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THE VIBRATIONAL SPECTRA OF PERFLUORO- AND PERCHLOROBUTATRIENE*

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ABSTRACT

Raman data are reported for gas, liquid and solid perfluorobutatriene, $F_2C{=}C{=}C{=}CF_2$, and infrared data for gas and solid. They show clearly that the molecule has the expected planar structure of D_{2h} symmetry. With the aid of Raman depolarization ratios and infrared band contours, twelve of the seventeen spectroscopically-active fundamentals can be assigned with assurance. Frequencies are suggested for the remaining five modes.

Data for perchlorobutatriene are limited to the solid state except for some depolarization measurements in solution. Again only D_{2h} symmetry is acceptable. About half the fundamentals can be assigned with confidence.

INTRODUCTION

This paper presents IR and Raman spectra for perfluoro- and perchlorobutatriene, $X_2C{=}C{=}C{=}CX_2$. (They will often be referred to as C_4F_4 and C_4Cl_4 in the following discussion.) Some mid-IR data for both compounds have been reported previously, but complete vibrational spectra are given here for the first time.

Our laboratory has had a long-standing interest in molecules with linear skeletons of conjugated or cumulated multiple bonds such as carbon suboxide, dicyanoacetylene and dicyanodiacetylene. The most recent work was on perchloro- and periodoallene, $X_2C{=}C{=}CX_2$ [1]. Earlier we studied butatriene, and showed that it is a planar molecule [2]. As far as we are aware the only other structure determinations of any butatriene by a physical method are microwave [3, 4] and electron diffraction [5] studies of 1-chlorobutatriene. Thus this interesting class of compounds is virtually untouched. Furthermore the three cumulated double bonds constitute a

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*The work on the fluoro compound is from a thesis submitted by William Pingitore for the degree of Master of Science at the University of Pittsburgh (1975). That on the chloro compound is part of the thesis submitted by William F. Elbert for the degree of Doctor of Philosophy (1975) novel vibrational system. It therefore seemed worthwhile to study these two perhalogenated butatrienes as additional examples of an interesting type of molecular structure.

PERFLUOROBUTATRIENE

This compound was first prepared by Martin and Sharkey [6]. They gave a qualitative IR spectrum in the region 900—2000 cm^{-1}, but no other spectroscopic work has been reported.

Experimental

Preparation of the sample

Perfluorobutatriene was prepared by the following reactions

$$\underset{\text{I}}{F_2C{=}CH{-}CH{=}CF_2} \xrightarrow[85\%]{Br_2} \underset{\text{II}}{BrF_2C{-}CH{=}CH{-}CF_2Br} \xrightarrow[30\%]{KOH} \underset{\text{III}}{F_2C{=}C{=}C{=}CF_2}$$

Compound I is difficult to obtain; its preparation will be described in a forthcoming paper [7]. It was brominated as described by Anderson et al. [8] to give II in 85% yield. The latter is a stable, colorless liquid which freezes at about —78°C and boils at 107°C. It was purified by fractional distillation through a short vacuum-jacketed Vigreux column, using both IR and NMR spectroscopy to monitor the process. Careful purification of II greatly facilitated the later purification of III. Compound II was dehydrohalogenated as described by Martin and Sharkey [6] to give perfluorobutatriene (III) in 30% yield. The latter was purified by repeated trap-to-trap vacuum transfer, using changes in the IR spectrum as a guide. The final spectrum agreed well with that published by Martin and Sharkey.

Perfluorobutatriene, a colorless gas, melts at —103°C and boils at —5°C. The gas polymerizes to a dark yellow film on the walls of the container at pressures greater than 30 torr. It is reported to react violently with oxygen, and to explode when the liquid is heated to its boiling point [6].

Raman spectra

Raman spectra were obtained with a Spex Ramalog instrument which has been described elsewhere [9]. Excitation was with the 488.0 nm line from an Ar^+ laser, using 25 to 250 mw of power at the sample. Spectra were measured for the solid at 123 K, the liquid at 210 K and the gas at 298 K. The solid sample was obtained by condensing a jet of the gas on a liquid-nitrogen-cooled stainless steel wedge which was angled 15° relative to the incident laser beam. The wedge was suspended in an evacuated cold cell of conventional design [10]. For the liquid phase measurements the sample was sealed in a thin-walled capillary which was cooled with a controlled stream of cold nitrogen gas [11]. The gas phase sample was contained in a cylindrical

Pyrex cell with optically flat end windows. It was fitted with a side arm which was cooled to 250 K to keep the sample pressure at approximately 100 torr. A survey spectrum was obtained, but accurate band frequencies could not be measured because the sample polymerized too rapidly.

Infrared spectra

IR spectra were measured from 33—4000 cm^{-1} with Beckman IR-11 and IR-12 spectrophotometers. The solid was examined as a deposit on a liquid-nitrogen-cooled plate in a conventional cold cell [10]. The cooled plate and the windows were polyethylene for the region 33—350 cm^{-1}, and KBr for 350—4000 cm^{-1}. Gas phase data were obtained only above 200 cm^{-1} using a 10 cm gas cell having CsI windows. Pressures between 1 and 20 torr were adequate.

Results

The experimental results are given in Fig. 1 and Table 1. Frequencies are believed to be accurate to ±1 cm^{-1} in the infrared and ±2 cm^{-1} in the Raman spectrum unless a band is marked as broad, shoulder or approximate.

Assignments for a planar structure (D_{2h} symmetry)

Both simple valence theory and analogy with butatriene [2] indicate that a planar structure of D_{2h} symmetry is most probable. It will therefore be assumed initially, and will be found to be completely satisfactory. Later other possibilities will be mentioned briefly.

The symmetry and selection rules for vibrations of the D_{2h} model are summarized in Table 2. The z axis is taken along the C=C line and the x axis perpendicular to the molecular plane as recommended by the Joint Commission for Spectroscopy [12]. The conventions of Herzberg are followed throughout [13]. Table 2 contains the assignments for butatriene and the two perhalogen-derivatives. The order in which the vibrations are numbered is chosen for the halogenated compounds; it is not correct for C_4H_4. The usual disclaimer is made concerning the names for the vibrations; they are useful for purposes of bookkeeping and discussion, but may be poor descriptions for some of the actual modes.

Since D_{2h} contains a center of symmetry, the rule of mutual exclusion applies. Close examination of the data in Table 1 shows that there are a number of IR—Raman coincidences in the solid phase. In every case at least one of the two bands is weak. We believe that the coincidences are due to a lowering of the symmetry in the solid, or in a few cases are just accidental. In the gas phase, where the symmetry is that of the isolated molecule, there are no coincidences closer than 9 cm^{-1}. Unfortunately, the Raman values for the gas are less accurate than usual — ±5 cm^{-1} is estimated — because they are taken from a survey spectrum. It seems that mutual exclusion holds for the gas, however.

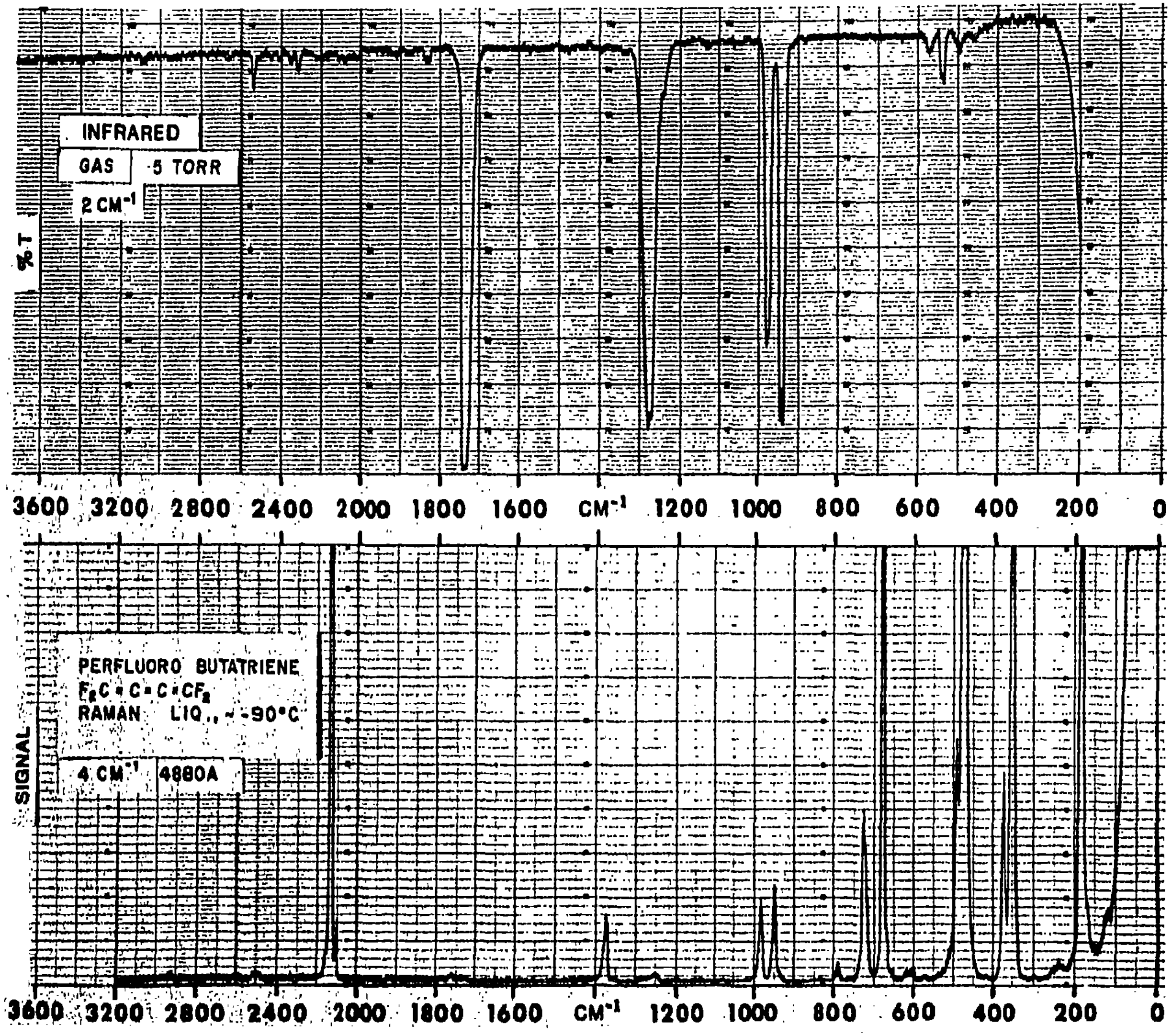

Fig. 1. IR and Raman spectra of perfluorobutatriene.

TABLE 1

Raman and IR spectra of perfluorobutatriene

Raman								IR					
Solid (123 K) cm^{-1}	int.	Liquid (210 K) cm^{-1}	int.^{a}	ρ	Gas (298 K) cm^{-1b}	int.^{a}	ρ	Gas (298 K) cm^{-1}	int.	type	Solid (123 K) cm^{-1}	int.	Assignment
51	690												lattice mode
78	135												lattice mode
								NE			95	vvw	lattice mode ?
								NE			129	vvw	ν_{18} ?
150	5	~130	1,sh,b										?
189	155	185	145	0.79	~180	420	dp						ν_{10}
					~220	60							imp. ?
260	2,b	~240	2,b		~280	30							?
358	130	353	200	0.27	~345	550	p						ν_4
379	20	375	45	0.19	~370	150							2 × 185 = 370, in F.R. with 353
464	3							460	vw,b				353 + 129 = 482, in F.R. with 494
477	1000	476	1000	0.73	~478	1000					475 480	vw w	ν_9
494	6	491	60	0.38	overlapped								?
								~487 494 501	w	C	498	s	ν_{17}
~540	1,b				~530	150							353 + 185 = 538 715 − 180 = 535
								535 539 543	w	A	539	m	ν_8
~570	1,b	~575	1,b		~560	70							ν_{16}
								565 (569) 574	w	B	571	m	ν_{13}

TABLE 1 (continued)

Raman								IR					
Solid (123 K)		Liquid (210 K)			Gas (298 K)			Gas (298 K)			Solid (123 K)		Assignment
cm^{-1}	int.	cm^{-1}	int.[a]	ρ	cm^{-1}[b]	int.[a]	ρ	cm^{-1}	int.	type	cm^{-1}	int.	
599	3				~600	60							?
~620	2,b	~613	2,vb		~640	30							ν_{15}?
682	110	681	250	0.0	~675	500	p						ν_3
726	18	724	40	0.0	~715	200							2 × 353 = 706, in F.R. with 681
					~735	180	p						imp.
											757	vvw	?
788	3	787	2										?
~840	1,b	~830	<1,b										353 + 476 = 829
								~840	vvw,b		832	vvw	353 + 494 = 847
								~890	vvw,b		890	vvw	353 + 539 = 892
								~920	vvw,sh		916	vvw	353 + 569 = 922
~940	1,b							940 943 947	vs	A	938	s	ν_7
951 959	7	949	17	0.10	958	100	p				949 962	vw,sh w	2 × 476 = 952
								976 (978) 980	vs	B	981 984	s	ν_{12}?
983 995	6	983	10	0.08	~988	100					995	vvw,sh	? ν_2 ?
					~1045	50							imp. ?
					~1058	80							imp. ?
								~1130	vvw,b				185 + 943 = 1128
											1153	vvw	?
								~1190	vvw,b		1168	w	613 + 569 = 1182
1200	1	~1200	<1,b										724 + 476 = 1200
											1219	w	726 + 498 = 1224

							1241	vvw		1223 1226 1230	vvw w vvw	681 + 569 = 1250
1239	3											?
										1245	vs	imp. ?
1251 1259	3	~1255	2,b									ν_{14}
							1274 (1278) 1282	vs	B	1259 1264	sh vs	ν_{11}
										1301	vw,b	?
										1318	vw	?
							~1340	vvw,b				978 + 353 = 1331
~1350	<1,b											?
										1367 1369	w	?
1364 1371	4	1373	10	0.14	~1380	50						2 × 681 = 1362 ?
1387	3									1379 1385	w	?
							~1400	vvw,b		1407	vvw,vb	539 + 681 + 185 = 1405
							1482	vw				3 × 494 = 1482
										1506	vvw,vb	?
							~1550	vvw		1531	vvw,vb	978 + ~575 = 1553
~1650	<1,vb											?
										1711 1717	w	?
							1738	vs	?	1729 1742 1760	vs,vb	ν_6
~1750	<1,vb	~1775	2,b									494 + 1278 = 1772
							1833 (1835) 1838	vw	A or B	1815 1824	w	1255 + 569 = 1824
							~1882	vvw,b		1865	vvw,vb	1278 + 613 = 1891
										1904	vvw	?

TABLE 1 (continued)

Raman								IR					
Solid (123 K)		Liquid (210 K)			Gas (298 K)			Gas (298 K)			Solid (123 K)		Assignment
cm^{-1}	int.	cm^{-1}	int.[a]	ρ	cm^{-1}[b]	int.[a]	ρ	cm^{-1}	int.	type	cm^{-1}	int.	
								1917	vvw,b		1919	vvw,b	1738 + 185 = 1923
								~1955	vvw,vb		1950	vvw,vb	1278 + 681 = 1959
											1980	vvw,vb	?
											2059	vvw	?
								~2077 2084 ~2091	vvw	C	2078	vvw	2 × 978 + 129 = 2085
2103	9	2103	8	0.29									ν_1 for ^{13}C?
								2110	vvw		~2103	vvw	1738 + 2 × 185 = 2108
2142	660	2140	700	0.24	2130	900	p				2141	vvw	
											2177 2181	sh vvw	
								2201 (2205) 2210	vvw	B?			1255 + 923 = 2198
											2214	vvw,vb	
								2233	vvw				1255 + 978 = 2233
											2293	vvw	
								2315 (2317) 2321	vw	B			1738 + ~575 = 2313
								2349 (2351) 2354	vw	B	2340	vvw	613 + 1738 = 2351
								2410 (2413) 2416	vw	B	2400 2402	vvw	2 × 569 + 1278 = 2416
											2427	vvw	
								2450	vvw,b		2447	vvw	724 + 1738 = 2462
~2490	1,b												

							2480	sh	?
							2490	sh	
							2503	w	
							2512	sh	
~2515	<1								?
				2533	w,b	?			1255 + 1278 = 2535
~2610 ~2620	<1	~2600	1,b						2140 + 476 = 2616
							2614	vvw	?
							2630	vvw	?

Abbreviations: NE, not examined; F.R., Fermi resonance. See also footnotes for Table 3.

[a] Peak intensity on a scale 1—1000, uncorrected for instrument response.

[b] Measured only from survey spectrum; ± 5 cm^{-1}

TABLE 2

Fundamental vibrations of $X_2C{=}C{=}C{=}CX_2$. (X=H,F,Cl)

D_{2h} Species	Activity	No.	Schematic description	Assignments (cm^{-1})		
				C_4H_4 [2]	C_4F_4[a]	C_4Cl_4[b]
a_g	R(p),—	1	Chain stretch	2079	2140	2071
		2	Chain stretch	878	983?	1112
		3	CX_2 sym. stretch	2995	681	416
		4	CX_2 scissor	1430	353	194
a_u	—,—	5	Torsion	736?	?	?
b_{1u}	—,IR	6	Chain stretch	1608	1738	1612
	(Type A)	7	CX_2 sym. stretch	2994	943	870
		8	CX_2 scissor	1370	539	294
b_{2g}	R(dp),—	9	CX_2 wag	544	476	321
		10	Skeletal bend A, O.P.	234	185	138
b_{2u}	—,IR	11	CX_2 antisym. stretch	~3080	1278	890
	(Type B)	12	CX_2 rock	~1060	978?	610?
		13	Skeletal bend B, I.P.	215	569	(341)
b_{3g}	R(dp),—	14	CX_2 antisym. stretch	3059	~1255	881
		15	CX_2 rock	663	613?	517
		16	Skeletal bend A, I.P.	330	~575?	482
b_{3u}	—,IR	17	CX_2 wag	854	494	434
	(Type C)	18	Skeletal bend B, O.P.	?	129[b]?	?

Skeletal bend A: $\underset{\downarrow}{C}=\overset{\uparrow}{C}=\underset{\downarrow}{C}=\overset{\uparrow}{C}$; Skeletal bend B: $\underset{\downarrow}{C}=\overset{\uparrow}{C}=\overset{\uparrow}{C}=\underset{\downarrow}{C}$.

[a] Raman: liquid phase. IR: gas phase.

[b] Solid phase.

O.P. = out-of-plane. I.P. = in-plane. ( ) Postulated from sum tones, so speculative.

Our assignments are included in Table 1, and are summarized in Table 2. Gas-phase frequencies are used for the IR-active modes, but the Raman-active ones are liquid values because these were measured more accurately. Fortunately there is little change of frequency with physical state, so sum tones calculated by combining values from different states are reasonably useable.

Some useful molecules for comparison are $F_2C{=}CF_2$ [14], $F_2C{=}CCl_2$ [15], $F_2C{=}CD_2$ [16] and $F_2C{=}C{=}CF_2$ [17].

Raman-active fundamentals

a_g species. These four modes consist of two stretches of the C=C chain, a CF_2 symmetric stretch and a CF_2 scissors. The higher chain stretch is easily assigned to the strong, polarized band at 2140 cm^{-1}. The second chain mode is a problem. Polarized bands which are possibilities are 681(250), 724(40), 949(17), 983(10) and 1373(10) cm^{-1}. (The numbers in parentheses are intensities in the liquid.) This mode is undoubtedly at 878 cm^{-1} in C_4H_4 and at 1112 cm^{-1} in C_4Cl_4 (Table 2). One would therefore expect it somewhere between these values in C_4F_4. Unfortunately both the indicated values, 949 and 983, are rather weak, and both can be explained as overtones: $2 \times 476 = 952$

and 2 × 494 = 988. Because 476 is the strongest Raman band in the spectrum whereas 494 is a weak infrared band, we have a slight preference for assigning 949 as the overtone of 476 and taking 983 as ν_2. The other three bands (681, 724 and 1373) are too far outside the expected range to be acceptable, and the first two can be explained well in other ways.

The 681 cm^{-1} band, the third strongest in the spectrum, is assigned to ν_3, the CF_2 symmetric stretch. The two polarized bands at 353 and 375 cm^{-1} probably involve Fermi resonance between the CF_2 scissors and 2 × 185 = 370 cm^{-1}. We therefore assign the fundamental to ~353 cm^{-1}, which is much the more intense of the two.

b_{2g} and b_{3g} species. Because there is no experimental way to distinguish between these species, they will be discussed together. Candidates for the five fundamentals are 185, 476, ~575, 613, 787, ~1200 and ~1255 cm^{-1}. The lowest of these fundamentals will be either ν_{10} or ν_{16}. On the assumption that an out-of-plane mode will be lower than the corresponding in-plane one, we assign 185 cm^{-1} to ν_{10}. It seems reasonable to describe this as a skeletal bend. The highest of the five fundamentals will be the b_{3g} CF_2 antisymmetric stretch ν_{14}. The only possibilities for it are the weak bands at ~1200 and ~1255 cm^{-1}. The latter is chosen on the basis of its slightly greater intensity and its usefulness in explaining the IR sum tones at 1835 and 2205 cm^{-1}. The band at ~1200 cm^{-1} may be the combination 724 + 476 = 1200 (B_{3g}).

A sum tone argument is also used to assign the Raman bands at ~575 and 613 cm^{-1} to b_{3g}, as follows. The IR bands at 2317 and 2351 cm^{-1} can be explained as the combinations (1738 + ~575 = 2313, $b_{1u} \times b_{3g} = B_{2u}$) and (1738 + 613 = 2351, $b_{1u} \times b_{3g} = B_{2u}$) respectively. Because of their contours, both sum tones belong to species B_{2u} (see later). Since 1738 cm^{-1} is unquestionably a b_{1u} fundamental, the two Raman values must belong to b_{3g} in order for the sum to be B_{2u}. Therefore, 613 and ~575 cm^{-1} are assigned to ν_{15} and ν_{16} respectively. Unfortunately both these bands are weak, so these assignments are questionable. With some hesitation we call 613 the CF_2 rock and ~575 the in-plane skeletal bend, but they are probably mixed.

This leaves only ν_9 to be assigned, and only 476 and 787 cm^{-1} as candidates. The choice is easy; the 476 cm^{-1} band is the most intense Raman band in the spectrum and must be due to a fundamental. (It is noteworthy that the most intense band is depolarized. Usually this distinction belongs to a polarized one.) We have no explanation for the weak band at 787 cm^{-1}.

IR-active fundamentals

Band contours. As an aid in attributing the IR bands to their proper symmetry species, the expected band contours were estimated. The moments of inertia were calculated after assuming the central C=C distance = 1.28 Å, outer C=C distance = 1.32 Å, C—F = 1.32 Å and F—C—F angle = 110°. These dimensions were chosen by analogy with butatriene [18] and 1,1-difluoroallene [19]. They gave $I_A = 88.8$, $I_B = 663$ and $I_C = 752$ amu A^2. From these values the P-to-R separations were calculated [20] and the intensity patterns estimated [21]. The calculated and observed P-to-R separations were as follows

Species	b_{1u}	b_{2u}	b_{3u}
Band Type	A	B	C
$\Delta\tilde{\nu}$(P—R) calculated (cm^{-1})	7.6	6.3	11.3
$\Delta\tilde{\nu}$(P—R) observed (cm^{-1})	7—8	4—9	14

The band types are included in Table 1.

b_{1u} species. The three b_{1u} fundamentals are a C=C chain stretch, a CF_2 symmetric stretch and a CF_2 scissors. The chain mode is assigned to the very strong band at 1738 cm^{-1}. Although its contour is not classifiable, there is no doubt that this must be ν_6. Bands at 943 and 539 cm^{-1} have type A contours and are assigned to ν_7 and ν_8. Their numerical values are reasonable [14—17].

b_{2u} species. There are three fundamentals in this species, described as a CF_2 antisymmetric stretch, a CF_2 rock and an in-plane skeletal bend. Type B contours are expected. We find just three possible candidates: 1278 (vs), 978 (vs) and 569 (w). The other observed type B bands are too high to be fundamentals. The 1278 band is a good choice for ν_{11}. The very strong 978 band is a serious problem because it seems to be too high to be one of the other b_{2u} fundamentals, it is not explainable as a binary combination, and its intensity demands respect. One might think that it is involved in Fermi resonance with the other nearby very strong band at 943, but this cannot be so because their band contours indicate different species. We see no alternative but to assign 978 to ν_{12}, but this is done with misgiving. That leaves 569 for ν_{13}, which is also too high by comparison with C_4H_4.

b_{3u} species. This contains a CF_2 wag and a skeletal out-of-plane bend. We expect the latter to be the lowest of all the allowed fundamentals, IR or Raman. The only observed C-type bands are 494 and 2084 cm^{-1}. The former is assigned to the CF_2 wag (ν_{17}), and the latter to a ternary sum tone.

In the gas phase data, which were obtained down to only 200 cm^{-1}, there is no acceptable candidate for the skeletal bend (ν_{18}). This is not surprising, for we now know that there is a Raman fundamental at 185 cm^{-1} and ν_{18} is expected to be still lower. In the solid phase IR spectrum, which was recorded down to 33 cm^{-1}, there are very, very weak bands at 95 and 129 cm^{-1}. We tentatively propose the band at 129 cm^{-1} for ν_{18}, but it is questionable.

Remaining bands

All the remaining IR bands, and most of the Raman bands, have been accounted for as the combination tones shown in Table 1. There are no adequate explanations for the Raman bands at 130, 240, 491 and 787 cm^{-1}.

Summary for D_{2h} assignments

Values have been suggested for all 17 of the spectroscopically-active fundamentals. Five of these are questionable; the others seem to be correct. The data fit D_{2h} symmetry well.

Consideration of other symmetries

If one CF_2 were twisted 90° with respect to the other the symmetry would be D_{2d}. Expectations for this model are $4a_1$ (R) + $1b_1$ (R) + $3b_2$ (R,IR) + $5e$ (R,IR). Thus eight fundamentals are allowed to be both Raman and IR active. Nothing remotely close to this is observed. The only other possible symmetry, D_2, fits the observations even less well. It can be concluded with assurance that this molecule is planar and D_{2h} like butatriene.

PERCHLOROBUTATRIENE

Perchlorobutatriene was first prepared by Heinrich and Roedig in 1968 [22]. They reported a few IR frequencies in the mid-IR. There has been no further mention of this substance in the literature.

Experimental

Preparation of the sample

Perchlorobutatriene was prepared by the following reactions as described by Heinrich and Roedig [22]

$$H_2C{=}CHOC_4H_9 \xrightarrow[\text{Benzoyl peroxide}]{CCl_4} \xrightarrow{H_2O} Cl_2C{=}CH{-}CHO \xrightarrow{LiCCl_3} Cl_2C{=}CH{-}CHOH{-}CCl_3$$

$$\xrightarrow{PCl_5} Cl_3C{-}CH{=}CH{-}CCl_3\ (+Cl_2C{=}CH{-}CHCl{-}CCl_3) \xrightarrow{KOC(CH_3)_3}$$

$$Cl_2C{=}C{=}C{=}CCl_2$$

It is a colorless solid which melts at 60°C and decomposes when heated above this. The sample was handled in a vacuum line and stored in an evacuated ampoule at 77 K to conserve the small quantity prepared.

Spectroscopic procedures

The instrumentation and procedures were the same as those described for C_4F_4. Infrared and Raman data were obtained only for the cooled solid, except for some depolarization ratios measured in solutions. No liquid or gas phase results were acquired. To obtain Raman spectra on either solid or solution, the sample was sealed in a capillary. Even though the solid was cooled to −150°C, it sublimed out of the path of the laser beam if there were more than 60 mW of power at the sample.

Results

The data for C_4Cl_4 are given in Table 3 and Fig. 2.

TABLE 3

Raman and IR spectra of perchlorobutatriene

Raman (solid 123 K)			IR (solid 77 K)		Assignment
cm^{-1}	Int.[a]	ρ	cm^{-1}	Int.	
70	243				lattice mode
138	390	0.74[b]			ν_{10}
194	586	~0.37[b]			ν_4
			294	m	ν_8
321	19				ν_{16}
416	212	0.10[c]			ν_3
			434	w	ν_{17}
482	142	0.75[c]			ν_9
517	13				ν_{15}
			610	s	ν_{12}
~643	6				2 × 321 = 642
			758	w	416 + (341) = 757
			857	vw	517 + (341) = 858
~864	1				2 × 434 = 868
			869	m	ν_7
			872	m	
881	12				ν_{14}
			890	vs	ν_{11}
			902	sh	?
~966	9				2 × 482 = 964
1029	31				2 × 517 = 1034
~1070	4				881 + 194 = 1075
1096	9				?
1112	690	0.34[b]			ν_2
~1205	2				881 + 321 = 1202
			1596	w	?
			1612	vs	ν_6
			1634	w	?
			1716	w	1112 + 610 = 1722
			~1778	w,b	890 + 881 = 1771
~1993	3				1112 + 881 = 1993
2043	36				1612 + 434 = 2046
2071	1000	0.34[b]			ν_1
2218	12				2 × 1112 = 2224
~2298	9				?
2495	11				1612 + 890 = 2502
			~2720	vw,b	1612 + 1112 = 2724

w,m,s = weak, medium, strong. v = very. b = broad. ~ = approximate. sh = shoulder.
ρ = depolarization ratio. For depolarized lines ρ = 0.75 ± 0.05.

[a] Peak intensity on scale of 1—1000, uncorrected for instrument response

[b] ρ measured in CCl_4 solution.

[c] ρ measured in THF solution.

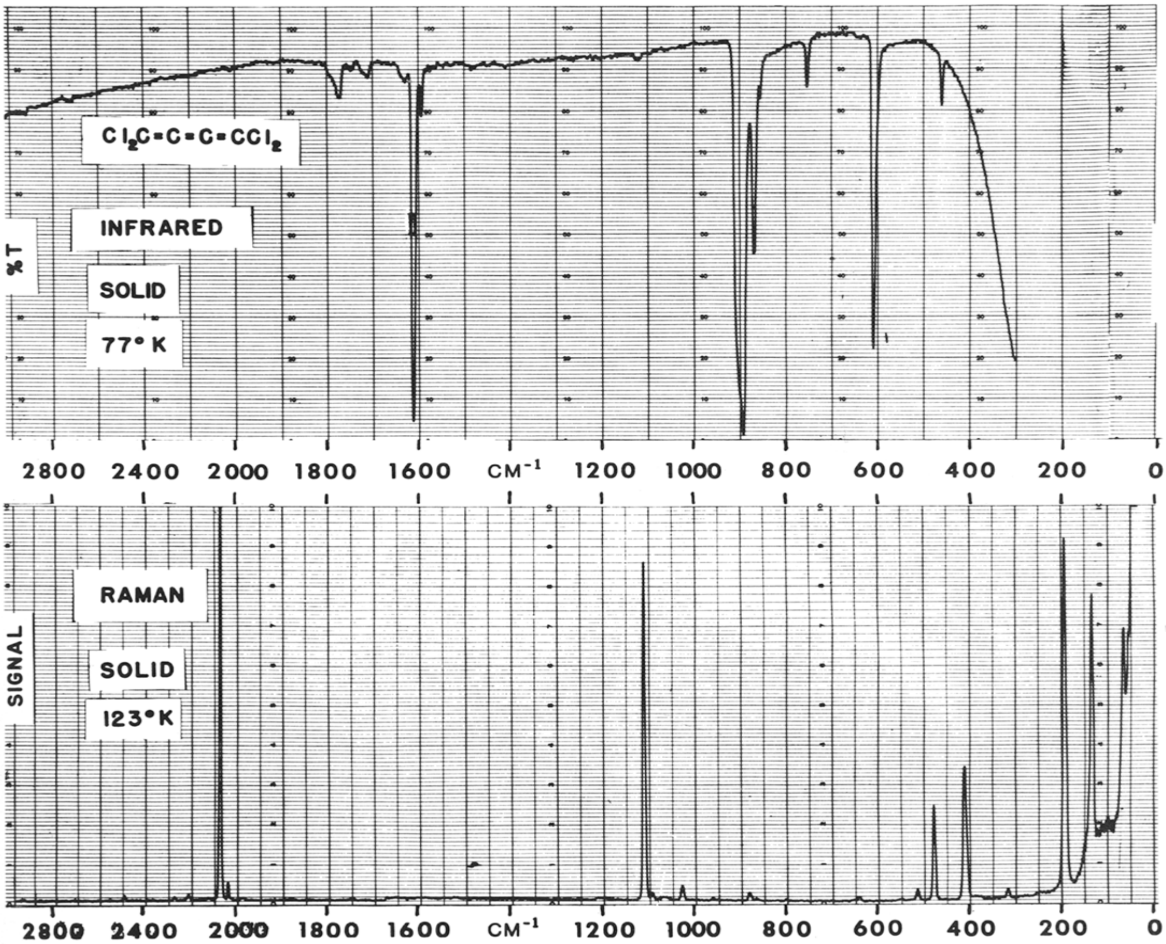

Fig. 2. IR and Raman spectra of perchlorobutatriene.

Assignments

The data are consistent with D_{2h} symmetry only. For example there are no Raman bands within 9 cm^{-1} of an IR one with the one trivial exception of 864 vs. 869 cm^{-1}. There is no need to consider any other point group. The assignments are included in Tables 2 and 3. Comparison with C_4F_4, as well as with $Cl_2C{=}CCl_2$ [23], $Cl_2C{=}CF_2$ [15], $Cl_2C{=}H_2$ [24] and $Cl_2C{=}C{=}CCl_2$ [1] is helpful.

Raman-active fundamentals

a_g species. The four a_g fundamentals are easily identified as the polarized bands at 2071, 1112, 416 and 194 cm^{-1}. The first two are C=C chain

stretches, 416 is the CCl_2 symmetric stretch, and 194 is the CCl_2 scissors.

b_{2g} and b_{3g}: There is no experimental criterion for distinguishing between these species. The highest frequency depolarized fundamental is the CCl_2 antisymmetric stretch (ν_{14}, b_{3g}). We assign the moderately strong band at 881 cm^{-1} to this because of its usefulness in explaining several combination tones. The lowest frequency Raman fundamental is expected to be the out-of-plane mode ν_{10} (b_{2g}), so 138 cm^{-1} is assigned to it. The remaining assignments are made somewhat arbitrarily: 321 cm^{-1} to ν_9, 482 to ν_{16} and 517 to ν_{15}.

IR-active fundamentals (species b_{1u}, b_{2u} and b_{3u})

Because there is no experimental method for differentiating between these species, they too will be discussed together. The very strong band at 1612 cm^{-1} is clearly ν_6, the b_{1u} chain stretch. The very strong band at 890 cm^{-1} is assigned to the CCl_2 antisymmetric stretch (ν_{11}, b_{2u}), while the CCl_2 symmetric stretch (ν_7, b_{1u}) can be either 870 or 610 cm^{-1}. There is ample precedence for having the antisymmetric stretch higher than the symmetric one — for example, the Raman-active modes of C_4Cl_4 and the assignments for C_4F_4. The two choices for ν_7 present a problem. We expected this frequency to occur around 600 cm^{-1}, so 610 cm^{-1} is a reasonable choice. However, this then leaves 870 cm^{-1} to be disposed of. It has no reasonable combination tone explanation. If it is a fundamental, the only possibility is ν_7. The problem with this is that 870, then a CCl_2 symmetric stretch, is nearly as high as the two antisymmetric stretches (890 and 881 cm^{-1}). In its favor is the fact that the corresponding CCl_2 symmetric stretch in $Cl_2C{=}CCl_2$ occurs at the high value of 777 cm^{-1}, which is far above 610 cm^{-1} [23]. The 610 band then has only one possibility as a fundamental, ν_{12}, by comparison with C_4F_4. We are disturbed by assigning a CX_2 rock to values as high as 978 in C_4F_4 and 610 in C_4Cl_4. However the high intensities of these two bands almost require that they be fundamentals. We assume that the schematic name is misleading.

There are only two more observed IR bands with appreciable intensity, 294 and 434 cm^{-1}, but four unassigned fundamentals (ν_8, ν_{13}, ν_{17}, ν_{18}). All four are expected to be below 500 cm^{-1}. We arbitrarily assign 294 cm^{-1} to ν_8 (CCl_2 scissors) and 434 to ν_{17} (skeletal bend). The two frequencies are probably fundamentals, but these may not be the correct modes. No other IR bands were observed below 500 cm^{-1}, even with very thick samples.

There are two weak, unassigned IR bands at 758 and 857 cm^{-1}. There are also two Raman-active fundamentals at 416 and 517 cm^{-1}. Is the 100 cm^{-1} separation between the bands in each pair accidental? Or are the Raman bands combining with an unobserved *u*-type fundamental near 341 cm^{-1} to give the IR bands as sum tones? The 341 value could be ν_{13}. Since we have found no other explanation for the IR bands at 758 and 857 cm^{-1}, we tentatively use this one.

Remaining bands

Explanations for most of the remaining bands as binary sum tones are given in Table 3.

Summary

The assignments for about half the fundamentals of C_4Cl_4 seem firm (numbers 1—4, 6, 10, 11, 14). The remainder are not reliable.

COMMENT ON THE CHAIN STRETCHES

Table 4 summarizes the three chain stretching modes. In the earlier paper on butatriene [2] these were discussed as examples of the classical resonance interaction. We point out here that ν_2 increases steadily through the series C_4H_4, C_4F_4 and C_4Cl_4. This illustrates that increasing the mass of a substituent (by a large factor) does not necessarily lower even a well-isolated frequency.

TABLE 4

The three chain stretching modes in butatrienes

Species	No.	Activity	Schematic form	C_4H_4	C_4F_4	C_4Cl_4
a_g	ν_1	Raman	$X_2\overset{\leftarrow}{C}=\vec{C}=\overset{\leftarrow}{C}=\vec{C}X_2$	2079	2140	2071
b_{1u}	ν_6	IR	$X_2\overset{\leftarrow}{C}=\vec{C}=\vec{C}=\overset{\leftarrow}{C}X_2$	1608	1738	1612
a_g	ν_2	Raman	$X_2\overset{\leftarrow}{C}=\overset{\leftarrow}{C}=\vec{C}=\vec{C}X_2$	878	983	1112

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