## The infrared and Raman spectra of octachloro-, octafluoro-, and octahydroxycyclobutane\*†

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**Abstract**—Infrared and Raman spectra are reported for  $cyclo-C_4Cl_8$ ,  $c-C_4F_8$ , and  $c-C_4(OH)_8$ . In each case the infrared measurements extended down to 35 cm<sup>-1</sup>. For  $c-C_4Cl_8$  infrared data were obtained on the solid, and Raman data on the solid at room temperature and at  $-168^{\circ}C$ , on a saturated  $CS_2$  solution, and on the melt at 280°C. For  $c-C_4F_8$  infrared measurements were made on the gas and on the solid at  $\sim -173^{\circ}C$  and Raman ones on the gas and the liquid (both at room temperature). For  $c-C_4(OH)_8$  infrared data were obtained on the solid and Raman data on the solid and n an aqueous solution.

These are the first vibrational results reported for  $c-C_4Cl_8$ , and almost the first for  $c-C_4(OH)_8$ . For  $c-C_4F_8$  our data are more extensive and accurate than those in the literature, and require modification of 8–10 of the assignments.

The results provide convincing evidence that the carbon rings in  $c \cdot C_4 Cl_8$  and  $c \cdot C_4 F_8$  are puckered, and that the molecules have  $D_{2d}$  symmetry. Unfortunately the frequency of the puckering mode could not be found. In  $c \cdot C_4(OH)_8$  the evidence is equally clear that the ring is planar and the symmetry is  $D_{4h}$ . It is suggested that this surprising result is due to internal hydrogen bonding, which provides an added constraint against folding the ring.

For each molecule assignments are made to nearly all the spectroscopically-active fundamentals. Typically about half of these are certain, while the remainder are in doubt to varying degrees.

#### INTRODUCTION

THERE has been much interest in the vibrational spectra of cyclobutane-like fourmembered ring systems in the past few years, especially with regard to the ringpuckering vibration and the barrier to inversion. It is well known that the planarity or non-planarity of the ring at equilibrium depends upon the resultant of two large opposing forces. On the one hand the bond angles of the four-membered ring are considerably strained when the ring is planar, and become more so if it is folded. This tends to keep the ring planar. On the other hand the repulsive interactions between the non-bonded substituents (e.g. hydrogen or halogen atoms) are at a maximum for a planar ring, and therefore this tends to drive the ring into a folded conformation. The equilibrium structure is determined by the balance between these forces. If one or more  $CH_2$  groups are replaced by C==O or by 0, the second force is reduced and the ring becomes planar. (A ring may be considered planar if the barrier to inversion is below the ground state vibrational energy level.) The ring is found to be essentially planar (low or zero barrier) in trimethylene oxide

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[1], cyclobutanone [2, 3], 2-bromocyclobutanone [4], and cyclobutane-1,3-dione [5]. On the other hand the ring is puckered (appreciable barrier) in the prototype cyclobutane [6, 7 and references therein], silacyclobutane [8], fluorocyclobutane [9] chlorocyclobutane [9, 10], bromocyclobutane [11] and, interestingly, trimethylene sulfide [2, 3] and trimethylene selenide [12].

Whether the ring is planar or folded, the puckering vibration is usually strongly anharmonic because of a large quartic term in the potential function. The importance of this for puckering vibrations was first pointed out by BELL [13]. The potential function is often represented by  $V = az^2 + bz^4$ , where z is a coordinate for the puckering vibration. The quadratic coefficient a can be either positive or negative. The ring strain makes a positive contribution to it, whereas the non-bonded repulsion makes a negative one. If the former dominates, (i.e. a is positive) the potential function has a single minimum with steep sides. (V is zero at z = 0, and increases rapidly for all values of  $\pm z$ .) If the non-bonded repulsion dominates and a is negative, and if a and b have appropriate magnitudes, a symmetric double minimum potential well can result. Again V is zero at z = 0. As z increases, V is at first negative, but ultimately the quartic term prevails and V becomes positive at large z. It is convenient to think of the pure quartic potential  $V = bz^4$  having an inverted parabola superimposed on it. For certain intermediate cases the minimum can be almost flat.

In this paper we report results for three added *cyclo*butane derivatives. One of these,  $cyclo-C_4(OH)_8$ , unexpectedly has a planar ring structure which indicates the presence of a third type of interaction in it.

Very little has been done on the vibrational spectra of the molecules reported here. Of the three,  $c-C_4F_8$  has received the greatest attention [14, 15]. However a number of its fundamentals are still unassigned, including the ring-puckering mode. We hoped to locate this frequency in these molecules and to calculate the barrier to inversion, but unfortunately it could not be found. We are reporting here: (1) the complete vibrational spectrum of  $c-C_4Cl_8$  for the first time (2) a more extensive Raman spectrum of  $c-C_4F_8$  gas, with polarizations for both the gas and liquid, and (3) a far more comprehensive infrared and Raman study of  $c-C_4(OH)_8$  than is presently available.

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The only structures which need be considered for the  $c-C_4X_8$  molecules are the planar ring model of symmetry  $D_{4h}$  and the folded or puckered ring structure of symmetry  $D_{2d}$ . Table 1 summarizes the normal vibrations and their spectroscopic activity for each model. It also gives our assignments for the three molecules. HERZBERG's conventions [16] are followed throughout except for the numbering of

No.	D <sub>2d</sub> (pue Species	kered ring) Activity	D <sub>4A</sub> (pl Species	anar ring) Activity	Schematic description	$\begin{array}{c} As\\ c\text{-}C_4F_8\\ (gas)\\ (D_{2d}) \end{array}$	signments $c \cdot C_4 Cl_8$ (solid) $(D_{2d})$	$(\mathrm{cm}^{-\mathrm{i}})$ $c \cdot \mathrm{C}_4(\mathrm{OH})_8$ $(\mathrm{solid})$ $(D_{4\lambda})$
1 2	<i>a</i> <sub>1</sub>	R(p), —	a <sub>19</sub>	R(p), —	Ring str. CX. str., sym.	$\begin{cases} 1433 \\ 700 \end{cases}$	1055 408	
3					CX. soissors	607	353	421
4			b.,,		CX, str., antisym.	1413?	822	
5				-	CX, rock	359	253	
6					Ring puckering	?	?	
7	a2	·····, ·····	a29	,	CX <sub>2</sub> wag			
8			b <sub>24</sub>	—, —	CX <sub>2</sub> twist			
9	<i>b</i> <sub>1</sub>	R(dp), —	b1,g	R(dp),	Ring str.	1010	987	937
10					CX <sub>2</sub> wag	259*	130	$\sim 150$
11			a <sub>14</sub>	,	CX <sub>2</sub> twist	274*	207	
12	b <sub>s</sub>	R(dp), IR(  )	b <sub>29</sub>	R(dp), —	CX <sub>2</sub> str., sym.	1224	853	864
13					CX <sub>2</sub> scissors	659	393	495
14					<b>Ring deformation</b>	350	228	319
15			a <sub>su</sub>	—, IR(  )	CX <sub>2</sub> str., antisym.	1290	948	1080
16					CX <sub>2</sub> rock	284	188	324
17	e	R(dp), IR(   )	eg	R(dp), —	CX <sub>2</sub> str., antisym.	1340	980	1167
18		(1)			CX, rock	569	272	256
19					CX <sub>2</sub> twist	439	220	224
20			eu	—, IR(⊥)	CX <sub>2</sub> str., sym.	1239	636	1170
21			-		Ring stretch	963	789	900
22					CX <sub>2</sub> scissors	604	337	455
23					CX <sub>2</sub> wag	197	154	287

fable !	1.	Fundamental	vibrations	for	cyclo-C.	F.	. cyclo-C	.Cl.	. and c	vclo-C	(OH)	10
ranio 1	×.	T. minamentai	vioravions	TOT	0900-04	L - 8	$, ugua - u_{z}$		, and o	y000-01	(OL)	9

\* Liquid values.

the vibrations. It is difficult to show in Table 1 how the species of  $D_{4h}$  combine to give those of  $D_{2d}$ , and still maintain the usual numbering convention for both symmetries. Furthermore the order of schematic descriptions varies somewhat for each of the three molecules. We have therefore chosen to use a single numbering scheme for all three molecules because this makes discussion and intercomparison simpler. We regret any inconvenience that this may cause.

It is emphasized that the schematic descriptions are convenient terms for discussion and bookkeeping, but that in some cases they may be far from correct. Also, we have arbitrarily assumed that the antisymmetric  $CX_2$  stretches have higher frequencies than the symmetric ones for lack of good evidence either way.

<sup>[16]</sup> G. HERZBERG, Infrared and Raman Spectra of Polyatomic Molecules, especially pp. 113, 117, 271-2. Van Nostrand (1945).

It will be seen from Table 1 that it should be easy to distinguish between  $D_{4h}$  and  $D_{2d}$ . The former has a center of symmetry, and therefore the only Ramaninfrared coincidences will be accidental ones. For the latter the five  $b_2$  and the seven e modes are allowed in both spectra. These differences and several others are listed in Table 2, together with a summary of the observations.

	Predicted for f	undamentals		Observed	*
	Puckered ring $D_{2d}$	$\begin{array}{c} {\rm Planar\ ring} \\ D_{4h} \end{array}$	c-C4Cl8 (solid)	$c-C_4F_8$ (gas) <sup>†</sup>	$c-C_4(OH)_8$ (solid);
No. Raman active	21	11	19-24	14-16	8-12
No. Raman polarized	6	3	4	6	2
No. Infrared active No. Raman–IR	12	6	11-22	19-35	7–10
coincidences	12	0	6-14	7	0–2

Table 2. Predictions and observations for  $D_{4h}$  and  $D_{2d}$ structures of cyclo-C<sub>4</sub>Cl<sub>8</sub>, -C<sub>4</sub>F<sub>8</sub> and -C<sub>4</sub>(OH)<sub>8</sub>

\* The lower number includes only weak or stronger bands; the higher includes everything.

 $\dagger$  Not considering bands above 1500 cm<sup>-1</sup>.

<sup>‡</sup> Omitting OH modes.

### 1. OCTACHLOROCYCLOBUTANE

No previous infrared or Raman work has been published for  $c-C_4Cl_8$ . OWEN and HOARD [17] concluded from an X-ray crystallographic study that the carbon ring is nonplanar. A refinement of their earlier X-ray results was made by MARGULIS [18], who obtained a dihedral angle of about 19°.

#### Experimental

Sample purity and characterization.  $Cyclo-C_4Cl_8$  is a solid which melts at 259°C. The sample was a gift from Professor W. T. MILLER of Cornell University [19]. It was put through a Varian 1520 A gas chromatograph equipped with a 10 ft OV-1 column. This revealed one small impurity peak totaling about 0.3% of the sample. The material was therefore used without further purification.

It was also characterized by mass spectroscopy. The parent peak at 332 m/e was not found. There are also other parent peaks because of the 3:1 ratio of  ${}^{35}\text{Cl}{}^{37}\text{Cl}$ , but mass 332 is the most abundant  $[C_4{}^{35}\text{Cl}_6{}^{37}\text{Cl}_2]$ . Although the parent was not present, clusters of fragment ions around  $295 \text{ m/e} (C_4\text{Cl}_7^+)$ ,  $260 \text{ m/e} (C_4\text{Cl}_6^+)$ ,  $225 \text{ m/e} (C_4\text{Cl}_5^+)$ ,  $213 \text{ m/e} (C_3\text{Cl}_5^+)$ ,  $190 \text{ m/e} (C_4\text{Cl}_4^+)$ , and  $166 \text{ m/e} (C_2\text{Cl}_4^+)$  were detected. The strongest peak is that of the  $C_2\text{Cl}_4^+$  ion, resulting from splitting the molecule in half. The measured relative amounts of isotopes for it compare well with those expected from the natural abundance of  ${}^{35}\text{Cl}{}^{37}\text{Cl}$ , as shown in Table 3.

Infrared spectra. Infrared spectra were measured from 35 to  $4000 \text{ cm}^{-1}$  with Beckman IR-11 and IR-12 spectrophotometers. The instruments were purged with dry air and calibrated in the usual manner [20, 21]. The spectral slit width was less than 2 cm<sup>-1</sup> over the entire region.

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Species	C2 <sup>35</sup> Cl4+	C2 <sup>35</sup> Cl3 <sup>37</sup> Cl+	$C_2^{35}Cl_2^{37}Cl_2^+$	C <sub>2</sub> <sup>35</sup> Cl <sup>37</sup> Cl <sub>3</sub> <sup>+</sup>	C2 <sup>37</sup> Cl4+
Calculated %	32.3	42.2	20.6	4.5	0.4
Observed %	32.9	41.3	20.1	4.9	<1

Table 3. Calculated vs. observed isotopic abundances for  $C_2Cl_4^+$  fragments from cyclo- $C_4Cl_8$ 

 $^{35}Cl = 75.4\%, \, ^{37}Cl = 24.6\%.$ 

 $Cyclo-C_4Cl_8$  was examined as pressed pellets in KBr and CsI and as a Nujol mull. The accuracy is believed to be  $\pm 1 \text{ cm}^{-1}$  for bands not marked broad or shoulder.

Raman spectra. Raman spectra were obtained with a Spex Ramalog instrument described elsewhere [22]. Two different excitation sources were used: a Carson Laboratories Model 300 argon ion laser with an output power of 500 mW in the 4880 Å line, and a Spectra Physics Model 125 He/Ne laser giving 80 mW at 6328 Å. The instrument was calibrated with some of the strong atomic lines from the laser discharge.

Raman spectra were obtained for the solid at room temperature and at  $-168^{\circ}$ C, for the melt, and for saturated CS<sub>2</sub> solutions. The solid was examined at  $-168^{\circ}$ C in a special cell [23] to see whether any of the degenerate bands can be identified by their splitting. With 1 cm<sup>-1</sup> resolution, the only band to be resolved was 272, which gave components at 271 and 268 cm<sup>-1</sup>. Quantitative polarizations were measured for both the liquid and CS<sub>2</sub> solution. The spectrum of the liquid at about 280°C was easily obtained by wrapping fine nichrome heating wire around a sealed and evacuated capillary tube containing the solid. After prolonged heating a band appeared at 1615 cm<sup>-1</sup>. This may be the C=C stretching mode of an olefin formed by thermal cracking of the ring. The frequencies for the solid are believed to be accurate to  $\pm 1$  cm<sup>-1</sup> for sharp bands.

## Results

The results for  $c-C_4Cl_d$  are given in Table 4 and in Figs. 1-3. Special comment is needed on the depolarized Raman bands at 987 and 945 cm<sup>-1</sup>. In the infrared, strong bands are found at 980 and 951 cm<sup>-1</sup>. It is bothersome to find a difference of 7 and 6 cm<sup>-1</sup> between the infrared and Raman values measured in the same physical state. We feel the difference should be no more than 4 cm<sup>-1</sup> unless marked broad or shoulder. We therefore believe that the 980 and 987 cm<sup>-1</sup> bands are due to two different vibrations. For 951 and 945 we are less certain, and in Table 4 have attributed them to the same vibration.

## Discussion of results

Examination of the data in Table 4 shows about a dozen infrared-Raman coincidences. (See also Table 2.) The results obviously fit expectations for  $D_{2d}$  far better than for  $D_{4h}$ . The evidence for a folded ring is so convincing that nothing more need be said about it, and we proceed to a discussion of the vibrational assignments on the basis of  $D_{2d}$  symmetry. Wavenumbers for the solid will be used. Analogy to the assignments for hexachlorocyclopropane [24] are of some assistance.

Species  $a_1$ . These six frequencies are Raman polarized and infrared forbidden. The four polarized Raman bands at 1055, 408, 353 and 253 cm<sup>-1</sup> are readily selected

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<sup>[23]</sup> F. A. MILLER and B. M. HARNEY, Appl. Spectry 24, 291 (1970).

<sup>[24]</sup> F. A. MILLER and K. O. HARTMAN, Spectrochim. Acta 23A, 1609 (1967).

Infrare	ed (solid)	Ram	an (solid)	Raman (l	iquid, 280°C)	
(cm <sup>-1</sup> )	Intensity	(cm <sup>-1</sup> )	Intensity*	(cm <sup>-1</sup> )	Depolzn†	Assignment
				66		Difference tone,
						See text.
		~95	2, b			Lattice mode
		130	21	127	0.76	¥10
155	VW	154	7	152	0.73	V23
$\sim 185$	vw, b	188	3			¥16
		207	20	202	0.74	<i>v</i> <sub>11</sub>
~220	vw, sh	220	5, sh	224	0.80	$v_{19}$
229	w	227	10	1224	0.00	<i>v</i> <sub>14</sub>
		253	26	251	0.17	$v_5$
272	m	272§	35	269	0.78	v18
337	m	337	<1			$\nu_{22}$
		353	11	352	0.55	<i>v</i> <sub>3</sub>
393	w	392	6, sh			¥13
		408	100	407	0.04	<i>v</i> <sub>2</sub>
623	m, sh	~618	<b>&lt;1, sh, b</b>			353 + 272 = 625
636	VS	$\sim$ 632	1, b			P20
688	500					$(2 \times 337 = 674(7))$
000	**					(822 - 154 = 668)
742	m					393 + 353 = 746
789	vs	789	<1, b			v <sub>21</sub>
		822	2. sh. b		)	γ.
839	vvw. sh	839	4. sh		0.67(?)	636 + 207 = 843
853	m	853	7	852		V 10
903	vw. sh	907	<1, b		,	636 + 272 = 908
		935	1. sh			839 + 95 = 934
951	8	945	8	951	0.72	P15
980	s, b					¥17
		987	8	988	0.75	r.
1000	m, sh					(853 + 154 = 1007)
						822 + 188 = 1010
1027	m. sh					636 + 393 = 1029
1040	w.sh					(948 + 95 = 1046)
						636 + 408 = 1044
		1055	3	1063	0.45+	ι, Ψ-
1145	VW	*****		*****	0120+	789 + 353 = 1142()
1209	vw					(822 + 393 = 1215)
	• ••					980 + 228 = 1208
						(200 ; 200 - 200

Table 4. Infrared and Raman spectra of cyclo-C<sub>4</sub>Cl<sub>8</sub>

s, m, w = strong, medium, weak; v = very; b = broad; sh = shoulder. \* Relative peak intensities, not corrected for instrumental transmission and detector sensitivity. † For depolarized lines,  $\rho = 0.75 \pm 0.03$ . ‡ Depolarization value from CS<sub>2</sub> solution. § Splits into 271 and 268 cm<sup>-1</sup> in solid at --168°C.



Fig. 1. Cyclo-C<sub>4</sub>Cl<sub>8</sub>. Infrared spectrum of the solid. A-KBr disc, B-Nujol mull.



Fig. 2. Cyclo-C<sub>4</sub>Cl<sub>8</sub>. Raman spectrum of the solid. Spectral slit width 4 cm<sup>-1</sup>. Laser power about 500 mW at 4880 Å.

for the ring breathing, the CCl<sub>2</sub> symmetric stretch, the CCl<sub>2</sub> scissors, and the CCl<sub>2</sub> rock respectively. There are three possible candidates for the antisymmetric CCl<sub>2</sub> stretch  $v_4$ : 987, 935 and 822 cm<sup>-1</sup>. These are the only unassigned Raman bands above 250 cm<sup>-1</sup> that do not have infrared counterparts. Since the complex of three bands at 822, 839, and 853 cm<sup>-1</sup> may be polarized, we have a slight preference for 822 for  $v_4$ . The 987 band then is put in species  $b_1$  on the basis of its intensity, and 935 is explained as a sum tone.



Fig. 3. Cyclo-C<sub>4</sub>Cl<sub>8</sub>. Low frequency Raman spectra of solid (24°C) and melt (280°C). Spectral slit width 6 cm<sup>-1</sup>. Excitation by 4880 Å.

This leaves the ring puckering to be located. It will be the lowest of all the  $a_1$  modes. The search for it was hampered by an instrumental ghost displaced 102 cm<sup>-1</sup> from Ar<sup>+</sup> 4880 Å. Consequently we questioned the authenticity of a very weak and broad feature near 95 cm<sup>-1</sup>. It was confirmed by using 6328 Å excitation, which shifted the instrumental ghost out of this vicinity. The 95 cm<sup>-1</sup> band is found only in the solid, and not in the liquid, which suggests that it is a lattice frequency. (Alternatively in the liquid it may be hidden under the wings of the 130 cm<sup>-1</sup> band and the exciting line, which are much broader than in the solid. See Fig. 3.) Some support for the lattice assignment is provided by the sum tone 935 explained as 839 + 95 = 934. This is missing in the liquid as it should be.

In the liquid (280°C) there is a new band at about 66 cm<sup>-1</sup> which is not evident at all in the solid (24°C), even though this region is relatively free of background scattering in the latter (see Fig. 3). This suggests that it is a difference tone because the intensity is enhanced at higher temperatures. The frequency is approximate because the band is on the side of the Rayleigh line. At least seven reasonable difference tones can be postulated: (1) 220 - 154 = 66, (2) 253 - 188 = 65, (3) 272 - 207 = 65, (4) 337 - 272 = 65, (5) 853 - 789 = 64, (6) 907 - 839 = 68, and (7) 1055 - 987 = 68. We conclude that 95 cm<sup>-1</sup> is a lattice mode, 66 cm<sup>-1</sup> is a difference tone, and that the puckering fundamental does not appear.

Species  $b_1$ . These three fundamentals should give depolarized Raman bands having no infrared counterparts. The ring mode  $v_9$ , has already been assigned to 987 cm<sup>-1</sup>. The remaining two frequencies are easily located at 207 and 130 cm<sup>-1</sup>. The higher is tentatively called a CCl<sub>2</sub> twist and the lower a CCl<sub>2</sub> wag, but they may be badly mixed.

Species  $b_2$  and e. Differentiating between these species on the basis of the condensed state infrared and Raman spectra is nearly impossible. We have considered the effect of site symmetry on the degenerate internal modes. Since the space group is  $C_{2h}^2 - P 2_1/m$  with two molecules per unit cell [17], the molecules must be located on a crystal site of  $C_s$  symmetry. The vibrational selection rules are then no longer those for  $D_{2d}$  but rather those for  $C_s$ . All 30 fundamentals are now allowed, and the degenerate e modes should be split into two bands. Our data indicate that these predictions are not fulfilled. There is almost no evidence for crystal state splitting, the only possible exceptions being the pairs at 220-227 and 268-271 cm<sup>-1</sup>. We conclude that the effective potential still has  $D_{2d}$  symmetry to a very good approximation.

The twelve  $b_2$  and e fundamentals can be divided into two groups. The first, having frequencies greater than 600 cm<sup>-1</sup>, probably include all four remaining C—Cl stretches and one of the two ring modes. The remaining seven fundamentals will be below 600 cm<sup>-1</sup>. Good candidates for the first group are 980, 951, 853, 789, and 636 cm<sup>-1</sup>, and for the second 393, 337, 272, 228, 188, and 154 cm<sup>-1</sup>. One more is needed for the second group. We take 220 for it, but 220 and 227 may be due to the same internal mode split by the crystal symmetry. Assigning these several frequencies to either the  $b_2$  or e species, let alone to a particular mode, is nearly impossible. Our suggestions are shown in Tables 1 and 4, but we readily concede that they may be scrambled. Some of the assignments were aided by finding suitable combination bands, and 272 cm<sup>-1</sup> is put in species e because of its splitting. Infrared and Raman spectra of octachloro-, octafluoro-, and octahydroxycyclobutane 1121

## Summary

The vibrational spectrum of  $c-C_4Cl_8$  clearly supports the puckered ring structure. Values have been suggested for 20 of the 23 fundamental vibrations. With one or two exceptions, those for the  $a_1$  and  $b_1$  modes are quite reliable, but species  $b_2$  and eare essentially a basket into which the fundamental frequencies are poured but not well sorted. The ring puckering mode has not been observed.

#### 2. Octafluorocyclobutane

CLAASSEN [14] obtained good infrared and Raman data on this molecule, but unfortunately interpreted them on the basis of the  $D_{4\hbar}$  structure. BAUMAN and BULKIN [15] made additional measurements, and concluded that the data indicate a  $D_{2d}$  structure. This is in agreement with electron diffraction results [25, 26]. We concur. Our contribution is mainly three-fold: (1) a more complete gas phase Raman spectrum, (2) more accurate depolarization values, and (3) the identification of coincident infrared and Raman bands by measurements on the same physical state. These new data require revision of the earlier assignments.

## Experimental

Sample. Cyclo-C<sub>4</sub> $F_8$  was obtained from the Matheson Gas Products Co. Since the stated minimum purity was 99.99%, it was used without further treatment.

Infrared spectra. The instruments were the same as described in Section 1. Gas phase spectra were obtained with sample pressures ranging from 1 to 485 torr and path lengths from 0.1 to 8.2 m. The sample of the solid at  $\sim -173^{\circ}$ C was prepared by depositing the vapor slowly onto a cold KBr window in the usual type of low-temperature infrared cell [27].

Raman spectra. The Raman spectrum of the liquid was measured in a sealed capillary tube at room temperature. For the gas work, the output power of the 4880 Å line was 800 mW. The gas cell was a cylindrical ultraviolet type cell with a side arm. The flat windows were perpendicular to the incident laser beam, which was multi-passed through the sample a few times. The sample pressure was 710 torr. The Raman spectrum of solid  $c-C_4F_8$  at  $-160^{\circ}C$  was examined from 0 to 400 cm<sup>-1</sup> in an unsuccessful search for the puckering fundamental. The low temperature cell has been described elsewhere [23].

#### Results

The gas phase Raman spectrum is shown in Fig. 4. Table 5 gives our results, together with those of CLAASSEN [14] and BAUMAN and BULKIN [15]. Our infrared data for the solid were of no help in making the assignments, so they are given separately in Table 6.

Agreement with earlier work is, on the whole, quite good. Our Raman results for the gas are much more extensive than previous ones. It is worth noting that the  $351 \text{ cm}^{-1}$  band is depolarized, not polarized as reported earlier. It has an infrared counterpart at  $350 \text{ cm}^{-1}$ , clearly parallel, which was not reported before. Claassen did not go this low, but we are puzzled about Bauman and Bulkin's missing it. Claassen's sample seems to have been slightly impure, as noted by Bauman and Bulkin, and

<sup>[25]</sup> H. P. LEMAIRE and R. L. LIVINGSTON, J. Am. Chem. Soc. 74, 5732 (1952).

<sup>[26]</sup> C. H. CHANG, R. F. PORTER and S. H. BAUER, Am. Chem. Soc. meeting, Houston, Texas, 22–27 February (1970). Paper 79 in the Division of Physical Chemistry.

<sup>[27]</sup> R. C. LORD, R. S. McDONALD and F. A. MILLER, J. Opt. Soc. Am. 42, 149 (1952).

						Table 5	. Infrar	ed and F	taman s	pectra o	f cyclo.	04F8				
C) L147	R and i	Infra R [16]	red (gas)	dana nidr		CF LU LU	Rama	n (gas) This much				Raman	(liquid)	-		
cm <sup>-1</sup> )*	Inten.	Type	(cm <sup>-1</sup> )	Inten.	Type	(0m <sup>-1</sup> )	(cm <sup>-1</sup> )	Inten.†	Polzn.‡	ULAASS (0m <sup>-1</sup> )	EN [14] Inten.	Polzn.§	(1-mo)	work Inten.	Polzn.‡	Assignments
198			95 197	WVW B	-		194	4.1 1	0.72	199	Ē	- te	104		0 42	
		ł	•	ł	ł			2 C - C		(258	1 20	0.87	260	1 10	0.75	V23 V.a
							60Z~	a x	0.76	273	82	0.87	274	52	0.75	۲۱۰ ۲۰۱۸
283		-	284	22												¥18
			828 873	жл												607 - 284 = 323
			350 350 355	a			351	8, sh	dp	347.0	82	ል	350	m, sh	0.73	P14
						358.2	360 383	65 5. sh	0.13	360.6	vs, sh	0.22	363	V8 	0.09	V5
:			410	m, sh			000	172 60	4	-	E	•	000	m, sn	۵,	$2 \times 194 = 388$ 604 - 197 = 407
437 464	œ 13	ᅴᅴ	440 464	e m, sh	-1	439	439	16	0.75	440	84	0.82	440	VB	0.75	$\gamma_{19}$ 059 - 197 = 462
533	ផ		633	Ħ												440 + 95 = 535(?)
569	87	-1	569	84	-1										<b>U</b>	274 + 259 = 533** $v_{18}$
605	Ħ	<u></u>	604.0 604.0	M												<sup>2</sup>
1110			101770				607	63	0.29	602	*		607	w	0.41	V8
			615	vw, sh												(963 — 350 <b>—</b> 613 1359 — 2560 — 618**
634	W		632	M												(439 + 197 = 636 359 + 274 = 633**
640	▶ :		640	vw, sh												$350 + 284 = 634^{**}$ 359 + 284 = 643
669	w, sh		629	w, 8p			662	2, b, sh	đþ	659.5	m, sh	dp	661	m, sh	0.75	7 V18
682	МA		683	*						675	M		677	m, sh	Įď	$\begin{array}{l} 963 - 284 = 679 \\ 963 - 284 = 679(1) \end{array}$
725	w		725	₿		699.3 719.3	721	100 6	0.10 0.14	698.7 721.9	vvs m, sh	0.04 0.3	700 724	vs m, sh	0.01 P	$r_{2}^{r_{3}}$ 2 × 263 = 726 439 + 284 = 723
763)	MA															<b>6</b> -1
167	WV									161	MAA					Impurity

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439 + 359 = 798 $604 + 197 = 801$	<b>.</b>	659 + 197 = 856	000 1 010 00044	901 + 203 = 800 + 1	604 + 259 = 863	607 ± 984 — 801	100 - 107 - 100			$700 \pm 284 = 984$	$659 + 350 = 1009^{**}$	569 + 439 = 1008	Va T		11111111111111111111111111111111111111	700 + 350 = 1050	659 + 439 = 1098	<b>6</b> -+	1433 - 284 = 1149(1)	•	/18 Voc	$1010 + 259 = 1269^{**}$	659 + 607 = 1266	V15		? •.•	963 + 439 = 1402	* 1 1
• -	-	-							•	dp			<b>0.74</b>			dp ?	•				0.76			0.74		dp 1	•	P 0.38
										, sh						, sh					_			_				, sh, b
										976 w			008 B			054 w					814 m			284 m		340 w		L11 × 132 ×
										ĩ		-	4			1					8			H		ï		ĨĨ
												80.0	0.82											0.9				0.69
	MAA					MAA				₩			82			ΜΛ		WVW			<b>20</b>			E		ΜΛ		s, sh
	810					<b>504</b>				972			1006.5			1001		1117			1215.0			1283		1338		1429.2
													0.73								0.75			0.75				0.44
													9								4			2, b			,	<1, sh 3
													1011								1224			1289		~1340		1413 1434
													1008								1220			1285				1431.3
									-	4											•	1			-	-	4	
w, b			w				M			vs w, sh	w. sh				4	m, sn	Ħ		#2		vs, sh ve		Ħ	8A		RV		
795		845	860	865 Q1	870	-000	222	6407	690	98 <b>3</b>	~1001				1011	1044	1093		1148	(1911	1223.5 1930		2021	1287)	1295)	1339	1403	
									-	-1											=	=		<u>1000</u>	2	-	ł	
мл мл		M	W	Ħ	м		ΜΛ	8	ΜΛ	# ≥ w	ж	:	æ	₩	20	æ	E		82	Þ	8	8	¢۵	VVB		A	- 	
797 802	3	845	858	865	870		068	1.62	608	983 983	1003		1010	1030	1037	1042	1093		1149	1156)	1220	0071	R971	[289		1304	1403	

Table	5 (cont.)												
CI [14]	B and B	Infrared 15]	(gas) This	work		CI [14]	Raman (gas) This work		CLAASSEN [14]	Raman	liquid) This work		-
(,)	Inten. T	ype (c	(r-u	Inten.	Type	(cm1)	(cm <sup>-1</sup> ) Inten.	Folzn.T	(cm <sup>-1</sup> ) Inten.	Polzn.§	(cm <sup>-1</sup> ) Inter	1. Polan.T	Assignments
			433) 136										
1443	8	121	140	Ħ									1010 + 439 = 1449
		i i	444 448)										
1473	ťů	ri.	471 471	8									¢
1502	-	1.	661	w, sh									$\begin{cases} 1239 + 259 = 1498 \\ 11924 + 274 = 1498 \\ \end{cases}$
1631	80	5	528,5 299	r B									963 + 569 = 1532
1572	æ	33	569	Ma (m									$1224 \pm 350 = 1574^*$
1600	*	ī	299	w, sh									1340 + 259 = 1599
1621	24	I	622	8									$1340 \pm 284 = 1624$
1626	SC SC	Ĩ	627	m, sh									$1433 \pm 197 - 1630$
1649	M												9 
1658	8	ĩ	658	w, b									$\begin{cases} 1224 + 439 = 1663 \\ 963 + 700 = 1663 \end{cases}$
1680	ΝA												
1715	*	t	714	w,b					2721		0441		1433 + 284 = 1717
1795	ш		787	*					1417 AAM		MA 00/1		$1224 \pm 569 = 1793$
1825	aQ	Ā	826	m, b									1224 + 604 = 1828
1866	νw	Ē	887	vw, sh									
1893	w	-4	891	M									
1940	82	T	939	8								•	$f_{1239} + 700 = 1939$ $f_{1340} + 604 = 1944$
1971	в		696	w, sh									
<b>966</b> I	e, sh	ĩ	997	B									$f_{1340} + 659 = 1999$ $f_{1433} + 569 = 2002$
0027		ē	030	Þ					2020 vvw				
2136		•		•									
2141	M.A.												
2180	82	61	182	a									***
+ high	er	+	ligher										
W, 11	n, s — weak	k, medium	, strong;	v == ver	y; sh =	· shoulde	r; sp = sharp; b =	= broad; ]	p, dp = depolariz	ed; FR =	Fermi resonan	C0.	- Management of the state of th

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The brackets are ours. + Relative peak intensities, uncorrected for instrumental response. ‡ For depolarized lines  $\rho = 0.75$ . § For depolarized lines  $\rho = 0.87$ . || Forbidden for present assignments.



Fig. 4.  $Cyclo-C_4F_8$ . Raman spectrum of the gas. Pressure 710 torr. Spectral slit width 6 cm<sup>-1</sup>. Laser power 800 mW at 4880 Å. Time constant 1 sec. Scan speed 50 cm<sup>-1</sup>/min. Photon counting. For the two re-run bands both slit and gain were halved, so the signal is one-eighth.

this probably accounts for a number of bands, mostly weak, which only he lists. He also ignored rotational structure in the infrared gas spectrum and attempted to explain every absorption peak as a separate vibration. Many of them are clearly P, Q, and R branches.

## Discussion of results

Examination of Table 5 shows seven pairs of infrared-Raman coincidences in the gas phase: 197, 350, 440, 659, 1224, 1289, and 1339 cm<sup>-1</sup>. (The pairs at 604 and 569 must be accidental coincidences because the Raman band is polarized. Polarized Raman bands are infrared inactive for both  $D_{4h}$  and  $D_{2h}$ .) These coincidences provide convincing evidence for  $D_{2d}$  rather than  $D_{4h}$  symmetry. Bauman and Bulkin reached the same conclusion, but a few of their presumed coincidences were incorrect because they used some infrared gas values vs. Raman liquid values, and they ignored Raman polarizations. Their incorrect pairs are near 283, 569, 605, and 1010 cm<sup>-1</sup>. There is no doubt that  $c-C_4F_8$  has a folded ring, and we proceed to make the assignments on this basis. They are summarized in Table 1.

Species  $a_1$ . Four of these six Raman active and polarized fundamentals are easily identified as 1433, 700, 607, and 359 cm<sup>-1</sup>. We believe that the first two are the ring breathing and the symmetric CF<sub>2</sub> stretch which have interacted strongly and moved apart to give frequencies which are abnormally high and low. A similar

(cm <sup>-1</sup> )	Intensity	(cm <sup>-1</sup> )	Intensity	(cm <sup>-1</sup> )	Intensity
560	VS	1054	w	1271	VS
606	vvw	1156	m, sh	1280	m, sh
867	vvw	1169	m, sh	1300	m
904	vvw	1194	w, sh	1334	VS
951	vs	1214	vs	1398	m
990	m, sh	1249	vs	1484	w
1006	w, sh	1254	m, sh	1535	w
1013	w, sh				

Table 6. Infrared bands of  $cyclo-C_4F_8$  solid at  $100^{\circ}K$  (400-2000 cm<sup>-1</sup>)

result was found in  $c-C_3F_6$  [24]. The ring puckering,  $v_6$ , should be very low. To our great disappointment there is no evidence for it. Careful examination of the Raman spectrum of the gas, liquid, and low temperature solid (-160°C) revealed no band that could be assigned to this vibration. The region between 40 and 180 cm<sup>-1</sup> is clear of background and free of bands in both liquid and gas. Consequently nothing can be deduced about the barrier to ring inversion. The final  $a_1$  fundamental is another CF<sub>2</sub> stretch which should be above 1000 cm<sup>-1</sup>. The only unused polarized band above 750 cm<sup>-1</sup> is 1413 cm<sup>-1</sup>. This is close to  $v_1$ , suggesting that it is a combination tone acquiring intensity by Fermi resonance with  $v_1$ , but we adopt it for lack of an alternative.

Species  $b_1$ . These three modes are Raman active and depolarized, and infrared forbidden. We take 1010 for the highest. CLAASSEN found a weak infrared band here but we did not, so we do not regard this as an obstacle. We believe that his 1010 band was due to an impurity. For the other two  $b_1$  fundamentals we adopt 259 and 274 cm<sup>-1</sup>. These are liquid values because in the gas there is only a single broad band at about 263 cm<sup>-1</sup> which was not resolved with a 3 cm<sup>-1</sup> slit. These two bands might be suspected of being a Fermi resonance pair, but we cannot think of any way in which to make up a sum tone of symmetry  $B_1$  in this frequency region. Therefore we feel that they are  $b_1$  fundamentals in spite of being so close together.

Species  $b_2$  and e. These twelve fundamentals are both infrared and Raman allowed. They differ in that the  $b_2$  modes give parallel infrared bands (P-R separation about 11 cm<sup>-1</sup>), whereas the e modes give perpendicular ones. The appearance of the latter will vary depending on the value of the Coriolis coupling constant for the vibration. Some of the band contours are clearcut and indicate the species assignment. Thus the parallel bands at 284, 350, and 1290 may confidently put in  $b_2$ , and the perpendicular ones at 197, 439, 569, 963, and 1340 in e. This leaves one high frequency (above  $800 \text{ cm}^{-1}$ ) needed for each species. The 1239 band must be one of these because of its infrared intensity, and 1224 must be the other because of its Raman intensity. It is difficult to decide which to put in  $b_2$  and which in e, but since their values are close together it makes little difference. Bauman and Bulkin suggested that  $D_{4h}$  selection rules might be helpful in cases like this. They pointed out that if deviation from  $D_{4h}$  were small,  $D_{4h}$  selection rules would hold approximately. Therefore the fundamentals in  $b_2$  which are derived from  $b_{2g}$  of  $D_{4h}$  will be relatively strong in the Raman spectrum and weak in the infrared, whereas those derived from  $a_{2u}$  of  $D_{4h}$  will be relatively strong in the infrared and weak in the Raman effect. A similar argument applies to species e. This leads us to assign 1224 to  $b_2$ and 1239 to e.

There is still one fundamental in each species to be assigned, with the frequency expected below 800 cm<sup>-1</sup>. We arbitrarily attribute 659 to  $r_{13}$  on the basis of its moderate Raman intensity, and 604 to  $r_{22}$  on the basis of its being observed only in the infrared. Both are CF<sub>2</sub> scissoring modes, and the values are reasonable.

## Summary

This completes the assignments of the spectroscopically active modes. A large number of combination tones were observed in the infrared, as is usual in fluoro-carbons. We have attempted to explain the ones below  $1500 \text{ cm}^{-1}$  by using only

binary combinations. Above that we made no serious effort. The only lower ones of significant intensity with which we are not satisfied are the bands at 533, 1153, and  $1472 \text{ cm}^{-1}$ .

### 3. OCTAHYDROXYCYCLOBUTANE

WEST et al. [28] were the first to synthesize  $c-C_4(OH)_8$ . They reported five infrared bands for the solid between 400 and 4000 cm<sup>-1</sup> and five Raman bands measured in aqueous solution, and concluded that their results were consistent with a  $D_{4h}$ model. No absorptions were found in the infrared below 900 cm<sup>-1</sup>, and of the five above, three were interpreted as OH modes. Since then BOCK [29] has determined the crystal structure from an X-ray study and found that the carbon ring is indeed planar. Our contribution has been to add infrared frequencies between 35 and 900 cm<sup>-1</sup> and Raman results for the solid, and to offer an explanation why this cyclobutane derivative has a planar ring.

### Experimental

Sample preparation and purity.  $Cyclo-C_4(OH)_8$  was prepared by the three step method of WEST et al. [28]. Difficulty was experienced in the final step when nitric acid was used for the oxidizing agent, because the oxidation went too far and gave some oxalic acid. However when bromine was used the reaction proceeded smoothly to the desired product. The resulting white solid was purified by precipitating several times with acetone from an aqueous solution and then vacuum drying. Decomposition occurred at about 140°C with evolution of a gas [28]. The infrared spectrum of the sample gave no evidence of unreacted diketocyclobutenediol, the precursor to the hydroxy compound, nor of oxalic acid.

Infrared spectra. The instruments were those described in Section 1. Spectra of the solid were obtained in the mid infrared from KBr pressed pellets and Nujol mulls, and in the region from 35 to  $500 \text{ cm}^{-1}$  from a Nujol mull between polyethylene plates.

Raman spectra. The Raman spectrum of the solid was obtained with 4880 Å excitation at an incident power of approximately 150 mW. Power much in excess of this caused the sample to char. Polarizations were measured on aqueous solutions with He/Ne 6328 Å excitation. The sample was stable in solution for at least 20 hr.

The c-C<sub>4</sub>(OH)<sub>8</sub> results are given in Table 7 and in Figs. 5 and 6. It should be noted that WEST *et al.* report the highest band to be at 3250 cm<sup>-1</sup>, whereas we found it about 3350 cm<sup>-1</sup>. This may be a typographical error on their part, or may be due to the great breadth of the band and the poor dispersion of the NaCl prism instrument they used.

### Discussion of results

The vibrational assignment will be discussed on the assumption that the OH group is a single particle. The OH bands (stretches, bends, and torsions) are easily identified by their frequencies and unusual breadth, and are indicated in Table 7. They will not be discussed explicitly. Fortunately the broad O—H modes do not seem to overlay any of the other fundamentals except possibly  $v_1$ . This is good fortune. We did not prepare the deuterated compound because we felt that the OD bends and torsions would be lowered enough to overlap the skeletal modes. This would complicate rather than clarify the interpretation.

A study of Table 7 shows that the rule of mutual exclusion is clearly operating.

<sup>[28]</sup> R. WEST, H. Y. NIU and M. ITO, J. Am. Chem. Soc. 85, 2584 (1963).

<sup>[29]</sup> C. M. BOCK, J. Am. Chem. Soc. 90, 2748 (1968).

WESE of	Infrare	d (solid)	work	Rama	an (solid) s work	WEST et	Raman	(H <sub>8</sub> O soln.) This w	ork	
(cm <sup>-1</sup> )	Inten.	(cm <sup>-1</sup> )	Inten.	(em <sup>-1</sup> )	Inten.*	(cm <sup>-1</sup> )	Polzn.	(em <sup>-1</sup> )	Polzn.†	Assignment
·····		56	vw							Lattice mode
				$\sim 150$	24 sh	165		$\sim 160$	$\mathbf{sh}$	$v_{10}$
				224	7					V19
		237	vw, b		_					?
				256	7			250		P18
		287	m	010						V23
		004		319	3					<sup>1</sup> 14
		324	ш	200	2 ah					$256 + \sim 150 = \sim 406$
				~355 421	33	405	n	403	0.21	200   ····
		~455	m.h	101	00		P			1200
		100	, 0							$608 - \sim 150 = \sim 458$
				495	45	465	dp	462	0.71	v13
		$\sim 575$	m, vb				-			O—H torsion
		~608	m, vb							0—H torsion
				725	100	707	р	707	0.13	$\nu_{2}$
		~770	vw, sh							, ?
				864	1					$  \frac{\nu_{12}}{1119} - 256 = 863$
900		900	8							v <sub>21</sub>
				937	28			932	0.72	v <sub>9</sub>
1080	8	1080	vs							v <sub>15</sub>
				1119	5					$v_1$
				$\sim 1167$	<1					$v_{17}$
1160	8	1170	vs							$v_{20}$
		1188	m, sh							804 - 324 = 1188
		$(^{1264})$	w, b	1005	a h )					
				~1200	A vb					
				~1343	# VD				_	
1300		1369	m		<pre>&gt;</pre>	1215		1000-1400	vvb	O-H bends
1000		1398	m							
		1-000		~1410	4 vb					1
		1438	w, b		,					/
			•	$\sim 3290$	9 vb					)
3250	s	$\sim$ 3350	vvs, vvb							O-H stretches
				$\sim$ 3363	8 vb, sh					1
				$\sim 3415$	9 vb				_	,

Table 7. Infrared and Raman spectra of  $cyclo - C_4(OH)_8$ 

w, m, s = weak, medium, strong; v = very; b = broad; sh = shoulder; p, dp = polarized, depolarized. \* Relative peak intensities, uncorrected for instrument transmission and detector sensitivity.

† For depolarized lines,  $\rho = 0.75 \pm 0.03$ . ‡ Corresponding sum tone not observed.



Fig. 5. Cyclo-C4(OH)8. Infrared spectrum of the solid. A--Nujol mull, B-KBr disc.



Fig. 6.  $Cyclo-C_4(OH)_8$ . Raman spectrum of the solid. Spectral slit width 8 cm<sup>-1</sup>. Laser power about 150 mW at 4880 Å.

In the spectra of the solid one is immediately struck by the moderate number of observed bands and the lack of coincidences between the infrared and Raman frequencies. Of the twelve infrared and twelve Raman frequencies below 1200 cm<sup>-1</sup>, only the two pairs at 324–319 and 1170–1167 can be coincidences. All other infrared and Raman frequencies are separated by at least 12 cm<sup>-1</sup>, and usually much more. This is, in fact, one of the clearest examples for the rule that we have seen in a molecule of this size. When a molecule has several identical groups there are nearly always a few cases of accidental near-coincidence, so the two exceptions cited above are not serious obstacles. We regard the spectroscopic evidence for a center of symmetry as convincing. Therefore  $c-C_4(OH)_8$  has a planar ring, in striking contrast to cyclobutane and its perfluoro and perchloro derivatives.

The assignments will be discussed next, and then we shall return to the reason for the difference in symmetry. Frequencies for the solid will be used.

Species  $a_{1g}$ . Both the CO<sub>2</sub> symmetric stretch and the ring breathing of this species would probably be in the range 900-1100 cm<sup>-1</sup> if they were unperturbed, but we must be prepared to find the actual frequencies of  $v_1$  and  $v_2$  far apart by first order interaction as they are in c-C<sub>4</sub>F<sub>8</sub> and c-C<sub>3</sub>F<sub>6</sub> [24]. The highest observed polarized band is 725 cm<sup>-1</sup>. This is probably  $v_2$ , and  $v_1$  is then to be sought above 1100 cm<sup>-1</sup>. There is nothing there except weak bands at 1119 and 1167 cm<sup>-1</sup>. We adopt 1119, although without conviction. Alternatively  $v_1$  may be hidden under the collection of O—H bends between 1285 and 1410. The last  $a_{1g}$  fundamental, a CO<sub>2</sub> scissors, is readily located at 421 cm<sup>-1</sup>.

Species  $b_{1g}$ ,  $b_{2g}$ , and  $e_g$ . There are eight fundamentals in these three species. It is very difficult to assign a given frequency to the proper species, to say nothing of giving it the proper description. Our suggested assignments will be mentioned briefly, and are summarized in Tables 1 and 7.

Species  $b_{1p}$  contains a ring stretch which is expected around 1000 cm<sup>-1</sup> by analogy with the two preceding molecules. The closest Raman band to this is 937 cm<sup>-1</sup>. The other  $b_{1p}$  mode is a CO<sub>2</sub> wag, which will be the lowest Raman band. It is therefore assigned to 150 cm<sup>-1</sup>.

The  $b_{2\rho}$  and  $e_{\rho}$  assignments are more difficult. There are two CO<sub>2</sub> stretches which are expected to be above 1000 cm<sup>-1</sup>. There is only one unused Raman band there, the very weak 1167 cm<sup>-1</sup> one. We are not certain that it is a fundamental, but can find no other explanation for it. The next lower unused band is 864 cm<sup>-1</sup>, which is needed to explain 1188 cm<sup>-1</sup>. The 1167 band is arbitrarily assigned to the antisymmetric stretch  $v_{17}$  and the 864 one to the symmetric stretch  $v_{12}$  although we are uneasy about the low value for the latter. The weak Raman band at 399 can be explained as a combination tone. This leaves four fundamentals and just four unused frequencies: 224, 256, 319, and 495 cm<sup>-1</sup>. The highest is probably the CO<sub>2</sub> scissors  $v_{13}$ . We have no good reason for assigning the others to specific modes; our choices are almost arbitrary.

Species  $a_{2u}$  and  $e_u$ . These six fundamentals are infrared-active. Three of them will be above 800 cm<sup>-1</sup>: the CO<sub>2</sub> antisymmetric stretch  $v_{15}$ , the CO<sub>2</sub> symmetric stretch  $v_{20}$ , and the ring stretch  $v_{21}$ . There are three strong infrared bands there: 1170, 1080, and 900 cm<sup>-1</sup>. In the infrared spectrum obtained on the KBr wafer, the 1170 band splits into components at 1172 and 1150 cm<sup>-1</sup>, and the 900 band splits into 900 and 893 cm<sup>-1</sup>. If this is due to lowering of the site symmetry, it indicates that these are both  $e_u$  modes. Therefore we assign 1170 cm<sup>-1</sup> to  $v_{20}$ , 900 to  $v_{21}$ , and 1080 to  $v_{15}$ . This places the antisymmetric stretch  $v_{15}$  lower than the symmetric one  $v_{20}$  (1080 and 1170 cm<sup>-1</sup> respectively), contrary to our earlier assumption. This splitting argument is by no means certain, because a KBr wafer can alter a spectrum for several reasons—e.g. halogen exchange, formation of solid solution in KBr, or alteration of the crystal form of the sample. Consequently the splitting is not proof that the two vibrations are degenerate, but merely suggests it.

For the three fundamentals expected below 800 cm<sup>-1</sup>, the medium intensity bands at 455, 324, and 287 cm<sup>-1</sup> are reasonable choices for  $v_{22}$ ,  $v_{16}$ , and  $v_{23}$  respectively.

### Conclusions

Vibrational spectra distinctly show that  $c-C_4F_8$  and  $c-C_4Cl_8$  have a puckered ring  $(D_{2d})$  and  $c-C_4(OH)_8$  has a planar one  $(D_{4h})$  in the ground vibrational state. We now consider the reason for this difference. Obviously in the halogenated molecules the force producing the folded ring is the repulsion between halogen atoms of adjacent  $CX_2$  groups. With this as the dominant force the quadratic term in the equation  $V = az^3 + bz^4$  must be negative. To a first approximation,  $c-C_4F_8$  and  $c-C_4(OH)_8$  will have about the same ring strain, and also about the same torsional forces. One's first guess is therefore that  $c-C_4(OH)_8$  will also have a folded ring. Since it does not, there seems to be a third force operating in  $c-C_4(OH)_8$  which overcomes the torsional one and produces the planar ring. This is, we believe, provided by hydrogen bonds. Bock [28] mentioned this possibility earlier, but he seemed to be thinking only of intermolecular hydrogen bonds.

Figure 7 is a top view of the  $c-C_4(OH)_8$  molecule. Only one hydrogen atom is shown, and it is pictured as forming a hydrogen bond to a neighboring oxygen atom on the same side of the ring. The C—C and C—O distances are taken from the X-ray results of Bock [29]. From these and the average OCO angle of 111.8°, we calculate an  $O \cdots O$  distance in the hydrogen bond of 2.66 Å. This is reasonably close to the average  $O \cdots O$  distance of 2.74  $\pm$  0.11 Å for intermolecular hydrogen bonds in alcohols [30].

<sup>[30]</sup> G. C. PIMENTAL and A. L. MCCLELLAN, The Hydrogen Bond, p. 284. W. H. Freeman (1960).



Fig. 7.  $Cyclo \cdot C_4(OH)_8$ . Top view, showing one internal hydrogen bond. (The other seven H's are omitted for clarity.)

These hydrogen bonds act to constrain the carbon ring to a plane, because to pucker it requires doing the work of lengthening the hydrogen bonds. Thus this new interaction adequately compensates the effect of the oxygen-oxygen repulsions.

One possible structure for  $c-C_4(OH)_8$  has four hydrogen bonds forming one ring above the plane of the carbon atoms, and four more forming another ring below that plane. The actual case is probably not this simple. There must be some intermolecular hydrogen bonding in the crystal, judging from the decomposition point (~140°C), and in water solution there is probably dynamic formation and breaking of hydrogen bonds with solvent molecules. It is interesting to note that the rule of mutual exclusion holds for all the O—H modes toe, suggesting that the hydrogen bonds are arranged so that there is a center of symmetry. The latter would require that, if the hydrogen bonds do form rings, both the upper and lower rings must circle in the same direction—i.e. both clockwise or both counterclockwise when viewed from above. We do not have much confidence in this, however, in part because the bands are so broad and ill-defined.

The molecules  $c-C_4Cl_8$ ,  $c-C_4F_8$ ,  $c-C_4H_8$ , and  $c-C_4(OH)_8$  form an interesting series. The first two are definitely folded, and give no evidence in their vibrational spectra of inverting. *Cyclobutane* is also folded, but inverts easily and shows this clearly in its spectrum. Finally  $c-C_4(OH)_8$  has a planar ring beyond any doubt.

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