Molecular Vibrations of Cubane and Its Deuterated Derivatives

S. J. Cyvin, B. N. Cyvin, and J. Brunvoll
Division of Physical Chemistry, The University of Trondheim, Norway

Z. Naturforsch. **38a,** 1248 – 1262 (1983); received August 8, 1983

A harmonic field for cubane is developed by means of the following experimental data from literature: vibrational frequencies for C_8H_8, sym-$C_8H_6D_2$, sym-$C_8H_2D_6$ and C_8D_8, in addition to three Coriolis constants of C_8H_8. As a part of this analysis a new iteration method was developed for simultaneous fitting of vibrational frequencies and first-order Coriolis constants of a three-dimensional symmetry block. The force constants were used to calculate the vibrational frequencies of all the twenty existing partially deuterated cubanes, in addition to the unsubstituted (C_8H_8) and perdeuterated (C_8D_8) molecules. Also the first-order Coriolis constants, mean amplitudes of vibration and perpendicular amplitude correction coefficients for selected cubane molecules are reported.

Introduction

Cubane (pentacyclo$[4.2.0.0.^{2,5}\,0.^{3,8}\,0^{4,7}]$octane), C_8H_8, is a highly interesting hydrocarbon because of its symmetrical cage structure, a cube skeleton of carbon atoms. The compound was first synthesized by Eaton and Cole [1]. The crystal structure was investigated by Fleischer [2]. A theoretical study of the molecular vibrations of the cubane model is due to Brunvoll and Cyvin [3], who produced a complete set of symmetry coordinates.

Raman and infrared spectra of cubane and four of its deuterated derivatives are reported by Della et al. [4]. The spectra were recorded in the solid state and solutions. The vapour-phase infrared spectrum of cubane, along with Raman spectra in solid and solution, were published by Cole et al. [5], based partly on a dissertation by Pakes [6].

The existing force field analyses [5, 6] of cubane are considered as preliminary. In the present work we have performed a detailed normal coordinate analysis taking into account both the observed Coriolis constants [5] and isotopic frequencies [4] as additional data. Furthermore, the mean amplitudes of vibration [7] were computed for the first time.

Molecular Structure

The octahedral (O_h) symmetry for the cubane molecule has been established. We have adopted the CC bond distance of 1.551 Å from the x-ray work [2]. Modern *ab initio* computations [8] suggest this value to be about 0.03 Å too low, but that is not supposed to have a significant effect on the present analysis. The CH bond distance was estimated to be 1.085 Å.

Preliminary Force Fields

A simple, approximate force field was assumed in terms of a force-constant matrix based on valence coordinates including redundancies:

r CH stretchings , d CC stretchings ,
γ CCC bendings , δ CCH bendings .

A number of runs with different numerical values were executed in order to get a reasonable agreement of the calculated frequencies with observed data for cubane and cubane-d_8 [4]. In this process some nonvanishing interaction force constants seemed to be unavoidable. Table 1 shows the produced force constants, which are consistent with

Table 1. Preliminary force constants.

Coordinate	Pakes [6]	Present	
r	4.837 mdyne/Å	4.85 mdyne/Å	
d	3.559 mdyne/Å	3.8 mdyne/Å	
γ	0.758 mdyne Å	0.842 mdyne Å	0.35 mdyne/Å
δ	0.421 mdyne Å	0.454 mdyne Å	0.27 mdyne/Å
d/d	0.101 mdyne/Å	0	
d/γ	0	0.155 mdyne	0.1 mdyne/Å
d/δ	0.075 mdyne	0.283 mdyne	0.1 mdyne/Å

Reprint requests to Prof. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norwegen.

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Table 2. Vibrational frequencies (cm^{-1}) for C_8H_8 and C_8D_8 calculated from simple, approximate force fields, along with observed data.

Species (activity)[a]	No.	Cubane				Cubane-d_8		
		Calc. (a)	Calc. (b)	Calc. (c)	Obs. [4]	Calc. (b)	Calc. (c)	Obs. [4]
A_{1g} (Ra)	1	2991	2987	2991	2995	2225	2228	2259
	2	990	994	990	1002	944	941	956
E_g (Ra)	5	1167	1062	1083	1083	1007	1044	1027
	6	877	872	936	912	651	687	684
F_{1g} (ia)	9	1115	1073	1115	1130	837	869	884
F_{2g} (Ra)	13	2989	2984	2988	2970	2217	2219	2232
	14	1361	1282	1247	1182	1222	1181	1072
	15	887	879	910	821	643	671	715
	16	636	604	635	665	583	613	586
A_{2u} (ia)	3	2990	2984	2990	2978	2217	2224	~ 2239
	4	958	912	958	839	869	911	807
E_u (ia)	7	1136	1093	1136	1151	880	915	960
	8	387	367	387	617	323	339	527
F_{1u} (IR)	10	2990	2985	2988	2978	2221	2222	2240
	11	1301	1246	1237	1230	1153	1134	1083
	12	864	862	885	853	651	674	686
F_{2u} (ia)	17	1227	1120	1113	1036	1088	1086	924
	18	908	901	949	829	656	688	674

[a] Ra Raman active; ia inactive; IR infrared active.

(a) Present diagonal force field.
(b) Nondiagonal force field from Pakes [6].
(c) Present nondiagonal force field.

the calculated frequencies of Table 2. Here the column (a) shows the calculated frequencies for C_8H_8 with a diagonal force field (all interaction force constants neglected); the main constants have the same numerical values in the cases (a) and (c); cf. Table 1. The nondiagonal force-constant matrix was used to calculate the frequencies for both C_8H_8 and C_8D_8; cf. column (c). The set of column (b) is calculated with numerical force constants from Pakes [6], also given in Table 1. In this run we were not able to reproduce exactly the reported calculated frequencies in the mentioned work [6], but the general agreement was satisfactory. Pakes [6] has not calculated any isotopic frequencies. In Table 2 the calculated frequencies are compared with observed values from Della et al. [4]. Our results are seen to be comparable with those of Pakes [6], but give a slightly better general agreement with the observed frequencies. In general the calculations support the experimental assignment except for the lowest $E_u\,(\nu_8)$, which is spectroscopically inactive. Most probably this frequency has been mis-assigned in the experimental works [4, 6]. This conclusion is supported by the calculations of Pakes [6].

Species F_{1u} of C_8H_8

Experimental Data

The first-order Coriolis constants [7, 9–12] of the F_{1u} species of cubane (say ζ_1, ζ_2 and ζ_3; cf. Table 3) have been determined by means of an analysis of the rotational structure of the infrared bands in the gas phase [5, 6]: 2990, 1235 and 852 cm^{-1}. Nevertheless we have adopted the infrared solid state data [4] (Table 2) because we wish to have the corresponding experimental data for isotopic derivatives [4] for further considerations. In the first place, however, we have considered the F_{1u} species of light cubane. A force field was derived using the experimental ζ values as additional information along with the frequencies. The ζ-sum rule [7, 9–12] reads in the present case

$$\zeta_1 + \zeta_2 + \zeta_3 = 0\,. \qquad (1)$$

The observed ζ values (Table 3) add up to 0.005; hence the experimental error limits of about ± 0.003 are to be expected. We have modified the observed values within these limits so that they obey the ζ-sum rule accurately; cf. the parenthesized values of Table 3. This modified set is the one to be used in the force constant determination.

Symmetry Coordinates

The symmetry coordinates of Brunvoll and Cyvin [3] were utilized with some modifications concerning the removal of redundancies. In the F_{1u} species in particular the γ-type coordinates were left out of S_2. The complete expressions of the F_{1u} symmetry coordinates in terms of the valence coordinates are given in the following; cf. Fig. 1 for the notation used for the valence coordinates.

$$
\begin{aligned}
S_{1a}(F_{1u}) &= 8^{-1/2}(r_1 + r_2 - r_3 + r_4 - r_5 - r_6 + r_7 - r_8)\,,\\
S_{2a}(F_{1u}) &= 8^{-1/2}(d_{12} + d_{14} - d_{36} + d_{47} - d_{56}\\
&\qquad - d_{58} + d_{27} - d_{38})\,,\\
S_{3a}(F_{1u}) &= \tfrac{1}{4}(RD)^{1/2}(\delta_{14} + \delta_{27} - \delta_{85} - \delta_{36} + \delta_{12}\\
&\qquad - \delta_{38} - \delta_{65} + \delta_{47} - \delta_{58} - \delta_{63}\\
&\qquad + \delta_{41} + \delta_{72} - \delta_{56} + \delta_{74}\\
&\qquad + \delta_{21} - \delta_{83})\,;
\end{aligned} \tag{2a}
$$

$$
\begin{aligned}
S_{1b}(F_{1u}) &= 8^{-1/2}(r_1 + r_2 + r_3 - r_4 - r_5 - r_6 - r_7 + r_8)\,,\\
S_{2b}(F_{1u}) &= 8^{-1/2}(d_{12} + d_{13} - d_{46} - d_{47} - d_{56}\\
&\qquad - d_{57} + d_{28} + d_{38})\,,\\
S_{3b}(F_{1u}) &= \tfrac{1}{4}(RD)^{1/2}(\delta_{13} - \delta_{46} - \delta_{75} + \delta_{28} + \delta_{12}\\
&\qquad + \delta_{38} - \delta_{65} - \delta_{47} - \delta_{57} + \delta_{82}\\
&\qquad + \delta_{31} - \delta_{64} - \delta_{56} - \delta_{74}\\
&\qquad + \delta_{21} + \delta_{38})\,;
\end{aligned} \tag{2b}
$$

$$
\begin{aligned}
S_{1c}(F_{1u}) &= 8^{-1/2}(r_1 - r_2 + r_3 + r_4 - r_5 + r_6 - r_7 - r_8)\,,\\
S_{2c}(F_{1u}) &= 8^{-1/2}(d_{13} + d_{14} + d_{36} + d_{46} - d_{57}\\
&\qquad - d_{58} - d_{27} - d_{28})\,,\\
S_{3c}(F_{1u}) &= \tfrac{1}{4}(RD)^{1/2}(\delta_{13} + \delta_{46} - \delta_{75} - \delta_{28} + \delta_{14} - \delta_{27}\\
&\qquad - \delta_{85} + \delta_{36} - \delta_{57} - \delta_{82} + \delta_{31}\\
&\qquad + \delta_{64} - \delta_{58} + \delta_{63}\\
&\qquad + \delta_{41} - \delta_{72})\,.
\end{aligned} \tag{2c}
$$

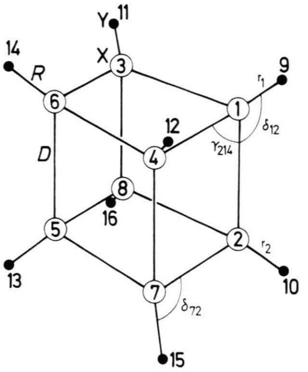


Fig. 1. The molecular model of cubane, X_8Y_8 (symmetry O_h). Valence coordinates: Eight r_i stretchings for the X_i-Y bonds; twelve d_{ij} stretchings for the X_i-X_j bonds; twenty-four δ_{ij} bendings for the $Y-X_i-X_j$ angles; twenty-four γ_{ijk} bendings for the $X_i-X_j-X_k$ angles. R and D are used to denote the XY and XX equilibrium distances, respectively.

Iteration Procedure with Linear Equations for Coriolis Constants

Observed Coriolis constants (ζ) are recognized as very useful additional information for determinations of force constants. General methods have been developed for ζ value fittings, based on the Jacobian elements, $\partial \zeta_k / \partial F_{ij}$ [15–17]. We have developed a new iteration procedure in the case of a three-dimensional species of degenerate vibrations, applicable to F_{1u} of cubane. Here the problem is to fit six independent force constants to five independent observed data, viz. three frequencies and two independent ζ values. By the new procedure we were able to deduce a set of symmetry force constants which reproduce accurately all the experimental frequency and Coriolis data. The iteration procedure is outlined in the following.

(i) Choose an initial force field in terms of the symmetry **F** matrix:

$$
\begin{bmatrix}
F_{11} & F_{12} & F_{13}\\
 & F_{22} & F_{23}\\
 & & F_{33}
\end{bmatrix}.
$$

(ii) A linear equation for the ζ constants in terms of the force constants is given by [7]

$$
\sum_{i=1}^{3} \zeta_i \lambda_i = \sum_{i=1}^{3} F_{ii} C_{ii} + 2(F_{12} C_{12} + F_{13} C_{13} + F_{23} C_{23})\,. \tag{3}
$$

Here λ_i are the familiar parameters proportional to the squared normal frequencies [7, 13]; C_{ij} are the elements of the appropriate symmetrical, three-dimensional block of the Coriolis $\mathbf{C}^\alpha$ matrix [7, 10]. The force constants are adjusted to the experimental $\zeta\lambda$ product-sum, i.e. the left-hand side of (3), through $F_{ij} + \Delta F_{ij}$, where

$$\Delta F_{ii} = (C_{ii}/D) \sum_k \zeta_k \lambda_k \, ,$$

$$\Delta F_{ij} = (2\,C_{ij}/D) \sum_k \zeta_k \lambda_k \quad (i \neq j) \, . \tag{4}$$

Here

$$D = \sum_{i=1}^{3} C_{ii}^2 + 4\,(C_{12}^2 + C_{13}^2 + C_{23}^2) \, . \tag{5}$$

(iii) Invert the adjusted **F** matrix block to obtain the compliants [7, 14]:

$$\begin{bmatrix} N_{11} & N_{12} & N_{13} \\ & N_{22} & N_{23} \\ & & N_{33} \end{bmatrix} .$$

(iv) Another linear equation for the ζ constants exists, viz. [7]

$$\sum_{i=1}^{3} (\zeta_i/\lambda_i) = \sum_{i=1}^{3} N_{ii} \bar{C}_{ii} + 2\,(N_{12}\bar{C}_{12} + N_{13}\bar{C}_{13} + N_{23}\bar{C}_{23}) \, . \tag{6}$$

Here $\bar{C}_{ij}$ are the appropriate elements of the $\bar{\mathbf{C}}^\alpha$ matrix [7, 10]. The compliants are now adjusted to the experimental ζ/λ quotient-sum through $N_{ij} + \Delta N_{ij}$, where

$$\Delta N_{ii} = (\bar{C}_{ii}/D') \sum_k (\zeta_k/\lambda_k) \, ,$$

$$\Delta N_{ij} = (2\,\bar{C}_{ij}/D') \sum_k (\zeta_k/\lambda_k) \quad (i \neq j) \tag{7}$$

and

$$D' = \sum_{i=1}^{3} \bar{C}_{ii}^2 + 4\,(\bar{C}_{12}^2 + \bar{C}_{13}^2 + \bar{C}_{23}^2) \, . \tag{8}$$

(v) The obtained **N** matrix block is inverted in order to produce the corresponding **F**.

Repeat (ii)–(v) until a self-consistent field is achieved (if possible) with a sufficient accuracy. This force field would reproduce accurately the experimental ζ values if the calculated frequencies were correct.

(vi) Adjust the **F** matrix deduced from the above iteration to the experimental frequencies according to the **L**-matrix approximation method [18–20]:

$$\mathbf{F} = \tilde{\mathbf{L}}^{-1}\,\lambda(\mathrm{exp})\,\mathbf{L}^{-1} \, . \tag{9}$$

Use the force field from (9) under point (i), and start over again from (ii).

Numerical Calculations

The preliminary force fields (see above) are not consistent with the experimental ζ values, as is seen from Table 3. The symmetry **F** matrix block of the force field (c) for the species F_{1u} reads (in mdyne/Å)

$$\begin{bmatrix} 4.850 & 0 & 0 \\ & 4.503 & -0.310 \\ & & 0.810 \end{bmatrix} .$$

The F_{11} constant was maintained during the determination of an initial force field. At first it was also attempted to keep $F_{12} = F_{13} = 0$. In that case (3) together with [7, 13]

$$\sum_{i=1}^{3} \lambda_i = \sum_{i=1}^{3} F_{ii} G_{ii} + 2\,(F_{12}G_{12} + F_{13}G_{13} + F_{23}G_{23}) \tag{10}$$

gave $F_{33} = 0.394$ mdyne/Å along with a linear dependence for F_{22} and F_{33}. Some pairs of solutions (in mdyne/Å) are (5.94, −0.31) and (6.16, 0.00). Further considerations were made with (6) included into the system, but none of the solutions gave acceptable calculated frequencies and Coriolis constants. In conclusion the approximations of $F_{12} = F_{13} = 0$ had to be abandoned. A nonvanishing F_{13} constant was introduced. The following numerical values were found, which obey (3) and (10), and where F_{23} and F_{33} were assumed as compatible with the preliminary set of (c); see above.

$$\begin{bmatrix} 4.850 & 0 & 0.249 \\ & 4.037 & -0.300 \\ & & 0.810 \end{bmatrix} .$$

Table 3. Preliminary calculated and observed F_{1u} Coriolis constants of C_8H_8.

Constant	Calculated		Observed [5, 6]	
	(b)	(c)		
ζ_1	−0.021	−0.019	−0.099	(−0.100)[a]
ζ_2	−0.051	0.025	0.258	(0.255)
ζ_3	0.072	−0.006	−0.154	(−0.155)

[a] Parenthesized values are modified in order to fit accurately the ζ-sum rule.

This set was used as the starting point of the iteration procedure described above. Convergence was obtained, and the result of the iteration reads

$$\begin{bmatrix} 4.784 & -0.083 & 0.279 \\ & 3.853 & -0.386 \\ & & 0.907 \end{bmatrix}$$

and is referred to as set (d). A similar result was obtained by Cole et al. [5] after computations according to the more conventional iteration procedure.

Refined Computations for C_8H_8 and C_8D_8

Valence Force Constants

A new set of valence force constants were derived in consistence with the force field of set (d) for the species F_{1u} of C_8H_8 (see above). This problem is indeterminate. We have selected nine nonvanishing parameters and determined the following numerical values (all in mdyne/Å): $f(r) = 4.784$, $f(d) = 3.400$, $f(\gamma) = 0.203$, $f(\delta) = 0.302$, $f(d/\gamma) = 0.100$, $f(d/\delta) = 0.085$, $f(r/d) = 0.075$, $f(r/\delta$ adjacent$) = -0.099$, $f(r/\delta$ opposite$) = 0.099$. The interaction terms all pertain to neighbouring coordinates, i.e. those having at least one C atom in common. Table 4 shows in column (d) the calculated frequencies from this force field for the whole molecule of C_8H_8. The corresponding symmetry force constants were deduced and subsequently adjusted according to the **L**-matrix approximation method (see above) to the frequencies listed in column (e) of Table 4. They are all equal to the observed values [4] except for ν_8, where it was supposed to be more correct to use the calculated value from column (c) of Table 2. The refined force field (e) was used to calculate the frequencies of C_8D_8 with the result displayed in Table 4. There are several significant discrepancies on comparing with the observed values [4]. Nevertheless, the general agreement seems good enough for our purpose, namely to use the force field as a starting point in an iteration procedure for frequency fitting of the two isotopic molecules.

Table 4. Vibrational frequencies (cm^{-1}) for C_8H_8 and C_8D_8 from different force fields, along with modified observed data.

Species	No.	Cubane				Cubane-d_8		
		Calc. (d)	Calc. (e)	Calc. (f)	Modified observed	Calc. (e)	Calc. (f)	Modified observed
A_{1g}	1	2956	2995	2995	2995	2218	2221	2221
	2	941	1002	1002	1002	957	956	956
E_g	5	1113	1083	1084	1083	993	1026	1027
	6	914	912	913	912	704	682	684
F_{1g}	9	1179	1130	1131	1130	881	882	884
F_{2g}	13	2995	2970	2946	2970	2219	2197	2135
	14	1202	1182	1180	1182	1060	1060	1072
	15	879	821	823	821	652	692	715
	16	497	665	663	665	626	590	586
A_{2u}	3	3010	2978	2978	2978	2236	2190	2190
	4	777	839	839	839	790	807	807
E_u	7	1190	1151	1151	1151	916	960	960
	8	297	387	387	387	344	328	328
F_{1u}	10	2978	2978	2969	2978	2216	2208	2184
	11	1230	1230	1234	1230	1081	1072	1083
	12	853	853	851	853	677	684	686
F_{2u}	17	1115	1036	1038	1036	936	921	924
	18	917	829	834	829	649	665	674

(d) Valence force constants consistent with observed F_{1u} frequencies and ζ values of C_8H_8.
(e) Adjusted to C_8H_8 frequencies, which are identical with observed values (cf. Table 2), except for ν_8.
(f) Result of the iteration procedure.

Iteration Procedure

A standard least-squares fitting was performed for the two isotopic molecules in question, cubane and cubane-d_8. For this purpose it was adherred to the frequencies of C_8H_8 from column (e) of Table 4. Some of the C_8D_8 frequencies were modified because of the inaccuracies in the Teller-Redlich product rule for the observed frequencies [4]; cf. Table 5.

Table 5. Teller-Redlich product rule for the C_8H_8/C_8D_8 frequencies.

Species (O_h)	Observed	Theoretical
A_{1g}	1.390	1.414
E_g	1.406	1.414
F_{1g}	1.278	1.282
F_{2g}	1.912	1.998
A_{2u}	1.383	1.414
E_u	1.404	1.414
F_{1u}	1.877	1.925
F_{2u}	1.379	1.414

In species A_{1g}, F_{2g} and A_{2u} we found it as reasonable to modify the CD stretching frequencies. The following values (in cm^{-1}) are consistent with the theoretical product rule along with the observed frequencies otherwise: $\nu_1 = 2220.6$, $\nu_{13} = 2135.3$, $\nu_3 = 2190.2$. The corresponding modification in species F_{1u} gives $\nu_{10} = 2184.4$. The frequencies of species E_g, F_{1g} and F_{2u} were not modified. Either (a) the Teller-Redlich product rule is satisfied with a sufficient accuracy (E_g, F_{1g}), (b) the frequencies are inactive (F_{1g}, F_{2u}) or (a & b) both (F_{1g}). In species E_u we have used a calculated value for ν_8 of C_8H_8. Hence it is reasonable to calculate the corresponding frequency of C_8D_8 in consistence with the product rule; the result is 328.2 cm^{-1}.

We do not report here the complete force field consistent with columns (f) of Table 4 since it is not yet the final one. It may be instructive, however, to show the symmetry force constant block of species F_{1u} for comparison with the preliminary results of sets (c) and (d); see above. All force constants are in mdyne/Å; standard deviations in parentheses.

$$\begin{bmatrix} 4.755\ (0.048) & -0.083\ (\text{ass.}) & 0.279\ (\text{ass.}) \\ & 3.710\ (0.576) & -0.380\ (0.107) \\ & & 0.941\ (0.144) \end{bmatrix}.$$

Inclusion of sym-$C_8H_6D_2$ and sym-$C_8H_2D_6$

Della et al. [4] have included sets of observed frequencies for sym-cubane-d_2 and sym-cubane-d_6 in their report.

Symmetry Coordinates

The partially deuterated molecules in question both belong to the D_{3d} symmetry. The normal vibrations are distributed into the different symmetry species according to

$$\Gamma_{\text{vib}}(D_{3d}) = 6A_{1g} + A_{2g} + 7E_g + 2A_{1u} + 5A_{2u} + 7E_u\,. \tag{11}$$

The correlations with the normal vibrations of the unsubstituted molecule of O_h symmetry are well known [13]. The O_h symmetry coordinates from Brunvoll and Cyvin [3] were utilized. A certain modification is described above for the $S_2(F_{1u})$ coordinate. The following coordinates were subjected to the same type of modification, i.e. leaving out the γ coordinates: $S_2(F_{2g})$, $S_2(A_{2u})$ and $S_1(F_{2u})$. The z-axis of the D_{3d} model was chosen through the atoms 9-1-5-13 (cf. Figure 1). Consequently the a and b coordinates of species E_g and E_u in the O_h model are consistent with the orientation of the corresponding tentatively standardized symmetry coordinates for a puckered hexagonal ring (symmetry D_{3d}) [21]. The different members (a, b and c) of the triply degenerate O_h coordinates had to be combined in order to fit into the D_{3d} scheme. The actual combinations are given below, where the O_h symmetry coordinates are symbolized by the species designations in small letters.

$$\begin{aligned} &f_{1g}(a) + f_{1g}(b) + f_{1g}(c) : A_{2g}, \\ &-f_{1g}(a) + f_{1g}(b) : E_g(a), \\ &-f_{1g}(a) - f_{1g}(b) + 2f_{1g}(c) : E_g(b)\,; \end{aligned} \tag{12}$$

$$\begin{aligned} &f_{2g}(a) + f_{2g}(b) + f_{2g}(c) : A_{1g}, \\ &-f_{2g}(a) - f_{2g}(b) + 2f_{2g}(c) : E_g(a), \\ &f_{2g}(a) - f_{2g}(b) : E_g(b)\,; \end{aligned} \tag{13}$$

$$\begin{aligned} &f_{1u}(a) + f_{1u}(b) + f_{1u}(c) : A_{2u}\,, \\ &f_{1u}(a) + f_{1u}(b) - 2f_{1u}(c) : E_u(a), \\ &-f_{1u}(a) + f_{1u}(b) : E_u(b)\,; \end{aligned} \tag{14}$$

$$\begin{aligned} &f_{2u}(a) + f_{2u}(b) + f_{2u}(c) : A_{1u}\,, \\ &f_{2u}(a) - f_{2u}(b) : E_u(a)\,, \\ &f_{2u}(a) + f_{2u}(b) - 2f_{2u}(c) : E_u(b)\,. \end{aligned} \tag{15}$$

Table 6. Teller-Redlich product rule for the C_8H_8/sym-$C_8H_6D_2$ and C_8H_8/sym-$C_8H_2D_6$ frequencies.

Species (D_{3d})	sym-$C_8H_6D_2$		sym-$C_8H_2D_6$	
	Obs.	Theor.	Obs.	Theor.
A_{1g}	1.389	1.414	1.949	1.998
A_{2g}	1.000	1.000	1.278	1.282
E_g	1.345	1.360	2.576	2.652
A_{1u}	~ 1.002	1.000	1.375	1.414
A_{2u}	1.371	1.400	1.911	1.943
E_u	1.378	1.400	2.690	2.746

Numerical Computations

Table 6 shows the observed and theoretical product rules for sym-cubane-d_2 and sym-cubane-d_6. The observed frequencies [4] were again modified in order to fit accurately the product rules. Also the reported ν_8 frequencies of sym-$C_8H_6D_2$ and sym-$C_8H_2D_6$ (574 and 538 cm^{-1}, respectively), were replaced by calculated values. The modified frequencies (Table 7) were used in a conventional iteration procedure of least-squares fitting for all the four isotopic molecules. The calculated frequencies from the resulting force constants (g) are given in Table 7.

Final Force Field

The force constants of the F_{1u} species were refined for the last time. Table 7 shows the calculated frequencies from the set (g). The corresponding Coriolis constants were computed with the result: $\zeta_1 = -0.101$, $\zeta_2 = 0.301$, $\zeta_3 = -0.200$; see Table 3 for the observed values. Starting from the

Table 7. Vibrational frequencies (cm^{-1}) from least-squares fittings for four isotopic molecules of cubane, along with modified observed data.

Species		C_8H_8		sym-$C_8H_6D_2$		sym-$C_8H_2D_6$		C_8D_8	
D_{3d}	O_h	Calc. (g)	Mod. obs.	Calc. (g)	Mod. obs.	Calc. (g)	Mod. obs.	Calc. (g)	Mod. obs.
A_{1g}	A_{1g}	3003	2995	2989	2993	2208	2199	2213	2221
		999	1002	989	991	968	967	959	956
	F_{2g}	2943	2970	2203	2197	2957	2978	2195	2135
		1181	1182	1166	1168	1081	1083	1062	1072
		825	821	815	821	707	725	693	715
		665	665	654	651	592	579	591	586
A_{2g}	F_{1g}	1132	1130	1132	1130	883	882	883	884
E_g	E_g	1086	1083	1015	1016	1033	1035	1027	1027
		914	912	880	875	690	704	683	684
	F_{1g}	1132	1130	1100	1100	982	985	883	884
	F_{2g}	2943	2970	2942	2938	2197	2165	2195	2135
		1181	1182	1169	1174	1139	1145	1062	1072
		825	821	728	738	751	758	693	715
		665	665	640	632	613	598	591	586
A_{1u}	F_{2u}	1037	1036	1037	1036	927	914	927	924
		831	829	831	829	658	665	658	674
A_{2u}	A_{2u}	2975	2978	2974	2968	2197	2206	2193	2190
		841	839	825	838	815	807	807	807
	F_{1u}	2971	2978	2210	2193	2970	2974	2210	2184
		1234	1230	1214	1201	1098	1100	1073	1083
		851	853	847	851	687	690	683	686
E_u	E_u	1150	1151	1118	1109	1013	1014	962	960
		388	387	368	368	339	340	328	328
	F_{1u}	2971	2978	2970	2977	2212	2205	2210	2184
		1234	1230	1207	1222	1159	1164	1073	1083
		851	853	840	844	790	786	684	686
	F_{2u}	1036	1036	966	958	934	962	927	924
		831	829	714	711	671	651	658	674

F_{1u} force constants of set (g) the force field was refined in order to fit accurately the observed frequencies and ζ values according to the techniques described above: iteration procedure with linear equations for Coriolis constants, combined with the **L**-matrix approximation method. For all the blocks except F_{1u} (referring to O_h symmetry) the force constant set (g) was considered as the final one. The final force field, referred to as set (h), is given in Table 8.

The calculated F_{1u} frequencies of C_8D_8 from the final force field (h) are: 2214, 1081 and 678 cm^{-1}; the result is satisfactory. For the other species of C_8H_8 and C_8D_8 the final calculations are identical to those of Table 7 under columns (g). The observed (unmodified) frequencies are found in Table 2. Table 9 shows the final calculated frequencies for sym-cubane-d$_2$ and sym-cubane-d$_6$ along with the observed data.

Table 9. Final calculated frequencies (cm^{-1}) along with observed data for sym-cubane-d$_2$ and sym-cubane-d$_6$.

Species (D_{3d})	No.	sym-$C_8H_6D_2$		sym-$C_8H_2D_6$	
		Calc. (h)	Obs. [4]	Calc. (h)	Obs. [4]
A_{1g}	1	2989	2993	2208	2254
	2	989	991	968	967
	13a	2203	2237	2957	2978
	14a	1166	1168	1081	1083
	15a	815	821	707	725
	16a	654	651	592	579
A_{2g}	9a	1132	(1130)	883	884
E_g	5	1015	1016	1033	1035
	6	880	875	690	704
	9b	1100	1100	982	985
	13b	2942	2970	2197	2229
	14b	1169	1174	1139	1145
	15b	728	738	751	758
	16b	640	632	613	598
A_{1u}	17a	1037	1036	914	927
	18a	831	~ 827	665	674
A_{2u}	3	2976	2968	2198	2242
	4	827	838	815	807
	10a	2214	2240	2975	2974
	11a	1209	1201	1108	1100
	12a	848	851	682	690
E_u	7	1119	1109	1018	1014
	8	368	574	339	538
	10b	2977	2977	2217	2236
	11b	1206	1222	1159	1164
	12b	840	844	790	786
	17b	968	995	934	975
	18b	712	711	668	651

Analysis of all Deuterated Cubanes

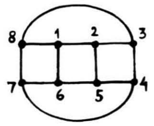
Survey and Notation

Exactly twenty partially deuterated cubanes are possible, in addition to the two pure compounds (C_8H_8 and C_8D_8). Figure 2 gives a survey of the fourteen different compounds of cubane-d$_0$, -d$_1$, -d$_2$, -d$_3$ and -d$_4$. In addition one has the -d$_5$, -d$_6$, -d$_7$ and -d$_8$ derivatives, which are complementary to -d$_3$, -d$_2$, -d$_1$ and -d$_0$, respectively. Complementary compounds are here defined as those where the H and D atoms are interchanged. The notation referring to standard (IUPAC) numbering for the eight compounds which complete the list from Fig. 2 is given below. The Roman numerals in parentheses refer to the appropriate complementary compounds in consistence with the numbering of Figure 2.

XV (VIII)	1,2,3,4,5-pentadeuterocubane
XVI (VII)	1,2,3,4,6-pentadeuterocubane
XVII (VI)	1,2,3,5,7-pentadeuterocubane
XVIII (V)	1,2,3,4,5,6-hexadeuterocubane

Table 8. Final symmetry force constants (mdyne/Å) of cubane, referred to as set (h). Standard deviations in parentheses.

Species (O_h)	**F** matrix block	
A_{1g}	4.993 (0.056)	
	0.446 (0.196)	3.826 (0.102)
E_g	3.578 (0.171)	
	0.114 (0.030)	0.273 (0.016)
F_{1g}	0.278 (0.006)	
F_{2g}	4.650 (0.015)	
	0.157 (ass.)	4.044(0.213)
	−0.061 (ass.)	−0.383 (ass.)
	−0.260 (ass.)	−0.697 (ass.)
	0.526 (0.025)	
	0.265 (ass.)	0.821 (0.028)
A_{2u}	4.870 (0.059)	
	−0.089 (0.072)	0.339 (0.013)
E_u	0.422 (0.104)	
	−0.075 (0.051)	0.243 (0.031)
F_{1u}	4.791 (0.016)	
	−0.050 (ass.)	3.841 (0.195)
	0.283 (ass.)	−0.383 (0.037)
	0.908 (0.046)	
F_{2u}	2.802 (0.114)	
	−0.094 (0.026)	0.263 (0.012)



	Numbering of Fig. 1									Standard (IUPAC) notation	
C:	1	2	3	4	5	6	7	8	Symm. group		
H/D:	9	10	11	12	13	14	15	16			
I	H	H	H	H	H	H	H	H	O_h	cubane	$-d_0$
II	D	H	H	H	H	H	H	H	C_{3v}	monodeuterocubane	$-d_1$
III	D	H	H	H	D	H	H	H	D_{3d}	1,4-dideuterocubane	$-d_2$
IV	D	H	H	H	H	D	H	H	C_{2v}^{I}	1,5-dideuterocubane	$-d_2$
V	D	D	H	H	H	H	H	H	C_{2v}^{II}	1,2-dideuterocubane	$-d_2$
VI	H	D	D	D	H	H	H	H	C_{3v}	1,3,5-trideuterocubane	$-d_3$
VII	D	D	H	H	D	H	H	H	C_s	1,2,4-trideuterocubane	$-d_3$
VIII	D	H	D	D	H	H	H	H	C_s	1,2,3-trideuterocubane	$-d_3$
IX	D	H	H	H	H	D	D	D	T_d	1,3,5,7-tetradeuterocubane	$-d_4$
X	D	H	D	D	H	D	H	H	C_{4v}	1,2,3,8-tetradeuterocubane	$-d_4$
XI	D	D	D	D	H	H	H	H	C_{3v}	1,2,3,5-tetradeuterocubane	$-d_4$
XII	D	D	H	H	D	D	H	H	D_{2h}	1,2,4,7-tetradeuterocubane	$-d_4$
XIII	D	H	D	D	D	H	H	H	C_s	1,2,3,7-tetradeuterocubane	$-d_4$
XIV	D	D	D	H	H	H	D	H	C_2	1,2,3,4-tetradeuterocubane	$-d_4$

Fig. 2. Survey of isotopic substitutions of cubane with deuterium. Notice that two different C_{2v} models are encountered, here designated C_{2v}^{I} and C_{2v}^{II}; cf. (22) and (26), respectively.

XIX (IV)	1,2,3,4,5,7-hexadeuterocubane
XX (III)	1,2,3,4,6,7-hexadeuterocubane
XXI (II)	heptadeuterocubane
XXII (I)	octadeuterocubane

The T_d Model

A cubane derivative of T_d symmetry is obtained on substituting the atoms number 9, 14, 15 and 16 (cf. Figure 1). The correlations between the species of the O_h and T_d models are well known [13]; one has

$$\Gamma_{\text{vib}}(T_d) = 4A_1 + 4E + 3F_1 + 7F_2 . \tag{16}$$

The *a*, *b* and *c* members of degenerate symmetry coordinates are simply correlated into the separate blocks.

The C_{4v} Model

In the C_{4v} model we have adherred to a standard orientation of symmetry coordinates applied to the pyramidal XY_4 model [22]. The cubane model was oriented so that the atoms number 1, 3, 6 and 4 (cf. Fig. 1) correspond to numbers 1, 2, 3 and 4 in the XY_4 model, respectively. In consequence, a σ_v plane [13] passes through the atoms 1 and 6 (with the *x* axis lying in this plane), while a σ_d plane intersects the bonds 1–3 and 4–6. With these definitions the symmetrical structure of the normal modes of vibration is

$$\Gamma_{\text{vib}}(C_{4v}) = 7A_1 + 3A_2 + 8B_1 + 4B_2 + 10E . \tag{17}$$

The correlations with the normal modes of the O_h model were worked out with the result surveyed in Figure 3. The $E_g(a)$ and $E_g(b)$ coordinates of the O_h model are correlated with A_1 and B_2 of the C_{4v} mode, respectively; the $E_u(a)$ and $E_u(b)$ with B_1 and A_2. For the triply degenerate coordinates the following scheme applies.

$$\begin{aligned} f_{1g}(c) : A_2 ; \quad & f_{1g}(a) - f_{1g}(b) : E(a) ; \\ & f_{1g}(a) + f_{1g}(b) : E(b) . \end{aligned} \tag{18}$$

$$\begin{aligned} f_{2g}(c) : B_1 ; \quad & f_{2g}(a) + f_{2g}(b) : E(a) ; \\ & f_{2g}(a) - f_{2g}(b) : E(b) . \end{aligned} \tag{19}$$

$$\begin{aligned} f_{1u}(c) : A_1 ; \quad & f_{1u}(a) + f_{1u}(b) : E(a) ; \\ & -f_{1u}(a) + f_{1u}(b) : E(b) . \end{aligned} \tag{20}$$

$$\begin{aligned} f_{2u}(c) : B_2 ; \quad & f_{2u}(a) - f_{2u}(b) : E(a) ; \\ & -f_{2u}(a) - f_{2u}(b) : E(b) . \end{aligned} \tag{21}$$

The considered C_{4v} model is simply correlated with one of the occurring C_{2v} models, namely the one which applies to cubane-d_2 with the substituted

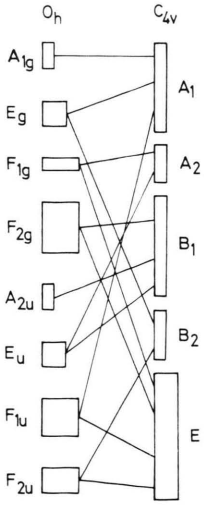


Fig. 3. Correlations between the normal vibrations in cubane (O_h) and 1,2,3,8-tetradeuterocubane (C_{4v} symmetry).

atoms number 9 and 14 in the numbering of Figure 1. The yz plane of reflection was chosen to go through the substituted atoms. One obtains consequently

$$\Gamma_{\text{vib}}(C_{2v}^{\text{I}}) = 15A_1(A_1+B_1) + 7A_2(A_2+B_2) + 10B_1(E) + 10B_2(E)\,. \tag{22}$$

Here the species designations in parentheses pertain to the C_{4v} group. The $E(a)$ and $E(b)$ blocks are correlated with B_2 and B_1 of the C_{2v} group, respectively.

The D_{2h} Model

Cubane-d$_4$ with the substituted atoms number 9, 10, 13 and 14 belongs to the symmetry group D_{2h}. In this model the z-axis was maintained as in the C_{4v} model, and the reflection plane through the substituted atoms was chosen as the yz-plane. Hence the appropriate symmetrical structure of the normal modes of vibration is

$$\Gamma_{\text{vib}}(D_{2h}) = 8A_g + 3B_{1g} + 5B_{2g} + 5B_{3g} + 4A_u + 7B_{1u} + 5B_{2u} + 5B_{3u}\,. \tag{23}$$

The correlation scheme with the normal modes of the O_h model is shown in Figure 4. Here the $E_g(a)$ and $E_g(b)$ coordinates of the O_h model are correlated with A_g and B_{1g} of the D_{2h} model, respectively; the $E_u(a)$ and $E_u(b)$ with B_{1u} and A_u. For the triply degenerate coordinates the below combinations may be applied to both sets of the g and u species.

$$f_1(c): B_1\,;\quad f_1(a)+f_1(b): B_2\,;\quad f_1(a)-f_1(b): B_3\,; \tag{24}$$

$$f_2(c): A\,;\quad f_2(a)-f_2(b): B_2\,;\quad f_2(a)+f_2(b): B_3\,. \tag{25}$$

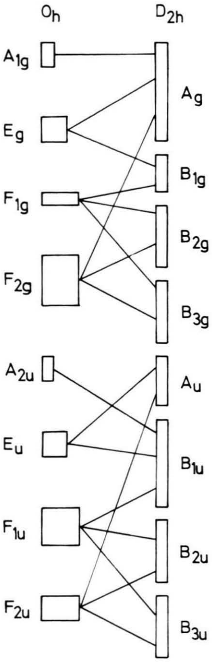


Fig. 4. Correlations between the normal vibrations in cubane (O_h) and 1,2,4,7-tetradeuterocubane (D_{2h} symmetry).

The D_{2h} model is simply correlated with another C_{2v} model, which applies to cubane-d$_2$ where the atoms number 9 and 10 are substituted. Again the yz plane was chosen to go through the substituted atoms. Then one has

$$\Gamma_{\text{vib}}(C_{2v}^{\text{II}}) = 13A_1(A_g+B_{2u}) + 9A_2(B_{2g}+A_u) + 8B_1(B_{1g}+B_{3u}) + 12B_2(B_{3g}+B_{1u})\,. \tag{26}$$

Here the species in parentheses pertain to the D_{2h} group.

The C_{3v} Model

Different substituted cubanes belong to the C_{3v} symmetry, *inter alia* cubane-d$_1$. The symmetrical structure of normal modes is simply correlated with the one of the D_{3d} model treated above. One has

$$\Gamma_{\text{vib}}(C_{3v}) = 11A_1(A_{1g}+A_{2u}) + 3A_2(A_{2g}+A_{1u}) + 14E(E_g+E_u)\,. \tag{27}$$

The C_s and C_2 Models

C_s and C_2 are the lowest possible symmetries of partially deuterated cubanes. For the C_s model one has

$$\Gamma_{\text{vib}}(C_s) = 25A'(A_1+B_2) + 17A''(A_2+B_1)\,, \tag{28}$$

where the species in parentheses pertain to either one of the C_{2v}^{I} or C_{2v}^{II} models. In the case of C_2 it was found

$$\Gamma_{\text{vib}}(C_2) = 22A(A_1+A_2) + 20B(B_1+B_2)\,, \tag{29}$$

where the parenthesized species pertain to C_{2v}^{II}.

Numerical Computations of Vibrational Frequencies

The final force field (h) was used to calculate the vibrational frequencies of all the possible deuterated cubanes. The final calculated frequencies of sym-cubane-d_2 (1,4-dideuterocubane, III) and sym-cubane-d_6 (1,2,3,4,6,7-hexadeuterocubane, XX) are shown in Table 9. Table 10 shows the results for the C_{3v} molecules of cubane-d_j with $j = 1$, 3, 5 and 7. The case of $j = 4$ (1,2,3,5-tetradeuterocubane, XI) is found in Table 11 along with the other tetradeuterocubanes. For the sake of brevity this table does not give the full listing of frequencies for the two least symmetrical compounds, 1,2,3,7-tetradeuterocubane (XIII) and 1,2,3,4-tetradeuterocubane (XIV). Also for the remaining isotopic molecules only some selected calculated frequencies are reported here; cf. Table 12.

Discussion of Vibrational Frequencies

A complete experimental assignment of the fundamentals of cubane-d_1 was furnished by Della et al. [4]. Table 10 shows a very good agreement between the observed frequencies and our calculations. It seems clear that ν_{15b} and ν_{18b} should be interchanged on comparing the calculations with experiments. This is not a real discrepancy, however, because of the ambiguities in numbering. Otherwise the mentioned investigators [4] have reported a few selected frequencies of partially deuterated cubanes from isotopic impurities in the sym-cubane-d_6 and cubane-d_8 samples. Their values are shown in brackets in Tables 10 and 12. Also the assignments of these fragmentary experimental frequencies [4] are astonishingly good. This is especially true for the ν_2 frequency, which was described as C–C stretch (breathing) in the experimental work [4]. The computations show this frequency to be characteristic for the abundance of D atoms in the molecule. In the four -d_4 molecules, for instance, the calculated ν_2 values do not deviate more than 3 cm^{-1} (cf. Table 11). We feel some

Table 10. Final calculated frequencies (cm^{-1}) for deuterated cubanes with C_{3v} symmetry: -d_1 (II), -d_3 (VI), -d_5 (XVII) and -d_7 (XXI), along with observed data from Ref. [4] in brackets. For -d_4 (XI), see Table 11.

Species (C_{3v})	No. [a]	-d_1	-d_3	-d_5	-d_7
A_1	1	2999 [2993]	2992	2982	2966
	2	994 [996]	986	975 [971]	964 [960]
	13a	2208 [2240]	2205	2204	2213
	14a	1172 [1174]	1098	1078	1067
	15a	817 [816]	705	692	701
	16a	659 [~ 659]	619	615	592
	3	2957 [2977]	2947	2196	2193
	4	837 [844]	823	819	811
	10a	2976 [2969]	2976	2217	2204
	11a	1221 [1219]	1203	1183	1100
	12a	850 [853]	840	827	679
A_2	9a	1132 [1132]	1090	1090	883
	17a	1037 [1036]	920	920	927
	18a	831 [834]	724	724	658
E	5	1069 [1062]	1033	1019	1032
	6	898 [898]	857	748 [716]	681
	9b	1104 [1101]	1091	974	913
	13b	2943 [2969]	2210	2208	2196
	14b	1173 [1179]	1160	1097	1070
	15b	721 [826]	708	702	692
	16b	651 [652]	634	607	600
	7	1144 [1145]	1118	1110	1003
	8	378 [590]	360	346	334
	10b	2978 [2977]	2959	2958	2216
	11b	1220 [1225]	1195	1167	1150
	12b	844 [847]	826	797	766
	17b	987 [1002]	964	919	938
	18b	829 [722]	757	670	665

[a] In some cases the numbering is tentative.

Table 11. Final calculated frequencies (cm^{-1}) for cubane-d_4 of different symmetries: T_d (IX), C_{4v} (X), C_{3v} (XI), D_{2h} (XII), C_s (XIII) and C_2 (XIV). Reported observed value for -d_4 [4] $\nu_2 = 978$ cm^{-1}.

Species (O_h)	No.[a]	T_d	C_{4v}		C_{3v}		D_{2h}		
A_{1g}	1	2989	2990		2990		2973		
	2	981	978		979		979		
E_g	5	1017	1038	1071	1037		1036	1004	
	6	780	878	862	856		868	753	
F_{1g}	9	1090	923	1017	1090	976	1106	1155	951
F_{2g}	13	2210	2195	2960	2196	2208	2205	2942	2199
	14	1097	1163	1127	1078	1153	1145	1040	1156
	15	702	738	692	695	712	699	721	749
	16	616	640	614	618	620	615	616	642
A_{2u}	3	2203	2959		2213		2205		
	4	822	825		821		824		
E_u	7	1119	1142	1027	1106		1109	1033	
	8	352	356	352	354		352	353	
F_{1u}	10	2958	2215	2206	2959	2959	2976	2219	2976
	11	1184	1178	1201	1202	1186	1193	1183	1160
	12	827	682	733	839	788	755	837	836
F_{2u}	17	920	979	949	920	962	933	944	995
	18	724	669	831	724	681	746	663	677

Species (O_h)	No.[a]	C_s			C_2		
A_{1g}	2	980			979		
E_g	6	850	853		852	863	
F_{2g}	16	632	611	620	613	628	624
A_{2g}	4	822			825		

[a] In some cases the numbering is tentative.

doubts as to the experimental assignment of 716 cm^{-1} as ν_6 of cubane-d_5 (cf. Table 10), but we have no better alternative. In general we find that ν_6, which was described as C–H bend [4], is not particularly characteristic for the number of D atoms in the molecule; cf. Tables 11 and 12. The ν_{16} frequencies (CC_3 deformation) appear to be moderately characteristic, namely within about 30 cm^{-1}. The calculated ν_4 frequencies (CC_3 def.) on the other hand, are found to vary less than 10 cm^{-1} for different cubane molecules with the same number of D atoms.

Della et al. [4] have suggested a linear dependence on j in cubane-d_j for the ν_2 frequency. This feature is confirmed with astonishing accuracy by our calculations. By least-squares fitting we have derived the formula

$$\nu_2/\mathrm{cm}^{-1} = 999.8 - 5.1\,j\,. \qquad (30)$$

Here the constant 5.1 is comparable with 5.75 reported in the experimental work [4]. Figure 5 shows the diagram of ν_2 as a function of j. The ν_4 frequency was treated in the same way, arriving at the formula

$$\nu_4/\mathrm{cm}^{-1} = 837.7 - 3.8\,j \qquad (31)$$

and the diagram of Figure 6. In this case the standard deviation from linearity is greater than in the case of ν_2; cf. legends of Figures 5 and 6.

Coriolis constants

The Coriolis constants are known to be rather sensitive for variations in the force constants [15–17, 23–30]. Nevertheless we believe that they may be calculated with good confidence from the present final force field, since it is based on a large

Table 12. Selected final calculated frequencies (cm^{-1}) for some partially deuterated cubanes. Observed values [4] in brackets.

Compound	Symmetry	ν_2	ν_6	ν_{16a}	$\nu_{16b,c}$	ν_4
-d_2 (III)	D_{3d}	989	880	654	640	827
-d_2 (IV)	C_{2v}^{I}	990	891 865	646	631 648	825
-d_2 (V)	C_{2v}^{II}	991	887 890	631	643 654	832
-d_2		[991]	[875]	[651]	[632]	
-d_3 (VI)	C_{3v}	986	857	619	634	823
-d_3 (VIII)	C_s	984	875 857	626	646 626	822
-d_3 (VIII)	C_s	985	884 864	644	621 629	827
-d_5 (XV)	C_s	974	792 744	619	610 607	820
-d_5 (XVI)	C_s	974	783 752	614	602 624	820
-d_5 (XVII)	C_{3v}	975	748	615	607	819
-d_5		[971]	[716]			
-d_6 (XVIII)	C_{2v}^{II}	970	848 780	601	611 602	816
-d_6 (XIX)	C_{2v}^{I}	969	799 750	605	609 598	815
-d_6 (XX)	D_{3d}	968	690	592	613	815
-d_6		[967]	[704]	[579]	[598]	

Table 13. Calculated Coriolis constants for C_8H_8, C_8H_7D, sym-$C_8H_6D_2$, sym-$C_8H_2D_6$ and C_8D_8.

Species (O_h)	No.[a]	-d_0 (I)	-d_1 (II)	-d_2 (III)	-d_6 (XX)	-d_8 (XXII)
E_g	5	0.000	0.345	0.528	0.114	0.000
	6	0.000	0.113	0.284	0.133	0.000
F_{1g}	9	0.500	−0.111	−0.203	0.388	0.500
F_{2g}	13	0.097	0.097	0.096	0.131	0.128
	14	0.574	0.409	0.434	0.901	0.673
	15	0.732	0.268	0.235	0.160	0.053
	16	−0.404	−0.105	0.089	−0.292	0.145
E_u	7	0.000	0.152	−0.033	−0.185	0.000
	8	0.000	0.087	0.165	−0.121	0.000
F_{1u}	10	−0.100	−0.100	−0.101	−0.132	−0.135
	11	0.255	0.171	−0.084	0.678	−0.004
	12	−0.155	−0.049	−0.020	0.524	0.139
F_{2u}	17	0.500	0.571	0.651	0.113	0.500
	18	0.500	0.635	0.421	0.123	0.500

[a] In some cases the numbering is tentative, but it is consistent with Tables 2, 4, 9 and 10.

number of observed frequencies for isotopic molecules, in addition to some observed Coriolis constants. It is difficult to give some definite error limits of the calculated Coriolis constants, but ±0.01 seems to be a reasonable estimate. The final force field (h) (cf. Table 8) was used to compute the Coriolis constants for all the twenty-two isotopic molecules considered here. The complete material is too voluminous to be reported here. We only give the first-order Coriolis constants of cubane,

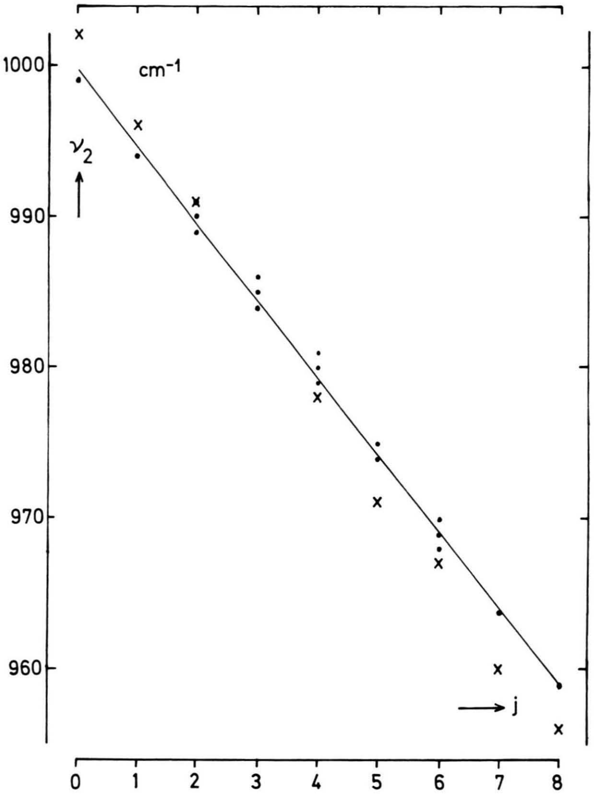


Fig. 5. The ν_2 frequency as a function of j in cubane-d$_j$ molecules. Standard deviation from linearity (for the calculated values): 0.83 cm^{-1}. Experimental values [4] are indicated by crosses.

Table 14. Calculated mean amplitudes of vibration (Å) for cubane and cubane-d$_8$.

Distance[a]	C_8H_8		C_8D_8	
	$T=0$	298 K	$T=0$	298 K
C−C (1.551)	0.0533	0.0539	0.0531	0.0538
C ... C (2.193)	0.0575	0.0597	0.0571	0.0595
C ... C (2.686)	0.0563	0.0576	0.0558	0.0573
C−H (1.085)	0.0785	0.0785	0.0671	0.0671
C ... H (2.351)	0.106	0.107	0.092	0.094
C ... H (3.142)	0.103	0.106	0.091	0.094
C ... H (3.771)	0.093	0.093	0.082	0.083
H ... H (2.804)	0.166	0.168	0.140	0.145
H ... H (3.965)	0.149	0.153	0.126	0.134
H ... H (4.856)	0.118	0.119	0.101	0.102

[a] H stands for both ^{1}H and ^{2}H = D. The equilibrium distances (in Å units) are included in parentheses.

Table 15. Calculated perpendicular amplitude correction coefficients (Å) for cubane and cubane-d$_8$.

Distance[a]	C_8H_8		C_8D_8	
	$T=0$	298 K	$T=0$	298 K
C−C (1.551)	0.0020	0.0023	0.0020	0.0023
C ... C (2.193)	0.0013	0.0014	0.0013	0.0015
C ... C (2.686)	0.0008	0.0008	0.0009	0.0009
C−H (1.085)	0.0161	0.0166	0.0115	0.0125
C ... H (2.351)	0.0077	0.0083	0.0056	0.0065
C ... H (3.142)	0.0056	0.0060	0.0040	0.0046
C ... H (3.771)	0.0045	0.0047	0.0032	0.0035
H ... H (2.804)	0.0104	0.0113	0.0073	0.0086
H ... H (3.965)	0.0077	0.0082	0.0052	0.0060
H ... H (4.856)	0.0063	0.0065	0.0042	0.0045

[a] See footnote to Table 14.

cubane-d$_1$, sym-cubane-d$_2$, sym-cubane-d$_6$ and cubane-d$_8$, i.e. the five molecules studied most extensively in the spectroscopical experiments [4]. These computational results are presented in Table 13. The unsubstituted molecule (C_8H_8) of O_h symmetry was also analysed in terms of the C_{3v} and D_{3d} symmetry coordinates, whereby the non-vanishing first-order ζ constants were reproduced numerically. The values of 0.5 for the $F_{1g} \times F_{1g}$ and

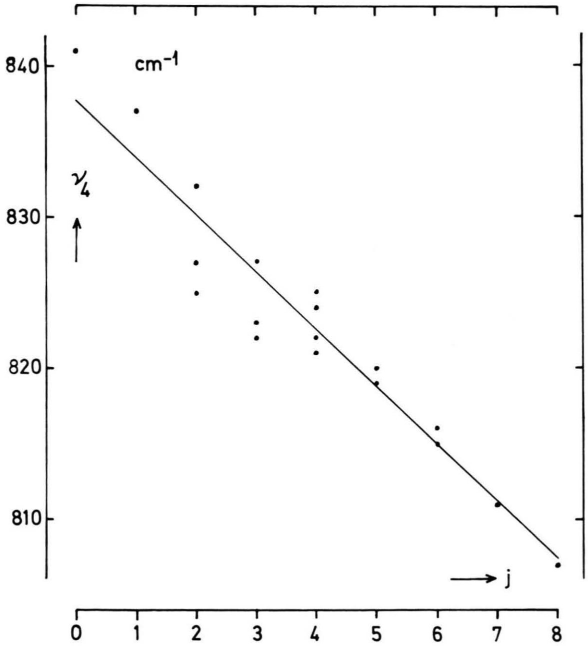


Fig. 6. The ν_4 frequency as a function of j in cubane-d$_j$ molecules. Standard deviation: 2.30 cm^{-1}.

$F_{2u} \times F_{2u}$ constants in the O_h models (C_8H_8 and C_8D_8) are exact; they do not depend on the force field.

Vibrational Amplitudes

The mean amplitudes of vibration, l [7], are of great interest in gas electron diffraction studies [7, 31]. The final force field (h) was used to compute the l values of C_8H_8 and C_8D_8 with the results shown in Table 14. These calculations are supposed to be quite reliable, especially because the mean amplitudes are not so sensitive for variations in force constants [7, 30]. The error limits are roughly estimated to about ±0.0005 Å for the bonded distances and about ±0.001 Å for the nonbonded ones.

Modern gas electron diffraction investigations also employ the perpendicular amplitude correction coefficients, K [7, 31, 32]. The K values for cubane and cubane-d_8 were also computed from the final force field and are shown in Table 15.

Acknowledgement

Financial support to BNC from the Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

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