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THE VIBRATIONAL SPECTRA OF 1,1,4,4-TETRAFLUORO- AND 1,1,4,4-TETRACHLOROBUTADIENE*

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ABSTRACT

Raman data are reported for gas, liquid and solid 1,1,4,4-tetrafluorobutadiene, $F_2C{=}CHCH{=}CF_2$, and IR data for gas and solid. The molecule has a planar *trans* conformation of C_{2h} symmetry. With the aid of Raman depolarization ratios and IR band contours, twenty of the twenty-four spectroscopically-active fundamentals can be assigned with assurance. Frequencies are suggested for the remaining four modes.

Raman and IR data are reported for the liquid and solid 1,1,4,4-tetrachlorobutadiene. Mid-IR gas phase data are also reported. Again the data can be satisfactorily explained under C_{2h} symmetry. Fourteen fundamentals can be assigned with confidence. Suggestions have been made for the frequencies of nine other fundamentals.

INTRODUCTION

For many years chemists have been interested in the conformation of the carbon skeleton in 1,3-butadienes. The three possible conformations include the two planar forms, *s-trans* and *s-cis*, which can be interconnected by a rotation of 180° about the single bond. Rotation by some angle less than 180° produces the non-planar *gauche* form. For the planar forms the "*s*-" indicates the configuration about the single bond. Since no confusion will result from dropping the "*s*-", it will not be used hereafter. While all three configurations have been experimentally observed in one or another butadiene, the *trans* and *gauche* conformers are most common.

It has been well established that in butadiene itself the lowest energy form is the planar *trans* conformer [1, 2]. Recently Carreira has experimentally determined that the less stable species is the *cis* conformer [3]. Unlike the parent compound the most stable conformer for perfluoro- or perchlorobutadiene is the *gauche* form [4—6].

Steric effects have been used to rationalize the observed configurations of

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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).

halogenated butadienes [4]. The *trans* conformer will be expected unless there are steric interactions between substituents on carbons 1 and 3 or 2 and 4. If these hindrances are present, the *cis* form will be favored. The *gauche* form will have the lowest energy only in molecules which have steric interactions between substituents on carbons 1 and 3 or 2 and 4 *and* 1 and 4; as in the perhalogenated derivatives. If this reasoning is correct a 1,1,4,4-tetrahalobutadiene should have the planar *trans* conformation.

The vibrational spectrum of tetrafluorobutadiene has previously been examined by Conrad and Dows [7]. Since we had to prepare this material en route to perfluorobutatriene we decided to reexamine this compound. Our results are more extensive including far-IR data, gas phase and depolarization Raman data not previously reported.

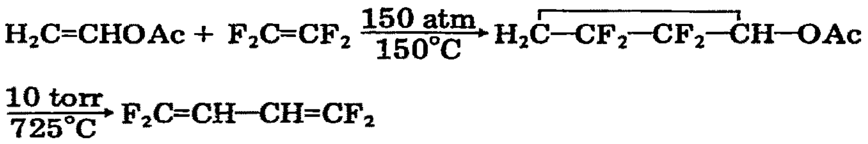
No vibrational study of the tetrachlorobutadiene has been previously reported.

1,1,4,4-TETRAFLUOROBUTADIENE

Experimental section

Preparation of the sample

The following reaction sequence used to prepare tetrafluorobutadiene was described by Coffman et al. [8]



$$H_2C{=}CHOAc + F_2C{=}CF_2 \xrightarrow[150°C]{150\ atm} H_2C{-}CF_2{-}CF_2{-}CH{-}OAc$$

$$\xrightarrow[725°C]{10\ torr} F_2C{=}CH{-}CH{=}CF_2$$

The required high pressure bomb reaction was carried out by Pressure Chemical Co., Pittsburgh, Pennsylvania. The final product was purified by repeated trap to trap vacuum transfers until the IR spectrum agreed with that reported by Conrad and Dows [7]. Tetrafluorobutadiene is a colorless gas with a boiling point of 269 K and a melting point of 188 K.

Raman spectra

Raman spectra were obtained using a Spex Ramalog instrument which has been described elsewhere [9]. Excitation was with the 488.0 nm line from an Ar$^+$ laser, using 30—300 mW of power at the sample. Spectra were measured for the solid at 123 K, the liquid at 298 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 liquid phase measurements the sample was sealed in a thin-walled capillary. The gas was contained in a cylindrical Pyrex cell with optically flat end windows. It was equipped with a side arm which was cooled to 268 K to keep the sample pressure at approximately one atmosphere.

Infrared spectra

Infrared 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 windows were polyethylene for the region 33—350 cm^{-1}, and KBr for 350—4000 cm^{-1}. Gas phase data were obtained above 200 cm^{-1} using a 10 cm gas cell having CsI windows. Sample pressures between 5 and 50 torr were adequate. The gas phase spectrum between 50 and 250 cm^{-1} was also examined using a Digilab FTS-14 Fourier transform interferometer.

Results

The results for 1,1,4,4-tetrafluorobutadiene are given in Table 1 and Fig. 1. The frequencies are believed to be accurate to ±1 cm^{-1} for the IR and ±2 cm^{-1} for the Raman, unless a band is marked broad, shoulder or approximate.

Assignments

Effective symmetry

The three most probable structures of 1,1,4,4-tetrafluorobutadiene are the *trans* planar form (C_{2h}), the *gauche* conformation (C_2) or the planar *cis* conformation (C_{2v}). The former has a center of symmetry, so there should be no coincidences between IR and Raman bands except accidental ones. The latter two permit coincidences for many modes, so it should be easy to decide whether the sample is all *trans* or includes *gauche* or *cis*. The earlier vibrational and microwave work indicated only the *trans* form.

We believe that our Raman frequencies are accurate to ±2 cm^{-1} and IR frequencies to ±1 cm^{-1}. Therefore any pair of bands within 4 cm^{-1} of one another will be considered as potential coincidences. Examination of the gas phase data in Table 1 shows the following five coincident Raman—IR pairs: ~690—696, 940—940, ~1170—1173, ~1390—1386 and ~2960—2964. In every case at least one member of the pair is weak, and all the values can be explained under C_{2h} symmetry except the 690 cm^{-1} Raman band. There are not enough coincidences to indicate the presence of any significant amount of *gauche* conformer.

In the solid phase there are 10—12 additional pairs of coincidences, but again nearly all have at least one member which is weak. In some cases a strong band in one spectrum appears very weakly in the solid phase of the other spectrum, as though the selection rules had been relaxed by solid state effects. In other cases a coincident pair appears only in the solid phase in each spectrum.

Certainly C_{2h} symmetry controls the main features of the spectra, and

TABLE 1

Raman and IR spectra of 1,1,4,4-tetrafluorobutadiene

Raman								IR					
Solid (123 K)		Liquid (298 K)			Gas (298 K)			Gas (298 K)			Solid (123 K)		Assignment
cm⁻¹	int.[a]	cm⁻¹	int.[a]	ρ	cm⁻¹	int.[a]	ρ	cm⁻¹	int.	type	cm⁻¹	int.	
								69	vw	C?	overlapped cell windows		ν_{13}
~95	100												lattice mode
					110	6,sh							?
											113	w	lattice mode
								114 121	w	C?	130	s	ν_{12}
~140	50	~150	<1,b		128	60,b	dp?				142	w	2 × 69 = 138 (p)
~195	20	200	20	0.74	188	60	dp						ν_{16}
232	180	236	160	0.30	234	170	p						ν_9
								230 240 247	vvw sh	A	239	w	ν_{24}
								298	vvw				234 + 69 = 303
387	170	387	150	0.20	386	110	p						ν_8
		~430	3										~195 + 232 = 427
								431	vvw				188 + 240 = 428
					~445	3							?
								490	vw		480 500	vvw	ν_{23}
		~500	2		~500	6							?
~550	1							546 (550) 553	m	B	547	s	ν_{22}
~560	5										567	m	?
573	750	576	360	0.71	580	150	dp						ν_{15}
								583	w		582	s	[illegible]

593	140	593	130	0.0	592	195	p						ν_7
608	170	610	130	0.04	609	110	p				~605	vw	ν_6
~620	1	~640	2		~635	6	dp						?
695	30	695	18	0.52	~690	15	?						?
								~689	sh				
								696	w	A	696	m	580 + 121 = 701
								704					
~710	<1												582 + 130 = 712
								721					
								729	vvw	C			609 + 121 = 730
~750	<1	741	9	0.19	~745	15	?						?
~770	<1												2 × 387 = 774.
815	240	816	100	0.72	812	60	dp						ν_{14}
								822		HB.			
								824	s	HB.			
								827		Q	829	s	ν_{10}
											837	vvw	608 + 239 = 847
								863					
								869	m	A	865	s	386 + 490 = 876
								875					
~860	5	~870	5		~880	5							?
											891	vw	?
											908	vvw	?
								919					
								(923)	vs	B	912 923	vs	ν_{21}
								926					
								937					
								(940)	w	B	934	vw	386 + 550 = 936, in F.R. with 923
								943					
945	310	938	280	0.04	940	225	p						ν_5
											951	s	?
								962	vvw,sh		966	w	386 + 583 = 969
											988	vw	?
											994	vvw	?
								1010	vvw		1001	vvw	940 + 69 = 1009

TABLE 1 (continued)

Raman								IR					
Solid (123 K)		Liquid (298 K)			Gas (298 K)			Gas (298 K)			Solid (123 K)		Assignment
cm⁻¹	int.ᵃ	cm⁻¹	int.ᵃ	ρ	cm⁻¹	int.ᵃ	ρ	cm⁻¹	int.	type	cm⁻¹	int.	
								1035	vvw				?
		~1040	1										923 + 121 = 1044
								1053					
								1058	vvw	A?	1052	vvw	234 + 827 = 1061 (C)
								~1064			~1070	vvw	940 + 121 = 1061 (C)
								~1110	vvw,sh		~1110	vvw,sh	188 + 923 = 1111
								~1148	vvw,sh		1139	s	234 + 923 = 1157
1129	50	1135	80		1141	sh							550 + 490 = 1140
1146	200	1148	210	0.87	1150	250	p						ν_4
1160	340	1150	180		1159	sh							580 × 2 = 1160
1173	100	1174	60		~1170	sh							940 + 234 = 1174
								1169					
								(1173)	vs	B	1170	vs	ν_{20}
								1177					
											1189	m	608 + 582 = 1190
~1200	1										1200	w	?
											1205		
								~1234	vvw,sh		1217	vvw,sh	?
								~1238	vvw,sh		1225	m	?
								1243					
								1256	w	C	1247	m	?
								1266					
1252	50	1258	27	0.47	1265	30							ν_3
~1295	1	~1280	2,sh										1170 + 130 = 1300
											1298	w	?
								1318					
								(1322)	vs	B	1320	s	ν_{19}
								1326					
		~1330	2										1150 + 188 = 1338

		~1370	12										?
											1373	vvw	1252 + 130 = 1382
								1382 (1386) 1390	w	B	1386 1390	vvw,sh w	1150 + 240 = 1390
1383	20	~1380	3,sh		~1390	6							812 + 580 = 1392 1322 + 69 = 1391
1406 1417	10 20	~1420	7								1406 1415	w vvw	?
								1430	vvw		~1430	w	609 + 827 = 1436
~1460	1	~1460	2										?
								1496	vvw		~1485	vvw	580 + 923 = 1503
								1519	vvw		1518	w	940 + 583 = 1523
											~1560	vvw,b	387 + 1170 = 1557
													812 × 2 = 1624
~1620	1	~1620	13		~1620	10							?
~1630	5												
								1633 1639	m sh	?	1646	m	812 + 827 = 1639
											1659	w,b	?
		~1680	2										?
											1686 1695	s	1146 + 547 = 1693
								1713 (1717) 1719	vvs	B	1705 1717	vvs	ν_{18}
~1725	5										1728	w	?
								~1737	w,b		1744	vs	812 + 923 = 1735
1760	1000	1759	1000	0.15	1765	1000	p						ν_2
								1778 (1782) 1784	w	B	1777	m	609 + 1173 = 1782
								1811 (1815) 1818	vw	B			1265 + 550 = 1815
~1840	1				~1830	6							1717 + 121 = 1838 923 × 2 = 1846

TABLE 1 (continued)

Raman								IR					
Solid (123 K)		Liquid (298 K)			Gas (298 K)			Gas (298 K)			Solid (123 K)		Assignment
cm⁻¹	int.ᵃ	cm⁻¹	int.ᵃ	ρ	cm⁻¹	int.ᵃ	ρ	cm⁻¹	int.	type	cm⁻¹	int.	
~1880	1	~1860	1,vb										945 × 2 = 1890
								1859 1867 1876	vw	A	1850	m	940 + 923 = 1863
		~1890	1										1320 + 582 = 1902
											~1925	vvw,b	?
								1959	vw		~1945	vw,b	234 + 1717 = 1951
								2097 2104 —	vw	A	2094 2106	vvw,sh vw	386 + 1717 = 2103
								2117	vw				940 + 1173 = 2113
~2140	1	~2140	3										387 + 1760 = 2147
								2187	vw		2162	vw	1265 + 923 = 2188
								2257 (2260) 2263	vw	B	2245	vw	940 + 1322 = 2262
								2297 (2301) 2305	vw	B?	2289	vw	592 + 1717 = 2309
~2310	1	~2300	3										?
~2320	1							2319 2324	w	?	2325	vvw	1150 + 1173 = 2323 609 + 1717 = 2326
											2340	vw	1760 + 582 = 2342
								2435	w		2413	m	1265 + 1173 = 2438
								2454	vvw,sh				1765 + 580 + 121 = 2466
~2480	1	~2480	1										1247 × 2 = 2494
		~2520	1										1265 × 2 = 2530
								2548	vvw,sh		2545	vw,b	827 + 1717 = 2544 1765 + 550 + 234 = 2549

								2584	w				1265 + 1322 = 2587
~2620	1	~2620	1										{1717 + 923 = 2640 1320 × 2 = 2640
								2651 (2654) 2656	vw	B	2644	m	940 + 1717 = 2657
								— 2684 ~2690	w	A	2672	m	1765 + 923 = 2688
~2695	1	~2680	2										1760 + 945 = 2705
~2805	1	~2810	2								~2800	vvw	?
								~2836	vvw,vb		~2825	vvw	940 + 580 + 1322 = 2842
		~2840	2										?
											~2850	vvw	1146 + 1717 = 2863
2890	20				2896	3,sh							1717 + 1173 = 2890
								2904	vvw		2920	w	580 + 609 + 1717 = 2906
2905	40	2906	60	0.0	2912	60	p						1765 + 1150 = 2915
								2956 2964 2972	w	A	2956	m	1265 + 1717 = 2982
		2963	30,sh	0.90	~2960	10,b	dp						{1765 + 812 + 386 = 2963 1717 + 1256 = 2973
~3015	3	~3020	3		~3030	3							1765 + 1265 = 3030
											3056	vw	?
								3070	vw		3078	vvw	1765 + 1322 = 3087
3088	100	3084	110	0.0	3091	110	p						ν_1
								3121	w		3104 3122	s	ν_{17}
		~3130	12										?
3161	8	~3160	12		~3153	6							1765 + 812 + 580 = 3157
								3466	vvw		3454	vw	1765 + 1717 = 3482
		~3510	2										1760 × 2 = 3520
											~3665	vvw	?

w, m, s = weak, medium, strong; v = very; ~ = approximate; F.R. = Fermi resonance; b = broad; sh = shoulder; NE. = not examined; Q = Q-branch; HB. = hot band; ρ = depolarization ratio; p = polarized; dp = depolarized. For depolarized lines, we obtain $\rho = 0.75 \pm 0.03$.

[a]Relative peak intensities uncorrected for instrument response.

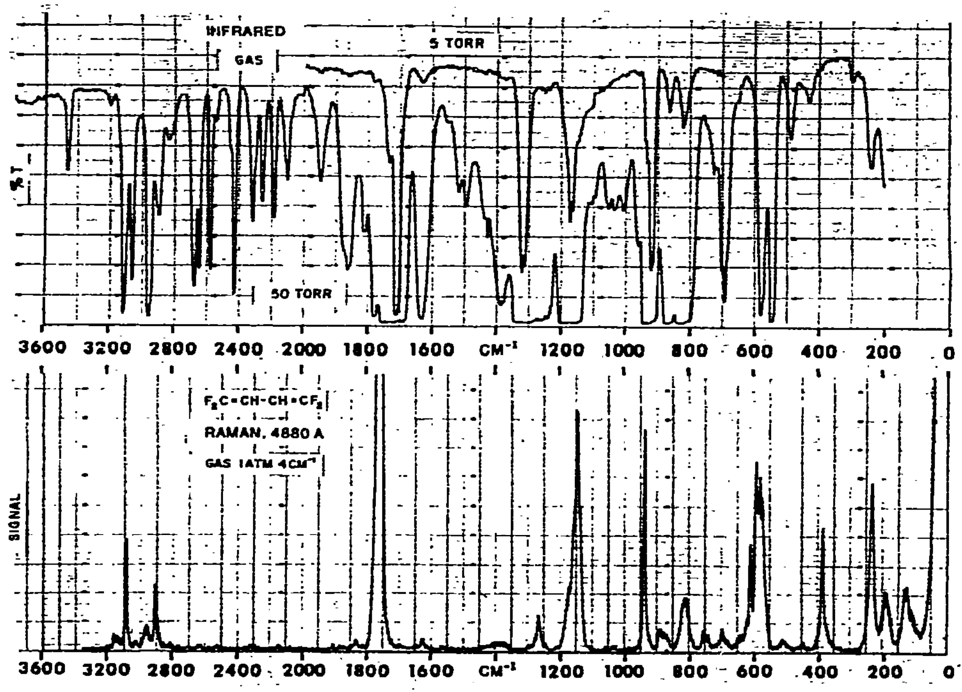


Fig. 1. IR and Raman spectra of 1,1,4,4-tetrafluorobutadiene.

most of the coincidences can be reasonably explained as accidental. Under C_{2h} symmetry the twenty-four fundamentals of 1,1,4,4-tetrafluorobutadien divide into the following symmetry species: $9a_g + 4a_u + 3b_g + 8b_u$. They are summarized in Table 2. The descriptive names of the vibrations are used for convenience and may not be accurate descriptions of the actual modes. Some useful molecules for comparison are: F_2C=CF_2 [11], F_2C=CH_2 [12] and F_2C=CD_2 and F_2C=CDH [13].

Raman-active fundamentals

a_g species. All nine fundamental frequencies belonging to this species were identified from their polarizations and intensities. The two candidates for the symmetric C—H stretch (ν_1) are 2912 and 3091 cm^{-1}. This mode is expected to occur above 3000 cm^{-1}. On this basis and its greater intensity the 3091 cm^{-1} is chosen as ν_1. The strongest Raman band, at 1765 cm^{-1}, is assigned to the symmetric C=C stretch (ν_2).

The C—C stretch, symmetric C—H in-plane bend and the out-of-phase C— stretch are expected to have similar frequencies. The band at 1265 cm^{-1} is attributed to the C—H bend since this mode is expected to be the highest frequency of the three [13]. By comparison with the hydrogen [1] and chlorine (Table 2) analogs of 1,1,4,4-tetrafluorobutadiene, ν_4, the C—C stretch is assigned to 1150 cm^{-1}. This leaves the band at 940 cm^{-1} to the

TABLE 2

Fundamental vibrations of $X_2C{=}CH{-}CH{=}CX_2$ (X = F,Cl)

Species	Activity	No.	Description	$C_4H_2F_4$	$C_4H_2Cl_4$
a_g	R(p),—	1	C—H sym. stretch	3091	3051
		2	C=C sym. stretch	1765	1609
		3	C—H I.P. bend	1265	1292
		4	C—C stretch	1150	1152
		5	CX_2 antisym. stretch	940	855 or 955
		6	CX_2 sym. stretch	609	691
		7	CX_2 sym. scissor	592	185
		8	CX_2 rock	386	374
		9	CCC deformation	234	462
a_u	—,IR(C)	10	C—H O.P. bend	827	889
		11	CX_2 wag	583	320
		12	CX_2 twist	121	96
		13	C—C torsion	69	—
b_g	R(dp),—	14	C—H O.P. bend	812	933 or 855
		15	CX_2 wag	580	477
		16	CX_2 twist	188	239
b_u	—,IR(AB)	17	C—H antisym. stretch	3121	3061
		18	C=C antisym. stretch	1717	1550
		19	C—H I.P. bend	1322	1242
		20	CX_2 antisym. stretch	1173	~866[a]
		21	CX_2 sym. stretch	923	609
		22	CX_2 scissor	550	306
		23	CX_2 rock	490	197
		24	CCC deformation	240	220

I.P. = in-plane; O.P. = out-of-plane.

[a] Fermi Resonance.

out-of-phase C—F stretch (ν_5). The four remaining strong polarized bands in the Raman spectrum are 609, 592, 386 and 234 cm^{-1}. We have chosen 609 cm^{-1} as the symmetric C—F stretch because it is slightly more intense than the band at 592 cm^{-1}. This band is then assigned to the CF_2 scissor (ν_7). These two assignments could easily be reversed. The remaining two bands 386 and 234 cm^{-1} are assigned to the CF_2 rock and C—C—C deformation respectively.

b_g species. The three vibrational fundamentals that belong to the b_g symmetry species are the out-of-plane C—H bend, the CF_2 wag and the CF_2 twist. Four depolarized bands of moderate intensities are observed at 812, 580, 188 and 128 cm^{-1}. The 812 and 580 cm^{-1} bands are assigned to the C—H out-of-plane bend (ν_{14}) and CF_2 wag (ν_{15}) respectively. Because the intensity of the 188 cm^{-1} does not fluctuate as much as that of the 128 cm^{-1} band we favor the 188 cm^{-1} band as ν_{16}. We then assign 128 cm^{-1} to the overtone of the torsion.

Infrared-active fundamentals: band contours

As an aid in assigning the IR fundamentals the expected band contours were estimated. The moments of inertia were calculated after assuming a geometry by analogy with similar compounds. The assumed parameters were: F—C bond 1.32 Å; C=C bond 1.35 Å; C—C bond 1.47 Å; C—H bond 1.06 Å; F—C—F angle 110°, C=C—C angle 124°, C=C—H angle 122°. The following moments of inertia were calculated: $I_A = 140$ amu Å^2, $I_b = 562$ amu Å^2 and $I_c = 702$ amu Å^2. From these values the P—R separations were calculated [14] and the intensity pattern estimated [15]. The calculated and observed P—R separation and band type are as follows

Species	b_u	b_u	a_u
Band type	A	B	C
$\Delta\tilde{\nu}(P-R)$ calculated	8.0 cm^{-1}	6.7 cm^{-1}	12.0 cm^{-1}
$\Delta\tilde{\nu}(P-R)$ observed	10—17 cm^{-1}	6—8 cm^{-1}	23 cm^{-1}

b_u *species.* In view of the expected contours, the following strong bands were chosen as candidates for b_u fundamentals: 1717, 1322, 1173 and 923 cm^{-1}. The band at 1717 is readily assigned to the C=C antisymmetric stretch (ν_{18}). By analogy with fluorinated ethylenes and the Raman-active fundamentals the C—H in-plane bend is expected at a higher frequency than the C—F stretches [13]. Therefore, ν_{19} is assigned to 1322 cm^{-1}. The C—F out-of-phase stretch and the C—F in-phase stretch are at 1173 and 923 cm^{-1} respectively.

Two additional bands of moderate intensity which belong to this symmetry species are 550 and 869 cm^{-1}. The former is chosen for the antisymmetric scissors (ν_{22}) while the latter is a combination band (490 + 386 = 876).

The antisymmetric C—H stretch is assigned to a weak band at 3121 cm^{-1}. Of the two candidates (3070 and 3121 cm^{-1}) only the 3121 cm^{-1} band had an intense counterpart in the solid phase. The 3070 cm^{-1} band is explained as a combination band (1765 + 1322 = 3087 cm^{-1}). The remaining two b_u fundamentals the CF$_2$ rock and the C—C deformation are assigned to 490 and 240 cm^{-1} respectively.

a_u *species.* There are four vibrational fundamentals which belong to the a_u symmetry species: the out-of-plane C—H bend, the antisymmetric CF$_2$ wag, the CF$_2$ twist, and the C—C torsion. The three C-type bands observed are either too high in frequency or too weak to be assigned to an a_u fundamental. Of the remaining bands the best candidates for these fundamentals are 827, 583, 121 and 69 cm^{-1}. The 827 cm^{-1} band is assigned to the out-of-plane C—H bend (ν_{10}) and the 583 band is assigned to the CF$_2$ wag. Since the torsion is expected to be at a lower frequency than the twist, the band at 121 cm^{-1} is attributed to the CF$_2$ twist, while the torsion is observed at 69 cm^{-1}.

Remaining bands. Most of the remaining bands are assigned to combination bands as shown in Table 1.

1,1,4,4-TETRACHLOROBUTADIENE

Experimental section

Preparation of the sample

The following reaction, first described by Roedig and Kloss [16], was used to prepare 1,1,4,4-tetrachlorobutadiene

$$Cl_2HC{-}ClHC{-}CHCl{-}CHCl_2 \xrightarrow{KOH} Cl_2C{=}CH{-}CH{=}CCl_2$$

Our sample was purified via preparative gas chromatography using a 10′ × 1/4″ 3% carbowax column operated at 110°C.

Spectroscopic procedure

The instruments and some of the procedures used were described earlier. The sample was contained in a 1 mm O.D. capillary for the Raman experiments. The spectrum of the liquid was obtained at room temperature. For the solid phase data the sample was cooled to 213 K in a conventional variable temperature cell [17]. The liquid phase infrared spectrum was obtained from a thin film between KBr plates or using a 1 mm sealed polyethylene cell. The gas phase was examined using a variable multi-pass cell [10] with a path length of 8.6m.

Results

The spectral results are listed in Table 3 and shown in Fig. 2.

Assignments

While several coincidences occur in the solid or liquid phases, only two pairs of bands are coincident in both phases. The other coincident pairs are certainly accidental or they would be coincident in both phases. These two coincidences are far less than should be observed for C_{2v} or C_2 symmetry. Clearly the selection rules for C_{2h} symmetry are followed and the molecule will be assigned under this symmetry. These assignments are summarized in Table 2. The numbering of the vibrations is for the fluoro compound and is not correct for the chloro compound.

Raman-active fundamentals

a_g species. The a_g bands are easily identified in the Raman spectrum by their polarized character. The band at 3051 cm^{-1} must be the C—H symmetric stretch. The symmetric C=C stretch certainly is the very strong band at 1609 cm^{-1}. The lowest a_g vibration, the CCl_2 scissors, is assigned to the band at 185 cm^{-1}. The C—C stretch is assigned to the band at 1152 cm^{-1}. A number of butadienes including C_4Cl_6 and C_4H_6 have a band between 1150 and

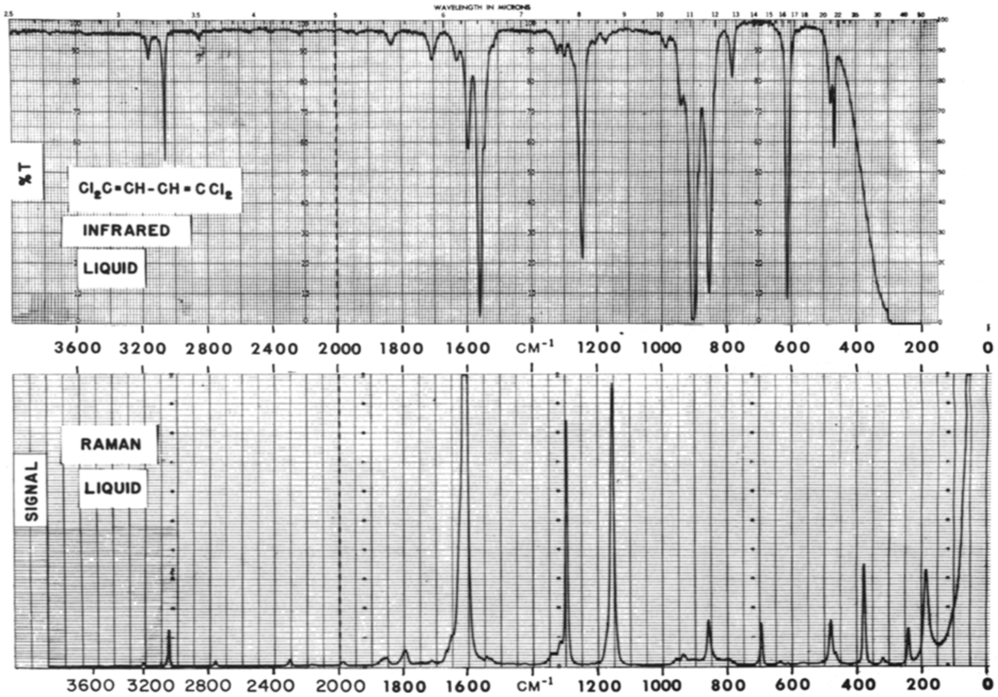


Fig. 2. IR and Raman spectra of 1,1,4,4-tetrachlorobutadiene.

1200 cm^{-1}. The only vibration common to all these molecules which would be expected in this region is the C—C stretch. If 1152 cm^{-1} is assigned to the C—C stretch, then the C—H in-plane bend must be at 1292 cm^{-1}. The only remaining a_g fundamental expected above 750 cm^{-1} is ν_5, the CCl_2 antisymmetric stretch. This vibration would be expected to occur between 800 and 1000 cm^{-1}. The only polarized Raman band in this region is at 955 cm^{-1}. However, this band is very weak and may arise from the combination $2 \times 477 = 954$ cm^{-1}. The next highest polarized band is at 691 cm^{-1}. If the antisymmetric stretch is assigned to this band the CCl_2 symmetric stretch would have to be assigned to the weak band at 564 cm^{-1}. The symmetric stretch is expected to be an intense band. Since the antisymmetric stretch (ν_5) would be expected at a much higher frequency than 691 cm^{-1}, we have assigned the 691 cm^{-1} band to the CCl_2 symmetric stretch. The depolarized band at 855 cm^{-1} is a candidate for the CCl_2 antisymmetric stretch. The fact that it is depolarized does not forbid this assignment. There are no definite arguments for choosing which band is due to ν_5. We have chosen ν_5 as 855 cm^{-1} because of its intensity. Its frequency is close to the frequency observed for the IR active CCl_2 antisymmetric stretch, as expected.

The remaining two a_g fundamentals, the skeletal in-plane bend and the CCl_2 rock, are assigned to 462 and 374 cm^{-1} respectively; they could well be reversed.

TABLE 3

Raman and IR spectra of 1,1,4,4-tetrachlorobutadiene

Solid				Liquid					Gas		Assignment
Raman 213 K		IR 77 K		Raman 296 K			IR 296 K		IR v.p. at 296 K 8.3 meters		
cm^{-1}	Int.[a]	cm^{-1}	Int.	cm^{-1}	Int.[a]	ρ	cm^{-1}	Int.	cm^{-1}	Int.	
		102	m				96	m			ν_{12}
~100	46										lattice
							138	w			462 — 320 = 142
		185	w				180	w			?
185	262			185	126	0.35					ν_7
		204	vw				197	vw			ν_{23}
		220	w				220	w			ν_{24}
238	48			239	45	0.77					ν_{16}
		251	vw				252	vw			?
		306	m				306	m			ν_{22}
323	12			317	7						220 + 96 = 316
		323	m				320	m			ν_{11}
				330	10						?
376	165			374	142	0.14					ν_8
				462	10	~.5					ν_9
		464	m				462	m	464	m	239 + 220 = 459
		472	m				474	m	474	m	374 + 96 = 470
482	101			477	58	0.75					ν_{15}
564	5,b			564	6,b	~.6					374 + 185 = 559
		614	s				609	s	614	s	ν_{21}
				~610	1						2 X 306 = 612
641	17			642	6						2 X 320 = 640
695	71			691	60	0.32					ν_6
		784	w								320 + 462 = 782
		787	w				786	m	773	m	691 + 96 = 787
799	17			800	1	~.8					?
860	76			855	55	0.78					ν_5
		880	m				856	s	851	m }	F.R. ν_{20} and
		905	vs				898	vs	911	vs }	691 + 197 = 888
		897	vs				889	sh	907	vs	ν_{10}
931	5			933	8	~.8					ν_{14}
		943	m				941	w	944	m	?
961	16			955	6	~.2					2 X 477 = 954
		985	vw				985	vw			609 + 374 = 983
1124	10										?
1155	233			1152	380	0.38					ν_4
							1165	vw			855 + 306 = 1161
		1189	vw				1185	vw			?
		1245	s				1242	s	1249	m	ν_{19}
1302	155			1292	333	0.32					ν_3
		1300	vw				~1300	vw			691 + 609 = 1300
~1330	5,b			1311	17	0.50					?
~1345	3,b			1355	8	~.4					?
~1543	5,b			1542	10	~.2					1242 + 306 = 1548
		1542	w				1543	m			856 + 691 = 1547
		1562	s				1550	vs	1564	vs	ν_{18}
		1590	sh								?
		1594	m				1592	m	1603	m	898 + 691 = 1589
1611	1000			1609	1000	0.26					ν_2
							1625	vw			?
				1715	2						2 X 856 = 1712
~1790	6,b			1793	18	~.3					1609 + 185 = 1794
		~1835	vw				1829	vw			1609 + 220 = 1829
~1855	3,b			~1854	8	~.4					1550 + 306 = 1856

TABLE 3 (continued)

Solid				Liquid					Gas		Assignment
Raman 213 K		IR 77 K		Raman 296 K			IR 296 K		IR v.p. at 296 K 8.3 meters		
cm^{-1}	Int.[a]	cm^{-1}	Int.	cm^{-1}	Int.[a]	ρ	cm^{-1}	Int.	cm^{-1}	Int.	
				1985	5	~.2					1609 + 374 = 1
							~2215	vw			1609 + 609 = 2
~2305	3,b			2299	7	~.2					1609 + 691 = 2
~2766	2			2759	6	~.5					1609 + 1152 =
		2845	vw				2838	w			1292 + 1550 =
				2895	2						1609 + 1292 = 2
3050	66			3051	44	0.09					ν_1
		3057	m				3061	m	3071	m	ν_{17}
		3155	w				3157	vw			1609 + 1550 = 3
~3218	3,b			3212	3	~.2					2 × 1609 = 321

w, m, s, = weak, medium, strong; v = very; b = broad; sh = shoulder; ~ = approximate; F.R. = Fermi Resonance; ρ = depolarization ratio. For depolarized lines we obtain ρ = 0.75 ± 0.05.

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

b_g species. The highest frequency b_g vibration, the C—H out-of-plane bend, is assigned to the band at 933 cm^{-1}. It is not surprising that a mode involving primarily the bending of two C—H bonds is weak in the Raman. The remaining two b_g fundamentals were assigned to bands at least three times more intense than the strongest combination band. The CCl_2 twist should be the lowest b_g fundamental, and is assigned to the band at 239 cm^{-1}. The remaining fundamental, the CCl_2 wag, is assigned to the band at 477 cm^{-1}.

Infrared-active fundamentals

In an attempt to distinguish between the IR-active species, a_u and b_u, a gas phase spectrum was obtained. Unfortunately the band contours could not be resolved; therefore we have no experimental method of distinguishing between the two species, and they will be discussed together.

a_u and b_u species. The C—H antisymmetric stretch (b_u) is observed at 3061 cm^{-1}. The very strong band at 1550 cm^{-1} is assigned to the C=C stretch (b_u). The only remaining fundamental expected above 1000 cm^{-1} is the C—H in-plane bend (b_u), assigned to the band at 1242 cm^{-1}. The lowest observed fundamental, at 96 cm^{-1}, is assigned to the CCl_2 twist. This value is too high to be reasonably assigned to the torsion, which should be the lowest IR-active fundamental. The intensity of this band also supports this assignment. Torsions are generally weak but this band is the strongest band below 400 cm^{-1}.

Between 850 and 920 cm^{-1} in the IR there are three bands of appreciable intensity. Two of these are surely due to the CCl_2 antisymmetric stretch and the C—H out-of-plane bend. We assign the C—H out-of-plane bend to 889 cm^{-1}. We believe the bands at 856 and 898 cm^{-1} to be members of a Fermi doublet involving the CCl$_2$ antisymmetric stretch and the combination band 691 + 197 = 888 cm^{-1}. The CCl$_2$ symmetric stretch is assigned to the band at 609 cm^{-1}.

The band at 306 cm^{-1} is assigned to the CCl$_2$ scissors (b_u). The combination band at 1542 cm^{-1} in the Raman spectrum is polarized, implying that the two bands from which it arises belong to the same species. The only reasonable explanation for this combination band is 1242 (b_u) + 306 = 1547. Therefore, the 306 cm^{-1} band must belong to the b_u species. The corresponding CCl$_2$ scissors is at 310 cm^{-1} in tetrachloroethylene and at 299 cm^{-1} in 1,1-dichlorethylene [18].

Excluding the torsion, this leaves three more low frequency fundamentals to be assigned. The bands observed at 197 and 220 cm^{-1} are useful in explaining combination bands. They are assigned to the CCl$_2$ rock and the C—C deformation respectively. The remaining fundamental the CCl$_2$ wag is assigned to the band at 320 cm^{-1}.

Most of the other bands tabulated in Table 3 are explained as combination bands. Only binary combinations were tried, since it was felt that due to the large number of fundamentals almost any number between 400 and 3000 cm^{-1} could be explained by a tertiary combination.

CONCLUSIONS

The vibrational spectra of both 1,1,4,4-tetrafluoro- and tetrachlorobutadiene can be satisfactorily explained under C_{2h} symmetry. We saw no evidence of a second conformer for either compound.

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REFERENCES

1 D. J. Marais, N. Sheppard and B. P. Stoicheff, Tetrahedron, 17 (1962) 163.
2 A. Almenningen et al., Acta Chem. Scand., 12 (1958) 1221.
3 L. A. Carreira, J. Chem. Phys., 62 (1975) 3851.
4 C. H. Chang, A. L. Andreassen and S. H. Bauer, J. Org. Chem., 36 (1971) 920.
5 J. C. Albright and J. Rud Nielsen, J. Chem. Phys., 26 (1957) 370.
6 G. J. Szaz and N. Sheppard, Trans. Faraday Soc., 49 (1953) 358.
7 R. M. Conrad and D. A. Dows, Spectrochim. Acta, 21 (1965) 1039.
8 D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, J. Am. Chem. Soc., 71 (1949) 490.
9 F. A. Miller, B. M. Harney and J. Tyrrell, Spectrochim. Acta Part A, 27 (1971) 1003.
10 R. C. Lord, R. S. McDonald and F. A. Miller, J. Opt. Soc. Am., 42 (1952) 149.

11 T. Shimanouchi, Tables of Molecular Vibrational Frequencies. Consolidated Vol. I. National Bureau of Standards, 1972. U.S. Government Printing Office, Washington, D.C., S.D. Catalog No. C13.48:39, p. 75.

12 D. C. Smith, J. Rud Nielsen and H. H. Claasen, J. Chem. Phys., 18 (1950) 326.

13 W. F. Edgell and C. J. Ultee, J. Chem. Phys., 22 (1954) 1983.

14 W. A. Seth-Paul and G. Dijkstra, Spectrochim. Acta Part A, 23 (1967) 2861.

15 T. Ueda and T. Shimanouchi, J. Mol. Spectrosc., 28 (1968) 350.

16 A. Roedig and R. Kloss, Justus Liebigs Ann. Chem., 612 (1958) 1.

17 F. A. Miller and B. M. Harney, Appl. Spectrosc., 24 (1970) 291.

18 T. Shimanouchi, Tables of Molecular Vibrational Frequencies. Consolidated Vol. I. National Bureau of Standards, 1972. U.S. Government Printing Office, Washington, D. C., S.D. Catalog No. C13.48:39, pp. 76, 83.