Spectroscopy at Very High Pressures. Part 11.[†] A Raman Study of Polymorphs of Carbon Tetrachloride and Tetrabromide and their Photodecomposition Products[‡]

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Raman spectra are reported for all the four solid phases of CCl_4, and for three of the four phases of CBr_4. All the spectra have been obtained under hydrostatic or near-hydrostatic conditions, and are shown to be compatible with such structural data as are available, except for CBr_4 (I) for which a pseudo-cubic monoclinic structure is proposed. The phases CBr_4 (IV) and CCl_4 (IV) have spectra compatible with predictions on the basis of the SnI_4 structure type. Carbon tetrachloride photodecomposes under pressure to yield, principally, C_2Cl_6 and some chlorine, whereas CBr_4 gives much bromine together with other (unidentified) products. The CCl_4 photodecomposition can be catalysed by the Cr^{3+} present in the ruby pressure calibrant: this alters the mode of decomposition yielding, principally, chlorine. The liquid-to-solid transition pressure of chlorine is *ca.* 7 kbar at 293 K, and that of bromine is 5.26 kbar at 308 K.

ALTHOUGH almost exhaustive attention has been paid to the vibrational properties of CCl_4, nothing is known about the spectra of its high-pressure phases apart from a mid-infrared spectrum of the recently discovered CCl_4 (IV).[1] In this paper we report the Raman spectra of the four known solid phases [1,2] of CCl_4, and of three phases [3,4] of CBr_4. The spectra were obtained at pressures of up to 50 kbar § under hydrostatic or near-hydrostatic conditions using a design of diamond anvil cell (d.a.c.) recently developed in these laboratories.

EXPERIMENTAL

The d.a.c. used was a modified version of one described by us earlier.[5] The central cylinder of the cell was insulated from the main cell body by placing it within a ring of Sindanio asbestos. An extended nose-piece on the fixed diamond-anvil holder was provided with a heater, and temperature was measured by a copper constantan thermocouple attached to the fixed diamond anvil with silver paste.

Samples were contained within molybdenum gaskets initially 0.2 mm thick and with a hole of initial diameter 0.3 mm; these dimensions change in the course of runs to high pressure. Pressure at room temperature was determined by following the R_1 and R_2 fluorescence lines of a grain of ruby powder contained within the sample. Details of this method of pressure calibration have been given elsewhere.[6,7] Although the behaviour of the R_1 and R_2 lines with increase of temperature is known over the temperature range we have used, these data cannot be used to correct a measurement of pressure made on the scale determined at ambient temperature as there are concurrent changes of pressure due to the thermal expansion of parts of the cell itself which slightly reduce the pressure on the sample. The loss of pressure (giving a positive shift to R_1 and R_2) due to the cell is partly offset by the negative shift due to the increase in temperature. Nevertheless, the cancellation is far from exact and the room-temperature calibration is no more than a guide to pressure at elevated temperature. This is why the spectra of phases prepared at elevated temperature have also been recorded at ambient temperature (when the pressure calibration is applicable).

Raman spectra were excited with either 514.5-nm argon-ion radiation (for the CCl_4 work) or 647.1-nm krypton-ion radiation (for CBr_4). Spectra were recorded using a Coderg T800 triple-monochromator Raman instrument with a thermoelectrically cooled E.M.I. 9558A photomultiplier and d.c. amplification. The laser beam was passed directly through the cell and scattered radiation was collected in the forward direction. The CCl_4 used was AnalaR grade. A commercial sample of CBr_4 was purified by sublimation, although some work was also done with the crude material in order to study the effect of impurities on phase properties.

RESULTS

Figure 1 shows the known phase diagram [2] of CCl_4 to which we have added the III–IV phase boundary as determined from our spectra. Piermarini [1] reported the discovery of CCl_4 (IV), noting that the transition is sluggish at room temperature but rapid at 520 K and >20 kbar, although he did not determine the boundary with CCl_4 (III). Spectra of CCl_4 as a liquid, and as phases I (in equilibrium

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[†] Part 10 is ref. 7.

[‡] No reprints available

§ Throughout this paper: 1 kbar = 10^8 Pa.

[1] G. J. Piermarini and A. B. Braun, *J. Chem. Phys.*, 1973, **58**, 1974.

[2] P. W. Bridgman, *Phys. Rev.*, 1914, **3**, 126, 153.

[3] P. W. Bridgman, *Proc. Amer. Acad. Sci.*, 1915, **51**, 55.

[4] P. W. Bridgman, *Proc. Amer. Acad. Sci.*, 1938, **72**, 227.

[5] D. M. Adams, K. Martin, and S. J. Payne, *Appl. Spectroscopy*, 1973, **27**, 377.

[6] G. J. Piermarini and S. Block, *Rev. Sci. Instr.*, 1975, **46**, 973 and refs. therein.

[7] D. M. Adams, R. Appleby, and S. K. Sharma, *J. Phys.(E)*, in the press.

with liquid), II, and III, were all obtained at 293 K by successively increasing the pressure. Representative spectra from a large number of runs are shown in Figure 2, and frequencies quoted in Table 1. On increasing the pressure on CCl_4 (III) at room temperature to *ca.* >20 kbar new features began to appear, eventually identified as due to phase IV intergrowing with III, but the new phase could not be obtained pure at this temperature. The procedure used was to apply a pressure of *ca.* 25 kbar at ambient temperature, heat to 403 K (the limit of our heater), and then pass *ca.* 1-W 514.5 nm radiation through the cell. This resulted in complete conversion into CCl_4 (IV) plus some slight decomposition (discussed below). Cooling to room temperature, still under pressure, gave samples from which spectra such as those of Figure 2 were obtained. It should be emphasised that, although we show spectra of (where possible) the pure phases, intergrowth of adjacent phases is a constant problem due to the sluggish nature of many transitions, both with CCl_4 and CBr_4.

TABLE 1

Raman wavenumbers (cm^{-1}) for CCl_4 polymorphs at 293 K

Pressure/kbar	0.66	1.12	2.30	6.25	12.8	24.3
Phase	Liquid	liquid + I	I	II	III	IV
Assignment						
ν_2, e	217.4s	218.9s	217.9s	*ca.* 217 (sh)	217.6m (0.25) *	231.4s (0.49)
			220.9s	219.1s	222.4m (0.17)	
				ca. 222.0 (sh)	226.9s (1.0)	
ν_4, t_2	313.6s	314.4s	*ca.* 309.5 (sh)	*ca.* 314.5 (sh)	*ca.* 314.5 (sh) (0.0)	319.4s (0.31)
			316.7s	317.1s	318.7s (0.25)	
				319.4s		
ν_1, a_1	459.9s	460.9s	462.4s	460.9s	*ca.* 463.0 (sh) (0.0)	466.4 (0.49)
				464.9s	464.4s (0.5)	
					465.9s (0.67)	
ν_3, t_2	*ca.* 759.5w, b	*ca.* 759.0w, b	*ca.* 751.5w, b	*ca.* 757.5w, b	*ca.* 752.5w, b (0.17)	748.4w (0.06)
+			*ca.* 765.5w, b	*ca.* 764.5w, b	*ca.* 765.0w, b (0.58)	768.4w (0.31)
($\nu_1 + \nu_4$) +	*ca.* 785.5w, b	*ca.* 789.5w, b	*ca.* 787.5w, b	*ca.* 776.0vw, b	*ca.* 782.0vw, b (1.0)	*ca.* 788.0vw, b (0.43)
Others		*ca.* 799.5w, b	*ca.* 799.5w, b	*ca.* 785.5w, b	*ca.* 800.02, b (0.0)	*ca.* 804.5vw, b (0.6)

* $\Delta\nu/\Delta P$ in cm^{-1} $kbar^{-1}$.

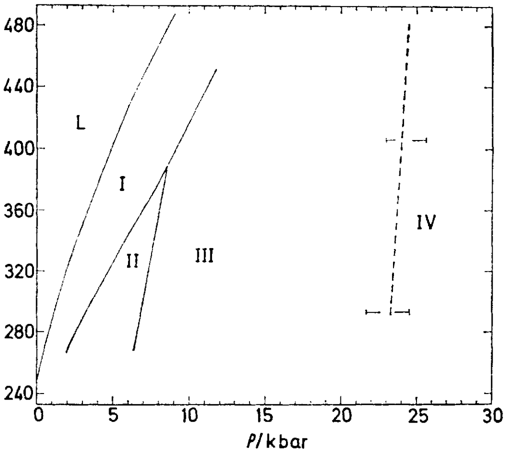

FIGURE 1 Phase diagram for CCl_4. The data are from ref. 5 (converted from kg cm^{-2} into kbar), except for the points for the III–IV boundary which are from this work

A study of CBr_4 similar to that above allowed spectroscopic identification of the known phases [3,4] I, II, and IV (Figure 3). Spectra are shown in Figure 4 and frequencies in Table 2. We were unable to characterise phase III as it always photodecomposed rapidly (see below). The phase CBr_4 (IV) was obtained by a procedure analogous to that used to isolate pure CCl_4 (IV), because the CBr_4 III–IV transition also is sluggish at ambient temperature: indeed, we found that it did not occur until 23.3—24.4 kbar in the pure material, and was delayed until *ca.* 31 kbar with impure samples. At 327 K the transition was relatively sharp; this, and other observations of the transition, straddled the III–IV phase boundary as determined by Bridgman. To obtain pure CBr_4 (IV) a sample of CBr_4 (II) at 322 K and 20.4 kbar was heated to 395 K whereupon a rapid and complete transformation took place. The sample was then cooled to room temperature to obtain the spectrum shown in Figure 4.

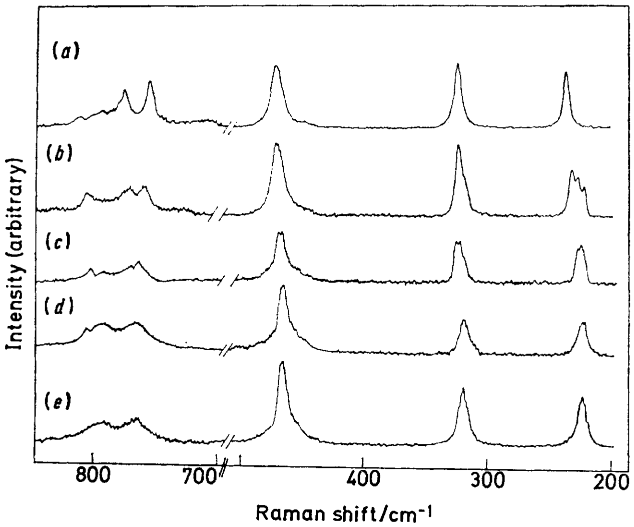

FIGURE 2 Raman spectra of CCl_4 polymorphs: see text for conditions of preparation. All the spectra were obtained with 300-mW 514.5-nm radiation at the sample. Spectral slit width was 1.0—1.2 cm^{-1} for the range 200—500 cm^{-1}, and 2.5 cm^{-1} for 500—800 cm^{-1}. Phases: (*a*) IV, 24.3 kbar (293 K); (*b*) III, 12.8; (*c*) II, 6.25; (*d*) I + liquid, 1.12; (*e*) liquid, 0.66

Phase IV was studied at 293—395 K and over a range of pressures, the varying band shapes revealing a number of components and shoulders which are not all necessarily clearly apparent in any one spectrum. Table 2 includes data on the mode-frequency changes with pressure for CBr_4

TABLE 2

Raman wavenumbers (cm^{-1}) for CBr$_4$ polymorphs

Pressure/kbar	0.26	0.001	0.001	20.4	5.26
T/K	396.3	322.4	293.0	293.0	307.6
Phase	Melt	I	II	IV	CBr$_4$–Br$_2$
Assignment					
ν_2, e	127m	128m	128m (0.4) *	138m (0.73)	130.5m
ν_4, t_2	184m	186m	185.0m (0.11)	188.5m (0.24)	188m
			186.5m (0.34)		190m
					230w, b
ν_1, a_1	269s	269s	268.5s (0.12)	272.5s (0.49)	271s
ν(Br$_2$)					310.5s
ν_3, t_2	*ca.* 665vw, b	*ca.* 663vw, b	*ca.* 662vw, b (0.58)	649w (0.67)	
		ca. 672vw, b	*ca.* 671vw, b (0.43)	666w (0.67)	
				686vw (1.0)	

* $\Delta\nu/\Delta P$ in cm^{-1} kbar^{-1}.

(IV), none of which calls for particular comment. The CBr$_4$ (II) spectrum was also rather sensitive to the particular P–T combination, especially in the ν_4 region: the higher component of this doublet was more pressure-sensitive (0.34 cm^{-1} kbar^{-1}) than the lower one (0.11 cm^{-1} kbar^{-1}) so that it was clearly a doublet at some pressures but not at others.

The effect of impurities in the commercial sample of CBr$_4$ was to stabilise CBr$_4$ (I) at ambient temperature: this phase is normally stable at room pressure only above 319 K.[3] This metastable CBr$_4$ (I) did not transform into CBr$_4$ (II) unless pressures >6 kbar were applied: it was then completely transformed. Impure CBr$_4$ was more susceptible to photodecomposition than was the pure material.

Decomposition of CCl$_4$ *and* CBr$_4$.—Both materials were photodecomposed under some of the conditions used in this work. With CCl$_4$ at ambient temperature, with a single ruby chip present (as pressure calibrant), and at various elevated pressures, no photodecomposition occurred with irradiation of up to 2 W and 514.5 nm. When the temperature was increased to 403 K at 25.66 kbar several new bands quickly developed in the spectrum; surprisingly, the process seemed to be reversible in that these new features all but disappeared on cooling to room temperature. A trace amount of Cl$_2$ is indicated [8] by weak broad bands near 550 cm^{-1}, those at 351w and 447s cm^{-1} most probably originating from C$_2$Cl$_6$ [9] which is a known photodecomposition product of CCl$_4$.[10] The two strongest bands in its Raman spectrum are at 340w and 431s cm^{-1}, the difference between these values and ours being accounted for by the pressure differential. The mechanism of the decomposition under these conditions undoubtedly involves creation of CCl$_3^{\cdot}$ radicals which dimerise to C$_2$Cl$_6$.

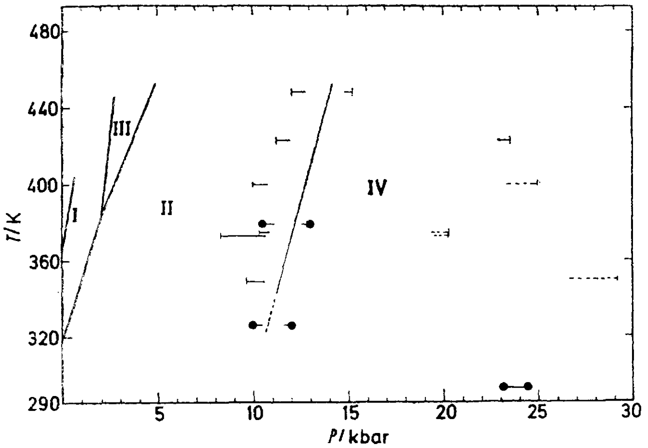

FIGURE 3 Phase diagram for CBr$_4$. The data are from ref. 3 (converted from kg cm^{-2} into kbar); (●), data points from this work

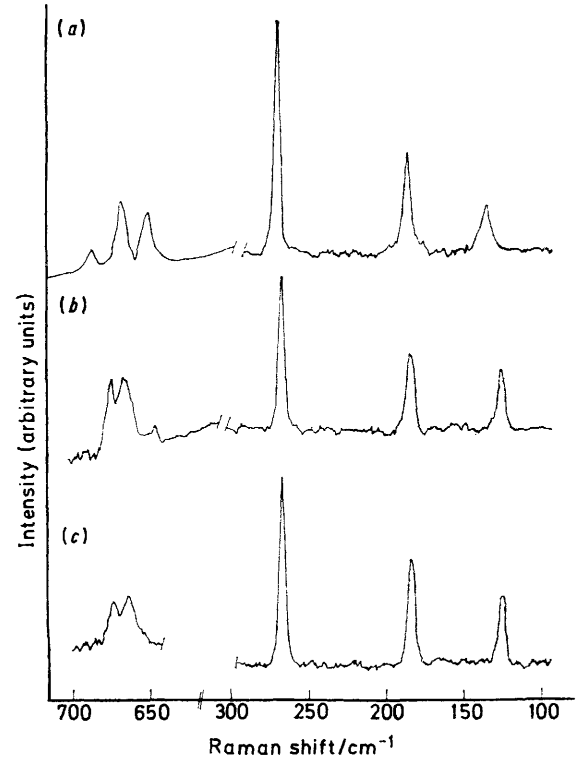

FIGURE 4 Raman spectra of CBr$_4$ polymorphs. All the spectra were obtained with 100-mW 647.1-nm radiation at the sample. Spectral slit width 1.2 cm^{-1} for the range 100—300 cm^{-1}, and 2.5 cm^{-1} for 600—700 cm^{-1}. Phases: (*a*) IV, 20.4 kbar (293 K); (*b*) II, 0.001 (293); (*c*) I, 0.001 (322.4)

In order to test whether the decomposition process was catalysed by Cr^{3+} ions in the ruby calibrant, further runs were made in which conditions differed from those above chiefly in that many grains of ruby (rather than one) were included with the sample. At ambient temperature, with *ca.* 500-mW 515.4-nm radiation, and a range of pressures up to 21 kbar, rapid and irreversible decomposition occurred yielding a large amount of Cl$_2$ together with other (so far

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[8] F. Wallart, *Canad. J. Spectroscopy*, 1972, **17**, 128.

[9] F. Watari and K. Aida, *J. Mol. Spectroscopy*, 1967, **24**, 503.

[10] R. Steudel, *Z. Naturforsch.*, 1968, **B23**, 1163.

unidentified) products, not C_2Cl_6. The principal features of the other products were a broad weak band at *ca.* 390 cm^{-1}, and two or three other bands which can be seen in the region

TABLE 3

Raman wavenumbers (cm^{-1}) for CCl_4 and photodecomposition products

Pressure/kbar	25.66	7.23
T/K	403	293
Laser power/W	1.0	0.5
Assignment		
ν_2, *e*	232.6s	220.6s
ν_4, t_2	320.4s	317.0s
C_2Cl_6	351w	
?		391w, b
C_2Cl_6	442.4m	
ν_1, a_1	467.4s	462.4s
$\nu(Cl_2)$		*ca.* 532.5 (sh)
		ca. 534.5 (sh)
	545w	539.7s
	548w, b	546.9vs
ν_3, t_2	745w	
	766w	762w, b
	783vw	
($\nu_1 + \nu_4$), *etc.*	806w, b	790w, b
	846w, b	
	854w, b	
	867w, b	

of ν_1 of CCl_4 in Figure 5(*b*). These bands do not correspond to C_2Cl_4, which might have been expected if the carbene CCl_2 is involved, as seems likely since sub-halogeno-species must be involved if one product is chlorine.

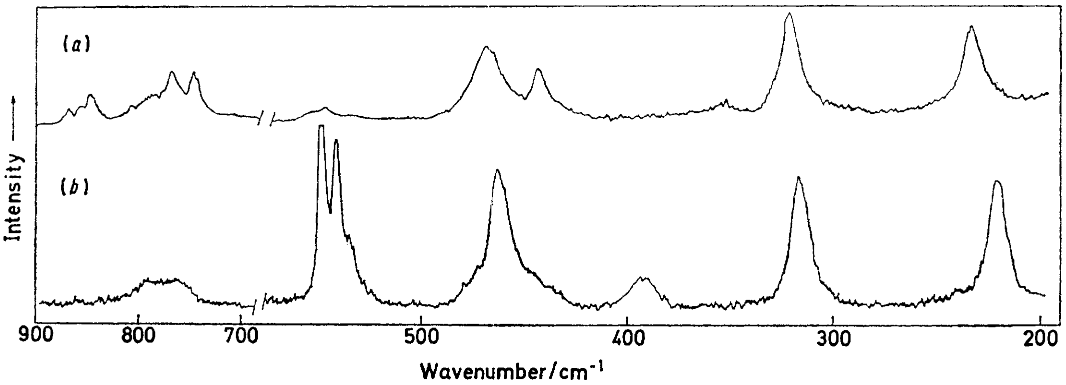

FIGURE 5 Raman spectra of (*a*) CCl_4 (IV) partly photodecomposed showing bands due to C_2Cl_6 (1-W, 514.5 nm radiation at the sample, spectral slit width 1.0 cm^{-1} for 200—600 cm^{-1}, 2.5 cm^{-1} for 700—800 cm^{-1}, 25.66 kbar, 403 K); (*b*) partly decomposed CCl_4 showing phase I plus Cl_2 (500 mW at the sample, spectral slit width 1.2 cm^{-1} for 200—500 cm^{-1}, 1.8 cm^{-1} for 700—800 cm^{-1}, 7.23 kbar, 293 K). The chlorine bands are pressure broadened

As a by-product, this work has yielded the first data on the effect of elevated pressure on the Raman spectrum of solid Cl_2. This was observed over the pressure range 7.23—21.0 kbar at 293 K: the chief effect was a pronounced broadening of all the bands, and an increase of 1 or 2 cm^{-1} in wavenumber. No data appear in the literature for the liquid-to-solid transition of Cl_2. We find that it solidifies at 293 K at *ca.* 7 kbar. This transition pressure was determined by photodecomposing CCl_4 under conditions that yield a large amount of liquid Cl_2 (*ca.* 3 kbar and plenty of ruby calibrant): a great deal of ' optical noise ' was seen in the sample compartment due to motion of solid particles within the liquid phase. The pressure was increased until this just ceased.

Photodecomposition data (647.1-nm excitation) for CBr_4 were obtained in the course of unsuccessful attempts to characterise CBr_4 (III). Indeed, under all the conditions of temperature and pressure used in this work CBr_4 decomposed if $>$100-mW 647.1-nm radiation (measured at the sample) was used. This contrasts with Bridgman's observation that at pressures $>$7 kbar no decomposition occurred due to heating alone.

The only new bands arising from products were a broad strong feature at 310.5 cm^{-1} due to Br_2 [11] (isotopic structure not resolved, probably due to pressure broadening), and a weak broad band at 230 cm^{-1} of unidentified origin, not C_2Br_6.[12,13] This mode of decomposition seems to parallel that found in CCl_4 when a large amount of ruby catalyst was present, although only a single chip was used in the CBr_4 work. In the early stages of the decomposition, patches of bromine could be seen clearly (under the microscope). After further irradiation the sample no longer supported the applied pressure and the spectrum corresponded to that of a solution of CBr_4 in Br_2. No Raman scatter could be observed in the ν_3 region of this mixture due to self-absorption. The liquid-to-solid transition pressure of Br_2 was determined (as described for Cl_2) as 5.26 kbar at 308 K. This compares with an approximate literature value of $<$5 kbar at room temperature.[14]

DISCUSSION

Carbon Tetrabromide.—Nothing is known of the structures of CBr_4 (III) (which we were unable to characterise) or of CBr_4 (IV). An early report indicates that CBr_4 (I) is cubic with a unimolecular primitive cell.[15] The room-temperature phase, CBr_4 (II), is monoclinic with $Z = 32$ but is constructed from eight of the cubic *F*-centred cells with only slight distortion of each.[16,17]

In contrast to CCl_4, the ν_3 region (650—700 cm^{-1}) is not complicated by the ($\nu_1 + \nu_4$) = 455 cm^{-1} combination as this lies well below ν_3. This is very clear from the ν_3

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[11] A. J. Melveger, J. W. Brasch, and E. R. Lippincott, *Appl. Optics*, 1970, **9**, 11.

[12] R. A. Carney, E. A. Piotrowski, A. G. Meister, J. H. Braun, and F. F. Cleveland, *J. Mol. Spectroscopy*, 1961, **7**, 209.

[13] R. D. McLachlan and V. B. Carter, *Spectrochim. Acta*, 1970, **A26**, 2247.

[14] C. E. Weir, G. J. Piermarini, and S. Block, *J. Chem. Phys.*, 1969, **50**, 2089.

[15] C. Finbak, *Structure Reports*, 1940—1941, **8**, 350.

[16] C. Finbak and D. Hassel, *Z. phys. Chem.*, 1937, **B36**, 301.

[17] A. E. Morgan and W. J. Dunning, *J. Crystal Growth*, 1970, **7**, 179.

region of CBr_4 as a melt (Figure 6) which shows only a single band at 665 cm^{-1}, *cf.* the broad doublet in CCl_4 due to ν_3 and $(\nu_1 + \nu_4)$. The structure in the ν_3 region of the CBr_4 polymorphs must therefore be accounted for by site- and/or correlation-field effects. Moreover, the spectra of CBr_4 (at least at room temperature) do not suffer from the complicating effects of isotopic structure.

It is obvious that the ν_3 region of CBr_4 (I), which shows two clearly resolved bands with a probable third on the low-frequency side, is not compatible with the structure claimed.[15] If the primitive cell is unimolecular there can be no correlation coupling and the observed splitting of $\nu_3(t_2)$ must be due to the site field. In a unimolecular cubic cell the molecule is required to be on a site of the same symmetry as that of the factor group and all the cubic factor groups retain triple degeneracies. On the grounds that it is easier to be mistaken about a space group than about occupancy, we suggest that the structure of this phase is in fact monoclinic but, in all probability, pseudo-cubic.

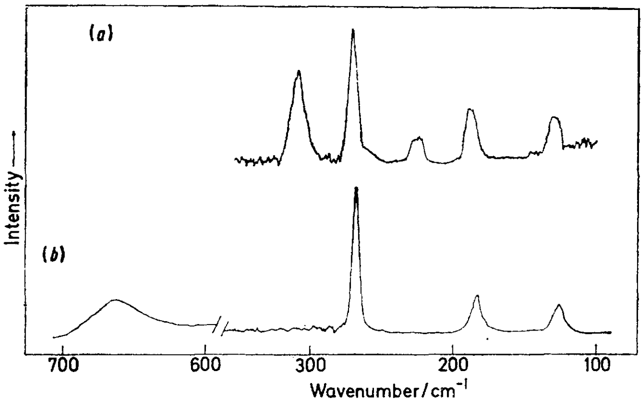

FIGURE 6 Raman spectra of (*a*) partly photodecomposed CBr_4 showing phase I plus Br_2 (100-mW 647.1 nm radiation at the sample, spectral slit width 1.2 cm^{-1}, 5.26 kbar, 307.6 K); (*b*) CBr_4 melt [conditions as for (*a*), except for 700—800 cm^{-1} for which the spectral slit width was 2.5 cm^{-1} and 0.26 kbar, 396.3 K]

The ν_3 region of CBr_4 (II), which is known to be monoclinic,[16,17] bears a strong similarity to that of CBr_4 (I). It is simply distinguished from phase I by the ν_4 region which shows a single band for CBr_4 (I) but a doublet for CBr_4 (II), which also has a broader and more complex ν_2 band. The spectrum of CBr_4 (II) is, thus, fully compatible with its reported structure. In a monoclinic cell all the degeneracy is necessarily lifted by the site symmetry (which, in a cell of high occupancy, can be C_1, C_2, C_i, or C_s according to the space group). The $\nu_2(e)$ band appears to have three unresolved components, thereby indicating that both site- and factor-group effects are at work, since only two components can originate from the site field alone. The $\nu_4(t_2)$ doublet can be accounted for by the site field alone, as can the $\nu_3(t_2)$ region although, in both cases, we incline to the view that most of the splitting originates in correlation coupling.

Spectroscopically, the most distinctive feature of CBr_4 (IV) is the structure shown in the ν_3 region, which indicates strong correlation coupling in a cell of multiple occupation. Examination of its spectrum over a considerable range of temperature and pressure caused the band shapes of ν_2 and ν_4 to vary progressively, revealing that $\nu_2(e)$ consists of a central peak flanked by unresolved shoulders (just visible in Figure 4 but more clearly seen at 394 K and 17 kbar). The ν_4 band has three components, most clearly seen at 326 K and 19.1 kbar. These data do not allow identification of the crystal class, let alone the space group. However, the distinctive change in the ν_3 region in passing from phase II to IV seems to imply a significant difference in structure such as is associated with a change of factor group. The phase CCl_4 (IV) is thought to be cubic [1] and it is not unreasonable that CBr_4 (IV) should be also. We note that the SnI_4 structure [18] ($Pa3$, $Z = 8$) would account for all the observed features of the CBr_4 (IV) spectrum. Thus, considering internal molecular modes only, we have the following where all the *g* modes are Raman active:

T_d	Site, $C_3 \longrightarrow$	Crystal, T_h^6
ν_1, a_1	A	$A_g + T_g + A_u + T_u$
ν_2, e	E	$E_g + 2T_g + E_u + 2T_u$
ν_3 and ν_4, t_2	$A + E$	$A_g + E_g + 3T_g + A_u + E_u + 3T_u$

In terms of numbers of observable Raman bands this correlation predicts (in terms of the three levels of symmetry involved):

Band	Molecule	Site	Crystal
ν_1	1	1	2
ν_2	1	1	3
ν_3	1	2	5
ν_4	1	2	5

Three components were found for each of ν_2, ν_3, and ν_4 and the possibility of others is clearly not ruled out by the spectra.

Carbon Tetrachloride.—Interpretation of the CCl_4 spectra is complicated by the well known isotope splitting[19,20] (especially on ν_1) due to $^{35,37}Cl$, and the proximity of and hence resonance between ν_3 and $(\nu_1 + \nu_4)$. Nevertheless, useful deductions can be made.

X-Ray diffraction data obtained at high pressures [12] indicate that CCl_4 (I) is rhombohedral with $Z = 21$, and that phase II is monoclinic with $Z = 32$. Even if these structures were fully characterised it is clear that the principal features of the vibrational spectra will be determined by much smaller pseudo-cells. In our experiments phase I was always obtained in equilibrium with liquid [Figure 2(*b*)] but differences from the liquid spectrum [Figure 2(*b*)] are apparent. Thus, the intensity ratio $\nu_1 : \nu_4$ is greater for phase I indicating that there has been a lifting of mode degeneracy in ν_4 and consequent spreading of the energy among levels which contribute to the ν_4 envelope. This process continues into phase II [Figure 2(*c*)] in which ν_2 and ν_4 now clearly reveal further structure. The spectrum of phase II bears strong similarities to that of CCl_4 at 80 K (allowing for the substan-

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[18] R. W. G. Wyckoff, 'Crystal Structures,' Interscience, New York, 1948, vol. 4.

[19] R. J. H. Clark and B. K. Hunter, *J. Chem. Soc.* (*A*), 1971, 2999.

[20] H. F. Shurvell, *Spectrochim. Acta*, 1971, **A27**, 2375.

tial sharpening due to cooling), including the complex ν_3–second-order region above 700 cm^{-1}. It is known [21,22] that below 225 K the structure is monoclinic, $C2/c$; although it appears that the space groups of this phase and of CCl_4 (II) differ, at least in occupancy, it is quite likely that the sites occupied will be identical, thereby generating similar spectra. It is certain that all the molecular-mode degeneracy will have been lifted by the site fields (since no degeneracy is possible in a monoclinic group) and that some further structure is generated by correlation coupling.

Phase III of CCl_4 is the only one that has been adequately characterised structurally.[1] It also is monoclinic, $P2_1/c$, with $Z = 4$, having all atoms on general sites. The correlation below (all g modes are Raman active) shows that ν_2 should give rise to four Raman bands ($2\ A_g + 2\ B_g$), three of which are clearly seen, and a fourth is probably under the rather asymmetric high-frequency side of the band. The six Raman components expected of ν_4 have combined to yield a broad and complex band in which several contributions can be discerned. The splitting for ν_4 is less pronounced than for ν_2, which is surprising. The magnitude of factor-group splitting, on the dipole-coupling model,[23] is related to the i.r. band intensities which are 0 and 20 mol^{-1} cm^{-1} for ν_2 and ν_4 respectively,[24] implying the reverse of what is found. It must be concluded that for the $\nu_2(e)$ mode the effect of the site field predominates.

Molecule, T_d	Site, C_1 $\longrightarrow$	crystal, C_{2h}
ν_1, a_1		
ν_2, e	$9A$	$9(A_g + B_g + A_u + B_u)$
ν_3 and ν_4, t_2		

The band $\nu_1(a_1)$ should be a doublet ($A_g + B_g$): it is relatively broad, suggesting that unresolved structure is present, but this is obscured by isotopic bands. The key experiments to settle assignment for this phase require the use of an isotopically enriched sample, studied at high pressure in combination with low temperature. The simplicity and almost classically Lorentzian shapes of ν_1, ν_2, and ν_4 of CCl_4 (IV) strongly imply a higher symmetry environment than in phases II and III and support the suggestion,[1] based on the absence of optical birefringence, that the structure is cubic.

The region >700 cm^{-1} in the vibrational spectrum of CCl_4 has long been a matter of controversy and is not yet adequately understood. It is certain that it contains ν_3, that ($\nu_1 + \nu_4$) and possibly other second- and third-order processes are involved, and that (at ambient temperature) hot bands make a contribution. Our high-pressure observations yield one particularly clear result: that with increase of pressure the lower-energy half of this complex region becomes dominant, suggesting that ν_3 is associated principally with it and that the higher-energy part is due to (at least) second-order processes. Indeed the sum ($\nu_1 + \nu_4$) = 785.8 cm^{-1} for CCl_4 (IV) places it sufficiently high to make our suggestion a reasonable one. Until more structural data become available for this phase further discussion of the spectrum is unprofitable. The observed features are accommodated on the same basis as those of CBr_4 (IV) above.

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[21] B. Post, *Acta Cryst.*, 1959, **12**, 349.

[22] R. Rudman and B. Post, *Science*, 1966, **154**, 1009; *Mol. Cryst.*, 1968, **5**, 95.

[23] D. A. Dows, ' Physics and Chemistry of the Organic Solid State,' eds. D. Fox, M. M. Labes, and A. Weissburger, Interscience, New York, 1963, p. 657.

[24] K. Tanabe and S. Saeki, *Spectrochim. Acta*, 1970, **A26**, 1469.