000
										3		0.129
Species B_2	1	5.317	-0.021	-0.017	0.015							
	2								5.024	-0.235	0.212	
	3									0.309	-0.001	
	4										0.668	

for the cyclopropene-1,2- d_2 molecule ¹ have not been used to determine the force constants, since some of the frequencies are questionable, and the assignment is incomplete.¹ The calculated frequencies for cyclopropene-1,2- d_2 with the present final force field still show satisfactory agreement with the observed frequencies; *cf.* Table 2, which includes the calculated frequencies for all isotopic cyclopropenes with C_{2v} symmetry.

CYCLOPROPANE

Molecular model. The cyclopropane molecule belongs to the D_{3h} symmetry group, and its normal vibrations are distributed among the various species as:

$$3A_1' + A_2' + 4E' + A_1'' + 2A_2'' + 3E''$$

The adopted set of symmetry coordinates (also without redundants) is given in a paper by Vizi and Cyvin ⁵ and is not reproduced here.

Structure parameters. The adopted molecular parameters for cyclopropane are:⁶

Table 2. Calculated frequencies (cm^{-1}) for all isotopic cyclopropenes with C_{2v} symmetry, including some observed values.

Species	Approxim. descript.	C_3H_4		$1,2-C_3H_2D_2$		$3,3-C_3H_2D_2$	C_3D_4
		Obs. ¹	Calc.	Obs. ¹	Calc.	Calc.	Calc.
A_1	C—H sym. stretch	3158	3158	2391?	2419	3158	2421
	CH_2 sym. stretch	2909	2909	2905.1	2910	2133	2130
	C=C stretch	1656.4	1656	1571.8	1572	1629	1519
	CH_2 scissor	1483.0	1483	1483.2	1454	1219	1213
	C—C sym. stretch	1110	1110	—	1081	1002	947
	C—H bend (in plane of ring)	905.0	905	669.4	668	867	663
A_2	CH_2 twist	1170	1170	—	1063	1147	978
	C—H bend (out of plane)	920	920	—	816	696	651
B_1	CH_2 antisym. stretch	2996.8	2997	2995.2	2997	2235	2235
	CH_2 rock	820	820	—	818	659	643
	C—H bend (out of plane)	570.4	570	433.4	432	546	421
B_2	C—H antisym. stretch	3124	3124	2450?	2308	3124	2308
	CH_2 wag	1043.2	1043	1039.7	1021	1040	980
	C—H bend (in plane of ring)	1010.9	1011	879.3	948	891	815
	C—C antisym. stretch	769.4	769	680.8	635	670	585

$$R(C-H) = 1.082 \text{ \AA}, \quad D(C-C) = 1.514 \text{ \AA}$$

$$2A(\angle HCH) = 116.3^\circ$$

Force field. Compliant⁷ from cyclopropene were successfully transferred to cyclopropane and served as a first approximation to the force field. The final force field shown in Table 3 was achieved after some refinements, following the same principles as used in cyclopropene (see above).

Table 3. Harmonic force field for cyclopropane in terms of symmetrized F matrix blocks. Units: mdyne/Å.

Species A_1'	1	5.112	-0.026	0.016	A_2'	0.437	
	2		4.068	0.279			
	3			0.616			
Species E'	1	5.199	0.007	-0.012	0.004	A_1'' 0.850	
	2		4.708	0.095	-0.438		
	3			0.556	0.015		
	4				0.616		
Species A_2''	1	5.153	-0.001	E'' 1	5.045	-0.005	0.002
	2		0.217	2		0.623	-0.003
				3			0.124

Calculated molecular constants and discussion of the force field. The calculated frequencies for cyclopropane and cyclopropane- d_6 from the force field of Table 3 are shown in Table 4. They are seen to be in good agreement with experimental values.^{6,8,9} In the most recent one of the cited works⁶ Duncan has given the

Table 4. Calculated and observed frequencies (cm^{-1}) for cyclopropane and cyclopropane- d_6 .

Species	Approxim. descript.	C_3H_6			C_3D_6			
		Obs. ⁶	Obs. ⁹	Obs. ⁶	Present calc.	Obs. ⁶	Obs. ⁹	Present calc.
A_1'	C—H stretching	3009	3020	—	3021	2236	2236	2226
	CH_2 deformation	1475	1475	—	1484	1270	1270	1265
	Ring breathing	1188	1188	—	1193	956	956	950
A_2'	CH_2 wagging	(975)	—	—	975	(790)	—	790
E'	C—H stretching	3028.1	3019	3024.4	3033	2211.4	2204	2204
	CH_2 deformation	1441.8	1434	1437.7	1413	1074.3	1068	1089
	Ring deformation	1028.7	1024	1028.44	1033	886.9	883	891
	CH_2 wagging	868.5	866	868.5	892	720.1	720	699
A_1''	CH_2 twisting	(1125)	—	—	1125	(800)	—	796
A_2''	C—C stretching	3102.9	3090	3101.7	3120	2338	2330	2324
	CH_2 rocking	(854)	854	—	854	614	614	614
E''	C—H stretching	3075	3075	—	3093	2329	2329	2316
	CH_2 twisting	(1050)	—	—	1067	(835)	—	822
	CH_2 rocking	741	741	—	728	528	528	538

Table 5. Rotational and centrifugal distortion constants (all in cm^{-1}) and the first-order Coriolis constants (ζ dimensionless) for cyclopropane and cyclopropane- d_6 .

	Observed ⁶	C_3H_6		C_3D_6
			Calc.	Calc.
A			0.4200	0.3196
B			0.6696	0.4608
D_J			9.89×10^{-7}	3.76×10^{-7}
D_{JK}			-12.04×10^{-7}	-3.33×10^{-7}
D_K			4.24×10^{-7}	0.815×10^{-7}
$E' \times E'$	ζ_5	-0.04 ± 0.003	-0.004	-0.019
	ζ_6	0.105 ± 0.002	-0.052	-0.412
	ζ_7	-0.073 ± 0.002	0.004	0.004
	ζ_8	-0.96 ± 0.03	-0.948	-0.574
$E'' \times E''$	ζ_{12}		0.015	0.024
	ζ_{13}		-0.426	-0.549
	ζ_{14}		0.615	0.804

experimental Coriolis constants (ζ) of the $E' \times E'$ type with respect to the C_3 axis (z) for cyclopropane. They are compared with the results of the present calculations in Table 5. The agreement is very good for ζ_3 . The three other $E' \times E'$ type ζ constants are all seen to be relatively small, but there is poor quantitative agreement between the observed and calculated values. This fact suggests that a further refinement of the force field could be made. Table 5 also gives the calculated rotational constants and centrifugal distortion constants, as well as the $E' \times E'$ type Coriolis constants for cyclopropane and cyclopropane- d_6 .

CONCLUSION

It is intended to use the reported force fields to calculate the mean amplitudes of vibration⁷ and related quantities. For this purpose and similar computations the force fields are believed to be sufficiently accurate, in spite of the failure of quantitative correspondence between three observed and calculated Coriolis constants for cyclopropane. These quantities are known in general to be very sensitive to force constant variations; hence it is reasonable to assume that agreement with the observed ζ values could be achieved by relatively small changes in the force constants. It seems, however, not worth while performing further refinements of the force fields at the present stage.

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Received January 30, 1969.